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CRYSTAL STRUCTURES OF PALLADIUM DIMETHYLGLYOXIME,

BIS(M-BROMOBENZOYL)METHANE, AND 3,4-FURANDICARBOXYLIC ACID

by

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INTRODUCTION

The hydrogen bond has been the subject of considerable study because of its importance in a wide variety of molecules and in interactions between molecules. X-ray diffraction provides a particularly powerful tool to investigate hydrogen bonding in the crystalline state. The fundamental parameters of the hydrogen bonding systems may be elucidated by this technique, although the accuracy with which the hydrogen atom itself may be located is limited by the low diffracting power and normally large thermal motion of hydrogen.

The X-ray diffraction method requires rather complicated experimental apparatus, however. In addition, large computers are required to utilize the diffraction data to successfully and precisely locate the individual atomic positions. Finally, no assurance can be given at the present state of the science that a given crystal structure can be solved at all. Nevertheless, the information obtained by the X-ray diffraction method is sufficiently valuable that a considerable expenditure of effort is justified.

The application of the X-ray diffraction method may be divided into five parts.

(1) The measurement of diffracted intensities, using a suitable X-ray source, a suitable orientation for the single crystal, and a suitable detector. In the past the Weissenberg and Buerger precession camera, using photographic film as the detector, have been extensively used as the measurement apparatus. The accuracy of measurement of diffracted intensities from these instruments left much to be desired. Frequently

an accuracy of 20% in the measured intensity was all that could be practically obtained by these photographic methods.

Fortunately, the demand for more accurate intensity data has been met by the availability of counter detectors. These counter detectors have evolved through several stages. The first of these was the Geiger-Muller detector, which had the disadvantage of a large recovery time after receiving an X-ray photon.

The gas-filled proportional counters successfully met the problem of minimizing the recovery time to a suitably low value. However, the proportional counter suffered from a very low counting efficiency at the shorter wave lengths used in crystal structure investigations.

The application of the scintillation crystal-photomultiplier detector to X-rays, long used in nuclear applications, provided crystallographers with an efficient, fast recovering detector suitable for general structural investigations. Intensity measurements of better than 10% accuracy are easily made, and the potential accuracy is much greater than this if suitable precautions are taken.

Early counters were merely attachments to existing film instruments. More recently the Harker-Furnas single crystal orienter was developed to fill the need for an orientation mechanism specifically for counter application. Other orientation devices specifically designed for counter detectors are now becoming available.

(2) The processing of the directly observed intensity data to obtain structure factors and their associated errors. Several well known corrections are necessary to convert the observed data into structure

factors. An absorption correction may be necessary if absorption is significantly large. A streak correction may be necessary if the incident X-ray beam is insufficiently monochromatized. An anomalous dispersion correction may be required. The Lorenz factor must be applied to correct for geometrical effects on the intensities. And finally, a polarization correction must be made for the effect of the polarized nature of the incident beam. These corrections are easily made by application of high speed computers.

(3) The solution of the phase problem and the arrival at an appropriate trial structure. This is the step in which no assurance of success can be given, except for very simple structures. Rapid evaluation of trial models is a necessity at this stage, and the method of the Fourier electron density map is especially useful in suggesting changes in the trial model.

(4) The refinement of the successful trial model by least squares. This step was formerly one of the most tedious. It is now perhaps the most straightforward and routine of the steps in the solution of a crystal structure. The use of a working crystallographic least squares program to refine a trial model to any desired degree is now almost completely mechanical and automatic, thanks to high speed computers.

(5) The presentation of the geometrical results of the calculations in the form of bond distances, bond angles, intermolecular distances, stereographic projections, three dimensional models, thermal motion analysis, and so forth, is the final step in the structure analysis. The details of presentation will vary according to the type of structure

considered, and the structural details considered to be of most interest.

The three crystal structures presented in this thesis, in addition to being of fundamental interest as representative hydrogen bonded structures, clearly illustrate the rapid progress that has been made in the experimental techniques of X-ray diffraction. In the cases of two of the structures there is a direct comparison between old photographic data and modern counter data. The third structure shows the potential of the more accurate counter data by yielding interatomic distances with standard deviations as low as 0.003 A.

PART I. CRYSTAL STRUCTURE OF PALLADIUM DIMETHYLGLYOXIME[1]

Introduction

Palladium dimethylglyoxime was found to be isomorphous with nickel dimethylglyoxime by Godycki and Rundle (1). Wohlauer (2) made an X-ray diffraction and infrared spectroscopic study of palladium dimethylglyoxime. The X-ray diffraction results were unsatisfactory. The structure contains a very short, possibly symmetrical, hydrogen bond, and it was decided to analyze Wohlauer's X-ray results to see if a more accurate structure could be obtained. The molecular configuration of palladium dimethyl-glyoxime and nickel dimethylglyoxime is shown in Figure 1.

Analysis of Wohlauer's Data

The three-dimensional X-ray intensities of Wohlauer were taken on a Weissenberg instrument by the equi-inclination method. The multiple film packs were judged against a standard set of spots obtained by exposing the same reflection for varying lengths of time. After correction for Lorenz and polarization factors, the data were subjected to least squares treatment beginning with the nickel dimethylglyoxime model. The least squares treatment was unsatisfactory, with the discrepancy index remaining at 22%.

The IBM 650 least squares program of Senko and Templeton[2] had become

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[1]This part has been published in abbreviated form in *Journal of the American Chemical Society* 81, 755 (1959).

[2]Senko, M. E. and Templeton, D. H. University of California (Berkeley). Crystallographic least squares program LS-2. Private communication. 1956.
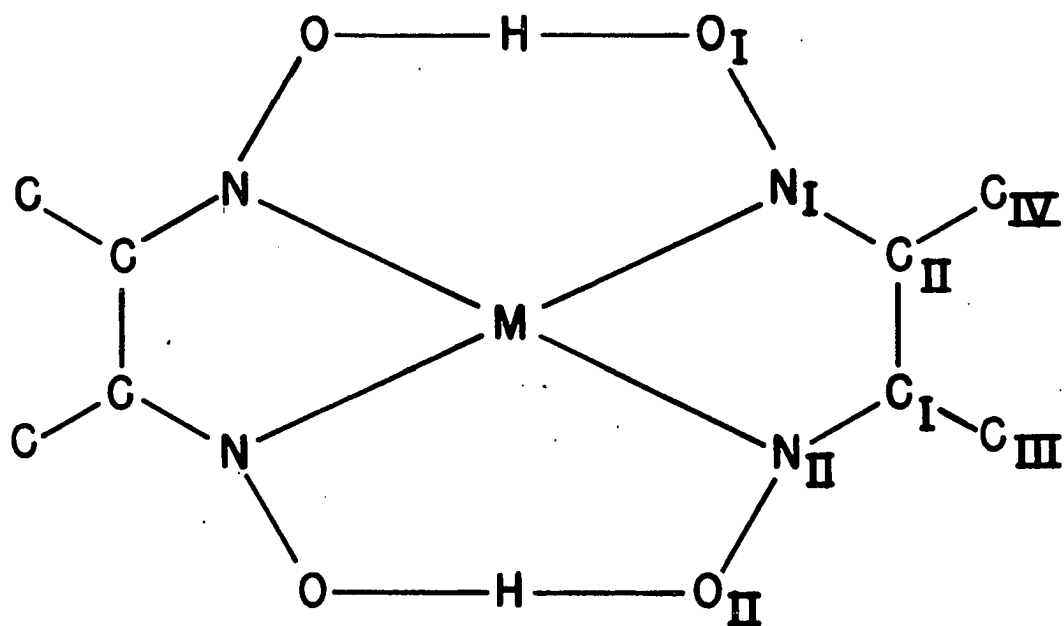
Figure 1.   The molecular configuration of palladium dimethylglyoxime and nickel dimethylglyoxime

available to us. An attempt to refine Wohlauer's data with this program led to immediate divergence, with the discrepancy index rising from 16% to 20% in three cycles of the (hk0) data.

Proportional Counter Intensity Data

New intensity data for palladium dimethylglyoxime were taken using a Norelco proportional counter. The (hk0) and (hkl) zones were measured by the omega scan equi-inclination method. An absorption correction was made based on a cylindrical approximation of the crystal shape.

The lattice constants were remeasured by the back reflection Weissenberg method. The new constants, along with Wohlauer's constants and Godycki's constants for the nickel compound are given in Table 3.

Refinement of Palladium and Nickel Dimethylglyoximes

The anomalous dispersion correction (3) had been neglected in the previous treatment of the nickel dimethylglyoxime data. Also, better computing facilities had become available, so it was decided to refine the two structures side by side using the IBM 650 program of Senko and Templeton. Table 1 lists the old and new values of the atomic parameters for the two structures. Table 2 lists the old and new values of the intramolecular distances. Table 4 lists the observed and calculated structure factors for the new data.

Table 1. Atomic parameters of nickel and palladium dimethylglyoximes

		Nickel dimethylglyoxime			Palladium dimethylglyoxime		
Atom	Parameter	Godycki	Williams	Std. dev.[a]	Wohlauer	Williams	Std. dev.[a]
M	x	.000	.0000	.0000	.0000	.0000	.0000
	y	.000	.0000	.0000	.0000	.0000	.0000
	B	6.46	4.83		5.26	2.58	
O_I	x	.158	.1577	.0009	.1620	.1618	.0012
	y	.098	.0991	.0014	.0962	.0960	.0020
	B	6.46	7.16		7.07	4.41	
O_{II}	x	.053	.0543	.0009	.0552	.0500	.0012
	y	.260	.2589	.0015	.2545	.2654	.0021
	B	6.46	7.50		6.89	4.92	
N_I	x	.114	.1111	.0009	.1125	.1179	.0013
	y	.986	.9931	.0019	.9853	.9901	.0025
	B	6.46	6.29		7.39	3.79	
N_{II}	x	.988	.9909	.0011	.9730	.9868	.0014
	y	.178	.1765	.0014	.2027	.1829	.0022
	B	6.46	6.01		8.03	3.83	
C_I	x	.082	.0808	.0013	.0892	.0864	.0017
	y	.778	.7741	.0022	.7724	.7744	.0028
	B	6.46	7.22		6.56	3.76	
C_{II}	x	.146	.1440	.0013	.1490	.1471	.0018
	y	.883	.8813	.0020	.8720	.8748	.0028
	B	6.46	6.52		7.52	3.89	
C_{III}	x	.102	.0988	.0015	.1023	.1076	.0019
	y	.636	.6334	.0024	.6345	.6305	.0031
	B	6.46	8.38		8.03	4.64	
C_{IV}	x	.232	.2348	.0015	.2358	.2373	.0020
	y	.854	.8575	.0023	.8502	.8522	.0031
	B	6.46	7.97		7.75	4.87	

[a]The standard deviations listed refer to the new values only.

Table 2. Intramolecular distances in the nickel and palladium
dimethylglyoximes

Distance	Nickel dimethylglyoxime			Palladium dimethylglyoxime		
	Godycki	Williams	Std. dev.[a]	Wohlauer	Williams	Std. dev.[a]
$M\text{-}N_I$	1.90	1.85	.015	1.92	1.99	.020
$M\text{-}N_{II}$	1.87	1.85	.015	2.17	1.93	.021
$O_I\text{-}O_{II}$	2.44	2.40	.021	2.46	2.59	.030
$O_I\text{-}N_I$	1.38	1.35	.023	1.43	1.33	.031
$O_{II}\text{-}N_{II}$	1.37	1.36	.023	1.50	1.37	.031
$N_I\text{-}C_{II}$	1.20	1.29	.028	1.31	1.31	.038
$N_{II}\text{-}C_I$	1.25	1.30	.028	1.14	1.31	.037
$C_I\text{-}C_{II}$	1.53	1.54	.031	1.46	1.47	.041
$C_I\text{-}C_{III}$	1.51	1.50	.033	1.46	1.55	.044
$C_{II}\text{-}C_{IV}$	1.46	1.53	.033	1.49	1.54	.045

[a]The standard deviations listed refer to the new values only.

Table 3. Lattice constants of nickel and palladium dimethylglyoximes

Constant	Nickel dimethylglyoxime	Palladium dimethylglyoxime	
	Godycki	Williams	Wohlauer
a	16.68	16.85	17.01
b	10.44	10.49	10.47
c	6.49	6.52	6.50

Table 4. Observed and calculated structure factors for palladium dimethylglyoxime

The three columns comprising each section are, from left to right, the h index, the observed and the calculated structure factors respectively. Unless noted otherwise the signs of the calculated structure factors are positive. All structure factors are multiplied by ten

h00

2	246	287
4	133	112
6	165	175
8	210	199
10	98	99
12	118	119
14	73	75
16	55	61
18	59	64
20	38	49

h10

3	116	106
5	209	202
7	226	221
9	143	133
11	98	100
13	107	111
15	61	69
17	60	63
19	42	48

h20

0	110	116
2	101	94
4	91	88
6	199	197
8	176	178
10	127	126
12	86	85
14	67	73
16	65	67
18	58	59
20	31	37

h30

1	167	171
3	151	149
5	79	73
7	125	122
9	126	132
11	99	95
13	34	40
15	65	71
17	60	67
19	44	51

h40

0	141	145
2	234	250
4	167	159
6	86	86
8	89	91
10	120	120
12	58	60
14	56	68
16	67	69
18	45	47

h50

1	177	173
3	176	182
5	95	96
7	98	111
9	164	164
11	107	107
13	54	57
15	62	66
17	50	54
19	28	34

h60

0	118	125
2	119	121
4	130	136
6	110	101
8	151	146
10	115	108
12	55	63
14	53	57
16	57	61
18	36	41

h70

1	114	111
3	110	102
5	105	103
7	92	92
9	84	79
11	34	42
13	53	54
15	51	53
17	43	48

h80

0	139	134
2	90	83
4	50	50
6	59	63
8	79	77
10	55	51
12	48	48
14	45	43
16	37	39

h90

1	86	83
3	53	48
5	54	56
7	81	73
9	65	58
11	60	57
13	51	50
15	31	37

h·10·0

0	82	73
2	75	64
4	61	51
6	83	73
8	66	57
10	57	51
12	47	44

h·11·0

1	82	68
3	64	56
5	61	55
7	62	57
9	47	45
11	35	38

h·12·0

0	52	47
2	48	47
4	50	47
6	45	43

Table 4. (Continued)

The three columns comprising each section are, from left to right, the h index, the observed and the calculated structure factors respectively. Unless noted otherwise the signs of the calculated structure factors are positive. All structure factors are multiplied by ten

h11			h31			h51			h81		
2	55	53	2	17	7	2	35	37	1	14	16
6	41	50	4	48	46	6	19	22	3	19	22
8	51	53	6	12	14	8	15	23	5	24	20
10	25	30	10	28	33						
12	20	21	14	22	28	h61			h91		
14	22	30									
			h41			1	14	15	2	25	23
h21						3	52	53	4	17	15
			1	43	49	5	19	11	6	20	20
1	19	18	3	14	16	11	19	14			
3	37	27	5	22	24						
5	69	69	7	35	30	h71					
7	8	7	9	10	15						
9	34	35				2	15	14			
						6	19	20			
						8	22	24			

Nickel dimethylglyoxime

The refinement of Godycki's data showed that his results were essentially correct. The largest shifts obtained in the atomic parameters were less than three standard deviations from Godycki's values, based on his standard deviations. The new standard deviations are somewhat smaller, but only in one case are Godycki's values more than three standard deviations away from the new values, using the new standard deviations.

Similarly, only rather small shifts were obtained in the bond distances. These changes were generally in the direction of making the

molecule more symmetrical, and bringing the distances into closer agreement with the values predicted from other known structures.

The nickel-nitrogen distances became symmetrical at 1.85 A, as did also the nitrogen-carbon distances of 1.29 and 1.30 A. The C_{II}-C_{IV} single bond, which Godycki found to be 1.46 A, increased to a more reasonable 1.53 A. The very short hydrogen bond became even slightly shorter at 2.40 A. The C_I-C_{II} bond remained slightly long at 1.54 A. This bond between two trigonal carbon atoms would be expected to be about 1.48 A (4).

Palladium dimethylglyoxime

Refinement of the new counter data indicated significant changes from the results of Wohlauer. Several large shifts from Wohlauer's parameters were obtained, one of them almost ten standard deviations, based on the new standard deviations. The new discrepancy factor obtained for the counter data was 6.5%. It appeared that Wohlauer's values should be discarded as inaccurate.

Discussion

The palladium dimethylglyoxime molecule appears to be less symmetrical than the nickel compound. The two crystallographically different Pd-N distances and N-O distances differ from each other; the difference is three standard deviations for the Pd-N distances. The hydrogen bonded O-O distance in the palladium compound is also significantly greater than the corresponding distance in the nickel compound. The observed difference in symmetry would be the expected result if the nickel compound possessed a symmetrical hydrogen bond and the palladium compound an unsymmetrical one,

leading to nonequivalence of N-O and Pd-N distances in the latter. It has been estimated by Huggins (5) that at hydrogen bonded distances of 2.65 A and below, the hydrogen bond should become symmetrical. While this work is consistent with a symmetrical hydrogen bond for the nickel compound, the apparent lack of symmetry in the palladium compound would seem to indicate that Huggins' critical distance is perhaps somewhat high. The value obtained for the C_I-C_{II} distance (1.47 A) is closer to expectation for the palladium compound than for the nickel compound.

PART II.   CRYSTAL STRUCTURE OF BIS(M-BROMOBENZOYL)METHANE[1]

Introduction

The dibenzoylmethanes have been the subject of considerable study
because of their strong hydrogen bonding and their ability to chelate
with a variety of metal ions.   Infrared spectroscopy has been one of the
principal tools used to study both the parent compounds and their
chelates, along with studies of substituent effects on the ionization
constants.   In addition, several X-ray studies of the chelates have been
made.   It has been established that these β-diketones exist primarily in
the enol form, but whether the enol is symmetrical or not has remained a
matter of conjecture.

Dibenzoylmethane, bis(m-chlorobenzoyl)methane, and bis(m-
bromobenzoyl)methane crystallize in three different space groups, with
the halogen substituted compounds having unit cells of about half the
volume of the unit cell of dibenzoylmethane itself.   Preliminary evidence
indicated that the chloro derivative lacked a center of symmetry.   Crystals
of the bromo derivative were found to possess a center of symmetry, and
the molecule also has twofold symmetry in the crystal, reducing the number
of parameters.   The bromo derivative has a sufficiently heavy atom to
make the initial phases of the structure determination simple, but heavy
enough to be less than ideal for obtaining precise distances between the
lighter atoms.

Collection and Treatment of X-ray Data

Bis(m-bromobenzoyl)methane was prepared by reaction of m-bromoacetophenone with ethyl m-bromobenzoate in the presence of sodium amide (6). Crystals suitable for X-ray analysis, in the form of thin needles, were obtained by recrystallization from chloroform. Weissenberg and precession photographs indicated the unique space group Pnca, with lattice constants

$$a = 26.48, \ b = 4.054, \ c = 12.79 \ A.$$

The observed flotation density was 1.8 g/cc; for four molecules in the unit cell the calculated density is 1.85 g/cc.

Complete visually judged Weissenberg intensity data were taken using copper radiation, with rotation about the b (needle) axis. In addition to the usual Lorentz and polarization corrections, a beam divergence correction (7) was made, but no absorption correction was made. These data were used for the structure determination; however, because of the relatively high diffracting power of bromine, they were not of sufficient quality to obtain accurate bond distances between the light atoms in this structure.

For the refinement of the atomic positions a new set of data was obtained by counter methods, using a different crystal. The crystal selected for counter measurements was a needle 0.24 mm in length and of equilateral trapezoidal cross section. The thickness perpendicular to the parallel faces was 0.055 mm; the long parallel face measured 0.075 mm, and the short parallel face measured 0.048 mm. A General Electric XRD-5

X-ray unit equipped with a single crystal orienter and scintillation counter was used with the moving crystal-moving counter technique (θ, 2θ coupling), 3.0° take off angle and a 2.2° diffracted beam aperture. To eliminate errors involved in planimetering rate meter charts, the total count was recorded directly from the scaler. The copper radiation was filtered through nickel foil placed in the diffracted beam path. A 200 second scan, covering 3.33° in 2θ, was used for each reflection; average rate was ten reflections per hour. A standard reflection (24, 0, 0) was taken periodically and all data scaled to it. A slow variation of about 25% was observed in the standard reflection; this variation was probably caused by a faulty X-ray tube, which also showed about 25% iron radiation. Single crystal orienter settings were precalculated on the IBM 650 computer[1]. The background for each reflection was estimated from a plot of average background versus 2θ. All reciprocal lattice points up to $\theta = 77.5°$ were scanned, resulting in 839 observed and 615 unobserved reflections.

The estimated error of each intensity was calculated with the formula

$$\sigma^2(I_o) = C_T + C_B + [0.04(C_T - C_B)]^2 + [0.1C_B]^2 ,$$

where $\sigma(I_o)$ is the standard deviation of the observed intensity, C_T are the total counts, and C_B are the background counts. The first two terms in this formula represent the statistical counting error. The third term represents errors proportional to the net count, e.g., fluctuations in

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[1]Tulinsky, A. Yale University, New Haven, Connecticut. Single crystal orienter angles program. Private communication. 1960.

the beam intensity, errors in the absorption correction, etc. This term
sets a lower limit of 4% in the estimated relative error of I_o when
statistical counting errors and background errors become negligible. The
last term adds an error contribution caused by uncertainty in the
graphically estimated background count. Unobserved reflections were
assigned their probable intensity value and probable error depending on
the minimum intensity observable at the reciprocal lattice point in
question (8). Graphical corrections were made for those reflections most
seriously affected by noncharacteristic radiation (streaking) or by the
iron radiation component. The streaking correction subtracts from the
observed intensity, in addition to the normal background, the amount
contributed by the streak from reflections radially inward in the
reciprocal lattice. This correction can be relatively quite important
in those cases where a weak reflection is immediately outward radially
from a strong reflection. The streak may extend outward through several
reflections, so that the correction is cumulative. On the other hand,
the inward-extending shorter wave length streak (including the $\lambda/2$
component) is less important and its correction was neglected. The
Lorentz and polarization corrections were made in the usual way. No
extinction correction was used.

Absorption correction

With the more accurate counter data the absorption correction could
not be neglected. Attempts to grind spherical or ellipsoidal crystals
failed. It was decided, therefore, to carry out the necessary integration
for each reflection on the Cyclone computer. An absorption correction

correction program, designated ABCOR-I, was written for this purpose.

The mathematical method used was similar to that used previously (9), but

generalized to three dimensional data, and with the number of integration

grid points, m, variable from m = 4 to m = 7. Because of memory restric-

tions (only 1,024 words of memory were available on the Cyclone), it was

necessary to restrict the planes bounding the crystal to be either

parallel or perpendicular to the goniometer head axis, a condition

frequently met in practice, as it is indeed in this case. The crystal

coordinate system was defined by taking the y axis toward the X-ray source,

the z axis vertical, and the x axis toward the front of the orienter,

when $\emptyset = \chi = \Theta = 0$. The planes bounding the crystal were expressed on this

basis. For a general single crystal orienter setting $(\emptyset, \chi, \Theta)$, the

direction cosines of the incident beam vector, transformed to crystal

coordinates, are:

$$p_x = \cos\emptyset \cos\chi \sin\Theta - \sin\emptyset \cos\Theta ,$$

$$p_y = \sin\emptyset \cos\chi \sin\Theta + \cos\emptyset \cos\Theta ,$$

$$p_z = \sin\chi \sin\Theta.$$

The direction cosines of the diffracted beam vector are:

$$p_x = \cos\emptyset \cos\chi \sin\Theta + \sin\emptyset \cos\Theta ,$$

$$p_y = \sin\emptyset \cos\chi \sin\Theta - \cos\emptyset \cos\Theta ,$$

$$p_z = \sin\chi \sin\Theta.$$

The incident and diffracted beam path lengths to each grid point may then

be found with the formulas given in Busing's paper, and the integral

evaluated. The calculated absorption coefficient of 68.1 cm^{-1} was used

(10). To check the accuracy of the integration, the absorption correction

for a selected group of 11 reflections was calculated with m = 4, 5, and

6. The maximum difference between the m = 4 case and the m = 6 case was

0.96%, with an average of 0.22%. The maximum difference between the m =

5 case and the m = 6 case was 0.23%, with an average of 0.15%. It was

decided that m = 4 would provide sufficient accuracy. The value of the

transmission factor varied from 0.45 to 0.72, with an average near 0.65.

Each integration with m = 4 required approximately 6 seconds on the

Cyclone computer. Absorption corrections for the unobserved reflections

were obtained graphically.

For carbon and oxygen the scattering factors of Berghuis et al. (11)

were used; for bromine the scattering factor of Thomas and Umeda (12),

corrected for anomalous dispersion (3), was used.

Structure Determination

The projection onto the (010) plane, which has no overlapping atoms,

was solved first. The approximate bromine parameters were obtained from

the two dimensional Patterson function. After improving the bromine

parameters by calculation of an electron density projection, the oxygen

and all carbon atoms were placed in approximate positions based on a

planar molecular model with assumed distances and angles. After several

cycles of structure factor calculation and electron density projection

all atoms were well defined. The projection was then refined by the

least squares method.

The Patterson projection onto the (001) plane indicated a bromine y parameter of 1/4; however, a planar model based on this bromine y parameter diverged during attempted refinement by the least squares method. The situation was complicated by an ambiguity which remained from the (010) projection, which made possible the substitution of new z parameters $z' = 1/4 - z$ without affecting the fit to the (h0ℓ) reflections. A bounded Fourier electron density projection between $x = 0$ and $x = 1/4$ onto the (100) plane suggested that the bromine was shifted away slightly from $y = 0.25$ but did not indicate which way. The problem was solved by attempting to refine a large number of models having a bromine y parameter shifted by varying amounts both ways from $y = 0.250$, using a limited number of reflections with the ℓ index odd, and with the z transformation referred to above. Finally a model was found which would converge. The complete three dimensional film data were then refined by the least squares method (43 parameters); the final unweighted discrepancy factor was 0.155 for 587 observed reflections. The standard deviations of distances between light atoms were rather large, about 0.05 A, with the film data. It was decided to obtain more accurate intensity data using a scintillation counter.

Fourier calculations were made on the IBM 650 using the program of Fitzwater and Williams (13); least squares calculations, primarily using only diagonal matrix elements, with individual isotropic temperature factors and layer scale factors, were also made on the IBM 650 using the

program of Senko and Templeton[1].

Refinement of the scintillation counter data

The complete matrix program of Busing and Levy (14), for the IBM 704, was used for refinement of the scintillation counter data, using individual anisotropic temperature factors and a single scale factor (87 parameters). Convergence was obtained after four anisotropic cycles with a weighted discrepancy factor, including unobserved reflections, of 0.113. However, a study of the individual structure factors revealed unusually poor agreement, greater than six times the expected error, for 26 reflections. These reflections were given zero weight for the following three least squares cycles, which resulted in a drop of the weighted discrepancy factor, including unobserved reflections, to 0.068.

The intensities of the group of reflections showing poor agreement were remeasured, using a different crystal (the original crystal was accidentally lost). A marked improvement in the agreement between observed and calculated values of the intensities was noted in nearly every case. These remeasured intensities, plus the rest of the original data, were used to calculate three dimensional electron density and difference Fourier maps, using the IBM 650. These maps verified the correctness of the model by revealing no spurious holes or peaks in the electron density distribution. Both the electron density and difference maps clearly showed the presence of five of the six hydrogen atoms in the

[1]Senko, M. E. and Templeton, D. H. University of California (Berkeley). Crystallographic least squares program LS-2. Private communication. 1956.

asymmetric unit, the exception being the enolic hydrogen.

For the final refinement of the revised data these hydrogens were included isotropically at calculated positions along a line parallel to the intersection of the least squares benzene ring plane and the bisector plane between the neighboring ring atoms at a distance of 1.08 A from the attached carbon atoms. The C_8 hydrogen was placed on the twofold axis 1.08 A from C_8. At the end of the final two least squares refinement cycles the weighted discrepancy factor, including unobserved reflections, was 0.071; the unweighted discrepancy factor for 839 observed reflections was 0.057. Table 5 gives the final values of the parameters and their standard deviations. The quantity

$$[\Sigma w(F_o-F_c)^2/(m-n)]^{\frac{1}{2}}$$

was 1.48, indicating a reasonable assignment of weighting factors. All standard deviations quoted in this paper are based on the complete inverse matrix including covariances; analysis of the data was greatly facilitated by use of the IBM 704 Function and Error program of Busing and Levy (15). Figure 2 gives a comparison of the observed structure factors and the calculated structure factors based on the parameters shown in Table 5.

Discussion

The structure consists of nearly planar molecules, with their long axis along a and short axis along c, tilted $\pm$ 29.9° from the (010) plane (Figure 3). Least squares planes were fitted through the benzene ring (A), the enol ring (B), and the entire molecule (C); Table 6 shows the

Table 5. Final values of the parameters and their standard deviations. The form of the temperature factor is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}{}^2 - 2\beta_{12}hk - 2\beta_{13}h - 2\beta_{33}k)$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.03607	0.2306	0.15544	0.00107	0.0695	0.00737	-0.00052	0.00083	0.0007
σ	0.00003	0.0003	0.00007	0.00001	0.0006	0.00006	0.00009	0.00002	0.0002
O	0.2097	0.848	0.2068	0.00193	0.175	0.0023	-0.0083	0.0000	-0.001
σ	0.0002	0.002	0.0004	0.00009	0.009	0.0003	0.0008	0.0001	0.001
C_1	0.0883	0.399	0.0684	0.00080	0.054	0.0057	0.0007	0.0001	0.002
σ	0.0002	0.002	0.0006	0.00008	0.005	0.0005	0.0006	0.0002	0.001
C_2	0.1291	0.553	0.1166	0.00106	0.042	0.0039	0.0005	0.0002	-0.002
σ	0.0002	0.002	0.0005	0.00009	0.005	0.0004	0.0005	0.0001	0.001
C_3	0.1678	0.683	0.0546	0.00099	0.045	0.0033	0.0012	0.0001	-0.002
σ	0.0002	0.002	0.0005	0.00008	0.005	0.0003	0.0005	0.0001	0.001
C_4	0.1648	0.651	0.9450	0.00110	0.071	0.0040	0.0006	0.0000	0.000
σ	0.0002	0.002	0.0005	0.00009	0.007	0.0004	0.0006	0.0001	0.001
C_5	0.1234	0.494	0.9005	0.0015	0.075	0.0044	-0.0008	-0.0005	0.000

Table 5. (Continued)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
σ	0.0003	0.002	0.0005	0.0001	0.006	0.0004	0.0007	0.0002	0.002
C_6	0.0843	0.366	0.9618	0.0013	0.072	0.0050	-0.0009	-0.0006	0.000
σ	0.0003	0.002	0.0005	0.0001	0.007	0.0005	0.0007	0.0002	0.001
C_7	0.2101	0.850	0.1047	0.0013	0.078	0.0036	0.0004	-0.0002	-0.002
σ	0.0003	0.002	0.0005	0.0001	0.007	0.0004	0.0007	0.0002	0.001
C_8	0.2500	0.000	0.0520	0.0011	0.067	0.0028	-0.0005	0.0000	0.000
σ				0.0007	0.0001	0.008	0.0005	0.0009	
H_2	0.1308	0.574	0.2007	0.0018	0.076	0.0076			
H_4	0.1945	0.749	0.8962	0.0018	0.076	0.0076			
H_5	0.1212	0.471	0.8163	0.0018	0.076	0.0076			
H_6	0.0524	0.245	0.9262	0.0018	0.076	0.0076			
H_8	0.2500	0.000	0.9676	0.0018	0.076	0.0076			

Figure 2. Comparison of the observed structure factors and the
           calculated structure factors based on the parameters
           shown in Table 5

Figure 2.   (Continued)

Figure 3.   (a) Projection of the structure of the (010) plane,
including all hydrogens except the enolic hydrogen in
calculated positions
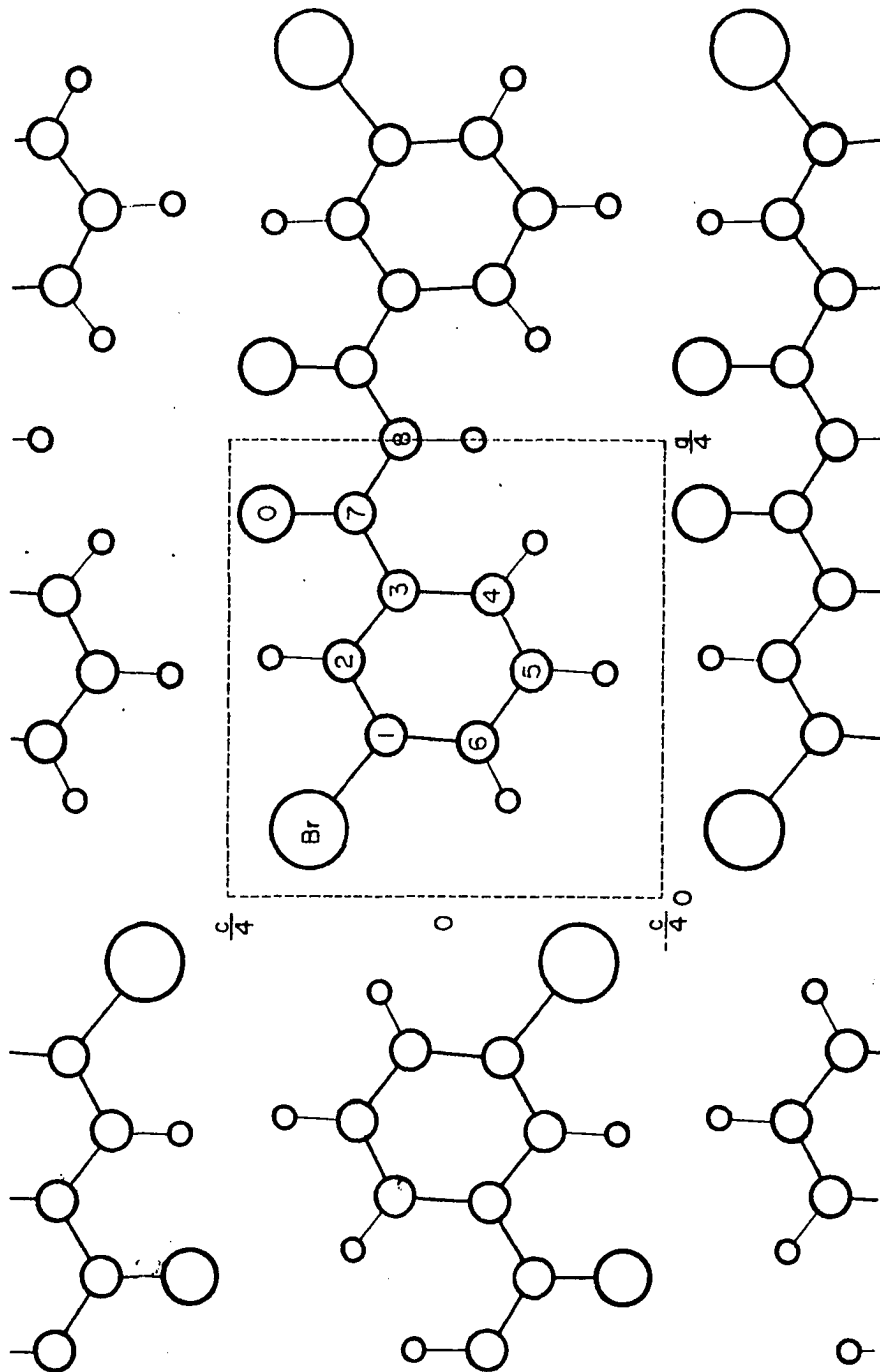
Figure 3.   (b) Projection of the structure onto the (001) plane, with
            hydrogens omitted for clarity. The light circles represent
            atoms behind the asymmetric unit, and the dotted circles
            represent atoms in front. The asymmetric unit is enclosed
            in dashed lines
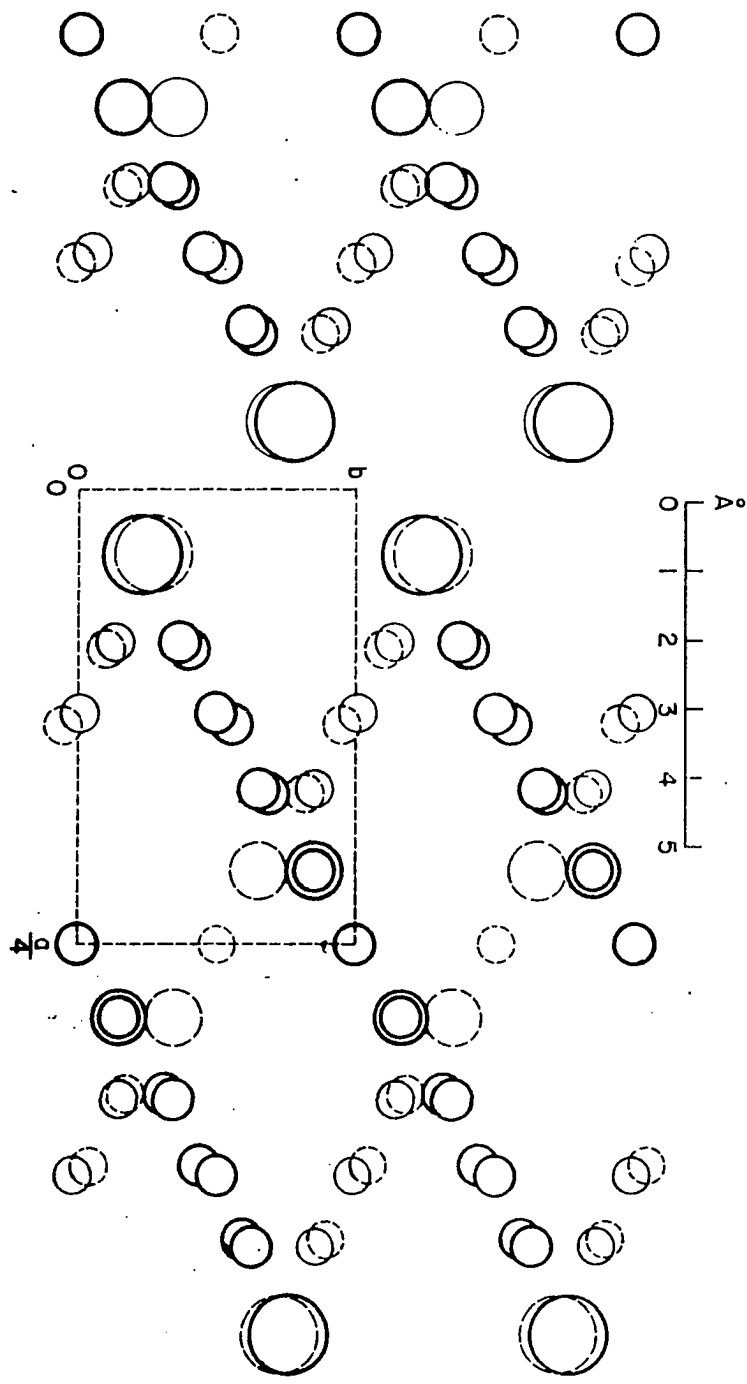
Table 6. Distances from the least squares planes and equations of
the planes in A units

Atom	A	B	C
Br	0.014	0.124	0.120
O	-0.041	-0.001	-0.001
C_1	0.001	0.026	0.022
C_2	-0.005	0.026	0.023
C_3	0.005	-0.026	-0.028
C_4	-0.002	-0.100	-0.102
C_5	-0.002	-0.104	-0.108
C_6	0.003	-0.038	-0.042
C_7	0.025	0.001	0.000
C_8	0.082	0.000	0.000

(A) $- 1.9794x + 3.5972y - 0.1270z = 1$

(B) $- 2.3866x + 4.1438y + 0.0000z = 1$

(C) $- 2.2797x + 3.9642y + 0.0000z = 1$

distances of the atoms from each plane and the equations of the planes in
A units. Both the benzene ring and the enol ring are planar within
experimental error; the maximum deviation of the entire molecule from its
least squares plane is 0.120 A, with the bromine atom being above the
plane, and C_4, C_5, and C_6 being below the plane. The inclination of the
benzene ring from the molecular plane is $\pm$ 1.7°. The intramolecular

distances and angles (Table 7), which are uncorrected for thermal motion, are all very close to the expected values, with an average benzene ring C-C distance of 1.394 A. The C-O bond (1.306) is intermediate between the normal $C = O$ (1.23) and C-O (1.43) distances, but perhaps slightly longer than expected for 50% double bond character (1.29). The C_7-C_8 distance (1.393) is the same as the C-C distances in the benzene ring within experimental error, and is considerably shorter than the normal single bond value. The C_3-C_7 distance (1.457) is also shorter than the single bond value, but in good agreement with a single bond C-C between carbons with planar trigonal coordination (4). The short O-O distance of 2.464 A confirms the presence of a strong hydrogen bond; the standard deviation for this distance is larger than the others because of the larger thermal motion and the twofold symmetry relationship between these atoms. The Br-C_1 distance (1.901 $\pm$ 0.007) is longer than the corresponding distance observed by electron diffraction methods in bromobenzene (1.86 $\pm$ 0.02), (16), or in p-fluorobromobenzene (1.87 $\pm$ 0.02), (17), or observed crystallographically in 1,3,5-tribromobenzene (1.86 $\pm$ 0.04), (18). The Br-C_1 distance is especially sensitive to systematic errors, which cause ripples in the electron density map in the vicinity of the heavy atom; during the process of refining the various sets of data this effect was noticed as erratic changes in this distance until the final cycles. In view of this fact, and of the rather large standard deviations reported in the literature cited above, no significance is attached to the difference between the value found here and those cited above.

The nearest nonbonded neighbors distance (Table 8), based on the

Table 7. Intramolecular bond distances and bond angles

Atoms	Distance	Atoms	Angle
Br-C_1	1.901 ± 0.007 A	Br-C_1-C_2	117.8 ± 0.5°
C_1-C_2	1.392 ± 0.009	C_6-C_1-C_2	122.7 ± 0.7
C_2-C_3	1.400 ± 0.009	C_6-C_1-Br	119.5 ± 0.6
C_3-C_4	1.410 ± 0.008	C_1-C_2-C_3	119.1 ± 0.6
C_4-C_5	1.389 ± 0.010	C_2-C_3-C_7	119.3 ± 0.6
C_5-C_6	1.397 ± 0.010	C_7-C_3-C_4	121.6 ± 0.6
C_6-C_1	1.375 ± 0.009	C_2-C_3-C_4	119.2 ± 0.6
C_3-C_7	1.457 ± 0.009	C_3-C_4-C_5	119.6 ± 0.7
C_7-C_8	1.393 ± 0.008	C_4-C_5-C_6	121.6 ± 0.6
C_7-O	1.306 ± 0.008	C_5-C_6-C_1	117.8 ± 0.7
O-O	2.464 ± 0.015	C_3-C_7-O	115.6 ± 0.6
		C_8-C_7-O	119.4 ± 0.7
		C_3-C_7-C_8	125.0 ± 0.6
		C_7-C_8-C_7	122.2 ± 0.8
		C_7-O-O	89.5 ± 0.8

calculated hydrogen positions, show that the oxygen atom is surrounded by H_2, H_4, and H_5 at 2.37, 2.49, and 2.83 A respectively, which restrict its lateral motion. The closest intermolecular nonbonded approaches are between H_2 and H_5, at 2.38 and 2.67 A. A close intramolecular approach occurs between H_4 and H_8, at 2.01 A, assuming that these hydrogens lie in

Table 8.   Nearest nonbonded neighbor distances less than 3 A

Atoms	Distance (A)	Atoms	Distance (A)	Atoms	Distance (A)
Br-Br	3.689	C_2-C_4	2.42	C_5-H_4	2.15
-C_2	2.83	-C_5	2.78	-H_6	2.16
-C_6	2.84	-C_6	2.43	C_6-H_5	2.14
-H_2	2.93	-C_7	2.46	C_7-C_7	2.44
-H_6	2.96	C_3-C_5	2.42	-H_2	2.68
O -C_2	2.71	-C_6	2.82	-H_4	2.73
-C_3	2.34	-C_8	2.53	-H_8	2.14
-C_7	2.78	-H_2	2.16	C_8-H_4	2.68
-C_8	2.33	-H_4	2.16	H_2-H_5	2.38
-H_2	2.37	-H_8	2.76	-H_5'	2.67
-H_4	2.49	C_4-C_6	2.43	H_4-H_5	2.47
-H_5	2.83	-C_7	2.50	-H_8	2.01
C_1-C_3	2.41	-C_8	2.99	H_5-H_6	2.48
-C_4	2.76	-H_5	2.14		
-C_5	2.37	-H_8	2.68		
-H_2	2.15				
-H_6	2.15				

the planes of the benzene and enol rings respectively. The perpendicular distance between least squares molecular planes is 3.514 A. Table 9 shows the amplitudes and directions of the principal thermal axes, referred to the least squares molecular plane. The standard deviations shown are based on the complete inverse matrix of the normal equations and thus include the effect of covariances. The rather large magnitudes of the standard deviations reflect the fact that the thermal parameters are more sensitive to errors in the experimental data than are the positional parameters. In particular it is seen that small differences in the orientation of the thermal ellipsoids are of no statistical significance. The thermal stereograms (Figure 4) do not show any pronounced oscillation of this rather rigid molecule about its major axes, as would have been expected. Possibly any such motion is masked by systematic errors in the observed light atom vibrations in the presence of the heavy atom, but it seems more likely that they are masked by the peculiarities of the enol ring (see below).

The greatest thermal anisotropy is shown by the bromine and oxygen atoms. The bromine atoms has its minor thermal axis nearly parallel to the Br-C_1 bond, as might be anticipated, with the mean and major axes nearly normal to this bond. These axes are consistent with some motion of the molecule as a whole with relatively large Br-C bending amplitudes.

Of special interest is the thermal stereogram for oxygen. The enol is required by crystal symmetry to have equivalent C-O bonds, but if these were statistically equivalent due to random arrangement of

Figure 4. Thermal stereograms for the atoms, transformed so that the plane of the paper is the least squares molecular plane. The X' axis is in the direction of the longest dimension of the molecule, and the Y' axis is perpendicular to the molecular plane. The directions of the r.m.s. thermal axes are shown stereographically, and the length of the axes are indicated in A
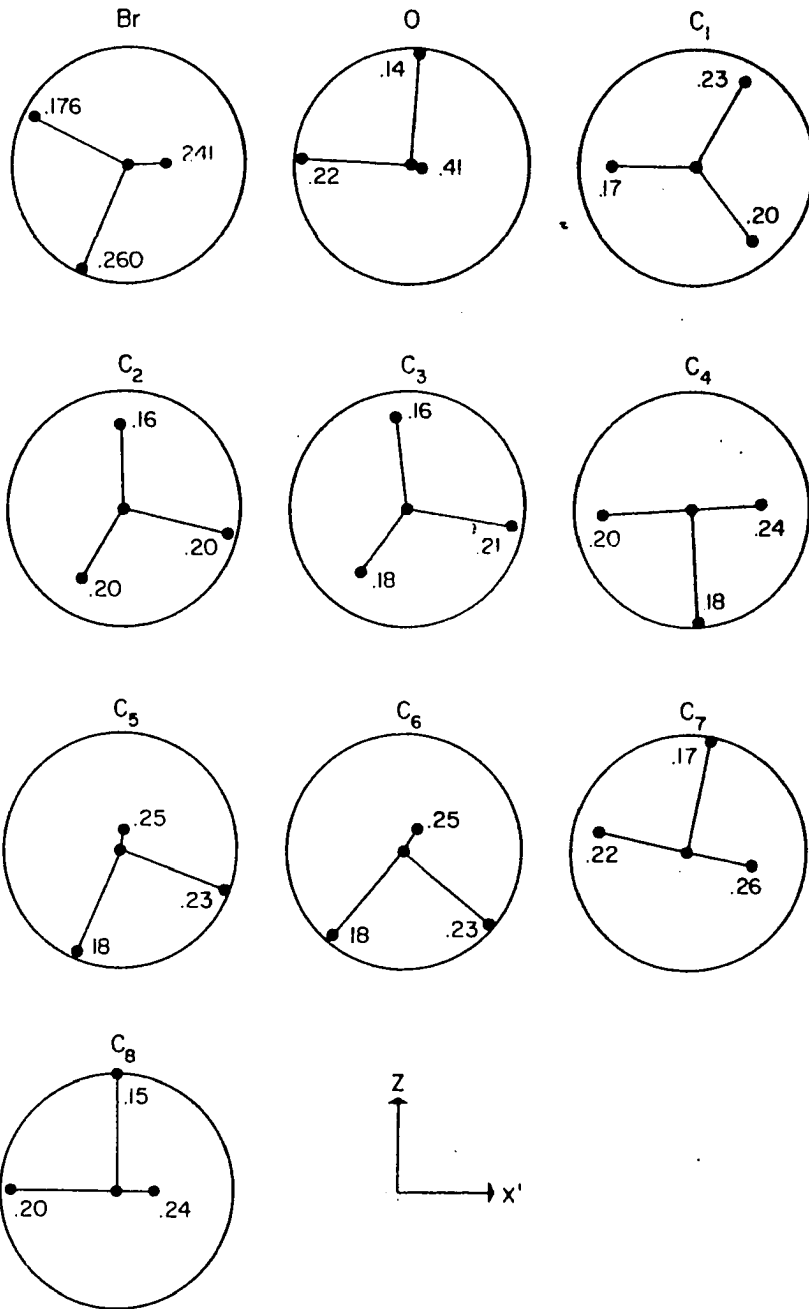
Table 9. Angle $\Theta(I)$ (degrees) between principal thermal axes R and
axes I of a Cartesian coordinate system defined by the least
squares molecular plane

(The X' axis is in the direction of the longest dimension
of the molecule and the Y' axis is perpendicular to the
molecular plane.)

Atom	R	R.m.s. amplitude (A)	$\Theta(X')$	$\Theta(Y')$	$\Theta(Z)$
Br	1	0.176 ± 0.001	32 ± 1	109 ± 1	115 ± 1
	2	0.241 ± 0.001	112 ± 2	158 ± 2	91 ± 3
	3	0.260 ± 0.001	67 ± 2	100 ± 3	25 ± 1
O	1	0.138 ± 0.008	86 ± 4	89 ± 1	4 ± 4
	2	0.219 ± 0.008	174 ± 3	86 ± 2	86 ± 4
	3	0.408 ± 0.010	94 ± 2	176 ± 2	89 ± 1
C_1	1	0.167 ± 0.009	41 ± 11	131 ± 11	90 ± 9
	2	0.202 ± 0.010	60 ± 13	55 ± 14	130 ± 15
	3	0.229 ± 0.010	65 ± 10	61 ± 11	40 ± 15
C_2	1	0.159 ± 0.010	88 ± 11	132 ± 10	137 ± 10
	2	0.198 ± 0.010	158 ± 59	107 ± 13	77 ± 5
	3	0.200 ± 0.009	68 ± 60	132 ± 67	50 ± 47
C_3	1	0.155 ± 0.009	96 ± 9	55 ± 15	36 ± 16
	2	0.180 ± 0.009	114 ± 15	44 ± 15	125 ± 17
	3	0.208 ± 0.010	25 ± 14	67 ± 12	99 ± 10
C_4	1	0.181 ± 0.009	94 ± 21	90 ± 17	4 ± 20
	2	0.196 ± 0.009	142 ± 10	52 ± 9	93 ± 26
	3	0.244 ± 0.012	52 ± 9	38 ± 9	88 ± 7
C_5	1	0.181 ± 0.010	68 ± 9	100 ± 7	24 ± 8
	2	0.233 ± 0.010	158 ± 9	92 ± 21	68 ± 9
	3	0.254 ± 0.011	91 ± 20	170 ± 9	100 ± 11
C_6	1	0.181 ± 0.010	51 ± 9	102 ± 7	42 ± 9
	2	0.228 ± 0.010	140 ± 10	92 ± 22	50 ± 10
	3	0.248 ± 0.011	96 ± 18	168 ± 8	101 ± 16

Table 9. (Continued)

Atom	R	R.m.s. amplitude (A)	θ(X')	θ(Y')	θ(Z)
C_7	1	0.169 ± 0.010	78 ± 8	90 ± 7	12 ± 8
	2	0.217 ± 0.009	142 ± 11	54 ± 11	80 ± 9
	3	0.257 ± 0.012	54 ± 11	36 ± 11	97 ± 6
C_8	1	0.152 ± 0.013	90	90	0
	2	0.196 ± 0.012	161 ± 15	71 ± 15	90
	3	0.238 ± 0.014	109 ± 15	161 ± 15	90
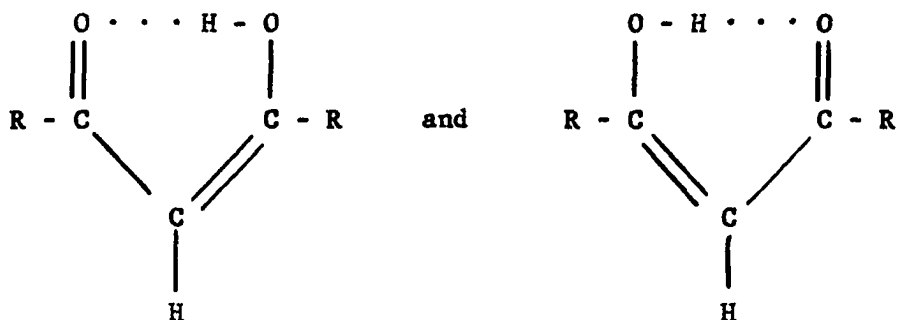
molecules within the unit cell, then the oxygen and neighboring carbon positions should show abnormally large apparent r.m.s. amplitudes parallel to the C-O bonds. This is clearly not so, and the thermal parameters strongly suggest that the two C-O bonds are equivalent, corresponding to resonance between the two forms shown above. All sensitive distances are also more compatible with this interpretation than any other. Note that C-O is 1.306, C_3-C_7 is 1.457 (trigonal single bond), and C_7-C_8 is 1.393 (50% double bond character).

The abnormally low thermal axes in the molecular plane may be the

result of the restriction of the oxygen in this plane due to very close hydrogen neighbors (see above). The very high amplitude out of the molecular plane is, however, unexpected and suggestive of an anomaly.

It is to be noted that $< C_7$-O-O is only $89.5°$, so that $< C_7$-O-H would be abnormally small if H were directly on the line of centers between the oxygen atoms. It seems likely, in the circumstances, that this hydrogen bond is bent, as shown in Figure 5 (a). If this is true, then the very close O-O contact of 2.46 A, among the shortest known for hydrogen bonds, may lead to strong O-O repulsion, and a warping of the oxygen atoms out of the molecular plane as shown in Figure 5 (b), so that the oxygen atoms are at random in positions m or positions n of that figure. This would lead to the apparently very high amplitude normal to the ring. Unfortunately, the X-ray data are not sufficient to confirm this conjecture. This suggestion does, however, have the additional merit that it would lead to some distortion or randomness in the carbon positions near the oxygens, that is, near the center of the molecule, lead-ing to apparently high thermal parameters for the atoms and obscuring the oscillations of this rigid molecule as a whole, which are to be expected. (Possibly the single bond character of C_3-C_7 reduces the rigidity, also giving some extra torsional freedom to the enol ring which would show most clearly in the thermal parameters of the oxygen atoms.)

In spite of the fact that this structure determination seems to settle the nature of the enols, at least of the aromatic β-diketones, the interest in this point and in the short hydrogen bond has caused us to regret the uncertainties introduced by such a heavy atom as bromine. Accordingly,

Figure 5.   (a) Postulated enol ring structure with non-collinear
            hydrogen bond; (b) side view of oxygen atoms showing
            effect of O-O repulsion
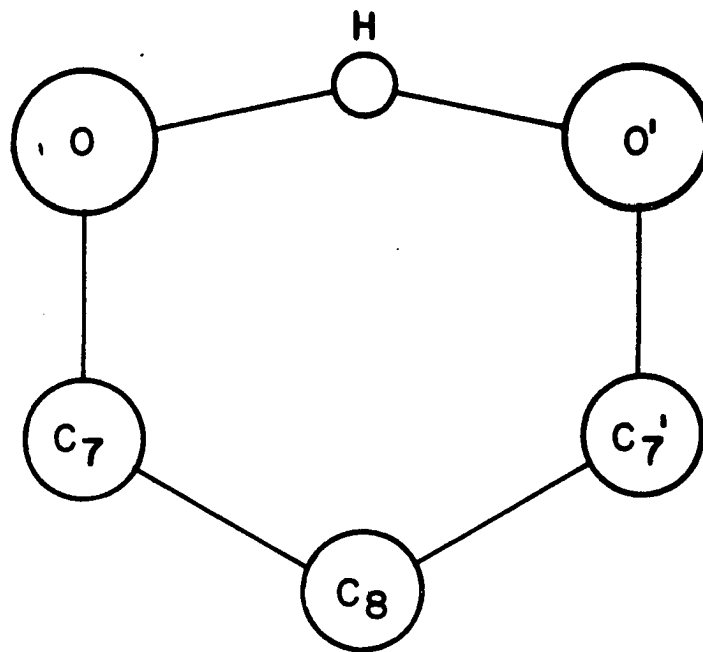
(a)
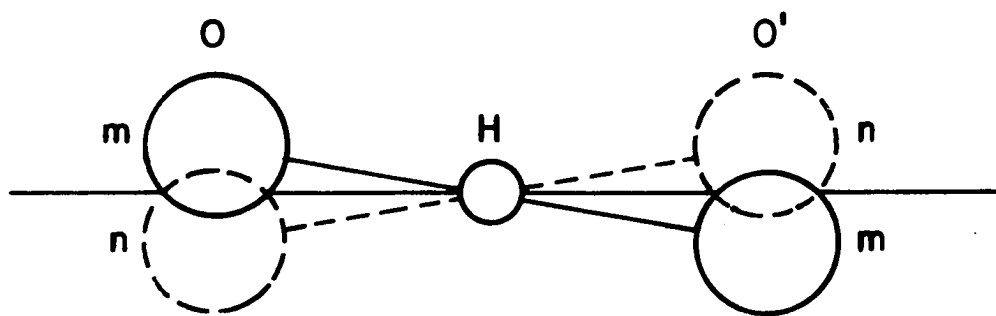
(b)

the structure of the corresponding (but not isomorphous) chloro-derivative is in progress.

This problem was suggested by Prof. G. S. Hammond in connection with his study of hydrogen bonding, lithium chelation, and other properties of these compounds.

PART III.   CRYSTAL STRUCTURE OF 3,4-FURANDICARBOXYLIC ACID[1]

Introduction

The acid dissociation constants of the furandicarboxylic acids have been determined by Oae, Hamada, Otsuji, and Furukawa (19). A very large difference between the values of the first and second ionization constants was found for the 2,3- and the 3,4-diacids. It seemed reasonable to conclude, as did Oae et al., that a very strong intramolecular hydrogen bond existed in 2,3- and 3,4-furandicarboxylic acid. Infrared absorption data also indicated the existence of a short intramolecular hydrogen bond. The present author found that the 3,4-diacid was suitable for an X-ray structural study of the hydrogen bonding in these compounds.

Collection and Treatment of X-ray Data

Dr. Hamada kindly supplied crystals of the disodium salt of 3,4-furandicarboxylic acid. The acid was prepared by acidification with HCl and recrystallization from water solution. The colorless monoclinic needles were found, as the result of the structure determination, to have space group symmetry $P2_1/m$. The lattice constants were obtained by a least squares extrapolation treatment of data for 18 reflections in the back reflection region, using the single crystal orienter with chromium radiation. The single crystal orienter was previously calibrated with an aluminum single crystal. The lattice constants obtained at room tempera-

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[1]This part has been published in substantially identical form in Journal of the American Chemical Society 86, 1660 (1964).

ture are: a = 6.0629 ± 0.0006, b = 3.6677 ± 0.0004, c = 14.4126 ± 0.0014, and γ = 92.60 ± 0.06.

The density calculated on the basis of two molecules in the unit cell is 1.57 g/cc. The crystals were elongated along b, and cleaved easily along ($\bar{1}$10) planes.

Complete three-dimensional X-ray diffraction intensity data (up to sin θ/λ = 1.15) were taken with molybdenum radiation from a crystal approximately 0.30 mm long and 0.18 mm in diameter. A General Electric XRD-5 X-ray unit equipped with a single crystal orienter and scintillation counter was used with the moving-crystal-moving-counter measurement technique (θ, 2θ coupling), 3.0° take-off angle, and a 2.8° diffracted beam aperture. A pulse selector admitted pulses to the scaler between 5 and 15 v., with the pulse distribution being centered in the selector window by varying the supply voltage to the scintillation counter photo-multiplier. A zirconium foil was placed in the diffracted beam path. A 200-sec. scan, covering 3.33° in 2θ was used for each reflection, followed by a repeat scan for background with an omega offset of 1.8°; all angles were set by hand and the average rate of measurement was six reflections per hour. Two standard reflections, (010) and (006), were measured periodically; the intensity of these reflections remained constant within ± 3%. Single crystal orienter settings were precalculated[1] on the Cyclone computer. A total of 768 reflections was measured.

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[1]Williams, D. E. Ames, Iowa. Single crystal orienter program SCO-5. Unpublished research. 1961.

Streak correction

With the experimental conditions used a considerable amount of non-characteristic radiation in the wave length range $\lambda_k < \lambda < 2\lambda_k$ was admitted into the counter window. This "streaking" is more intense with a molybdenum target tube than with a copper target tube for the usual experimental conditions. The ratio of characteristic to noncharacteristic radiation is highest when the applied voltage is approximately four times the excitation voltage of the target used (20, p. 59). For copper and molybdenum targets the optimum applied voltages are 36 and 80 kv. d.c., respectively. Since our present power supplies and X-ray tubes are limited to 50 kv. pk., Mo target tubes show a considerably lower characteristic to noncharacteristic radiation ratio than Cu target tubes.

Streaking may be eliminated by use of a crystal monochromator, but only with a large loss of incident beam intensity. Also, balanced filters (Ross filters) may be used to isolate the characteristic radiation component, although much less completely than with a crystal mono-chromator. This method is tedious since the filters must be accurately balanced, and it is necessary to make two intensity measurements and two background measurements for each reflection.

If, however, the noncharacteristic intensity distribution of the X-ray source is measured, a streak correction may be routinely applied to the observed data to eliminate noncharacteristic radiation components.

If the observed counting rate in the neighborhood of the character-istic wave length is approximated by a Gaussian, the observed integrated intensity I_k is

$$I_k = \int_{-\infty}^{+\infty} P_k \exp\left[-(\ln 2)\theta_{\frac{1}{2}}^{-2} (\theta_k-\theta)^2\right] d\theta$$

$$= P_k \pi^{\frac{1}{2}} (\ln 2)^{-\frac{1}{2}} \theta_{\frac{1}{2}}$$

where P_k is the peak counting rate, θ_k is the characteristic Bragg angle, and $\theta_{\frac{1}{2}}$ is the half-width at half-height of the Gaussian. This approximation assumes that the scan length is long enough that the value of the integrand is negligible outside the scan range. The wave length range, $\Delta\lambda_k$, is associated with the half-width constant, $\theta_{\frac{1}{2}}$. The observed integrated streak intensity, I_s, may be approximated by the integral

$$I_s = \int_{\theta-(\Delta\theta_s/2)}^{\theta+(\Delta\theta_s/2)} P_s d\theta = \overline{P}_s \Delta\theta_s$$

where P_s is the streak counting rate and $\Delta\theta_s$ is the scan length. Associated with the scan length is the wave length increment, $\Delta\lambda_s$.

For the reference reflection, r, the relation between the wave length increment, $\Delta\lambda_r$, and the fixed scan length, $\Delta\theta_s$, is given by the formula

$$\Delta\lambda_r = 2d_r \cos \theta_r \sin (\Delta\theta_s)$$

where d_r is the interplanar distance.

The quantity $W'(\lambda)$ may conveniently be defined as the relative experimental wave length distribution, corrected for the Lorenz factor, L, the polarization factor, p, and the wave length increments, $\Delta\lambda_k$ and $\Delta\lambda_r$

$$W'(\lambda) = \frac{I_s L_k P_k \Delta\lambda_k}{I_k L_s P_s \Delta\lambda_r} = \frac{I_s L_k P_k \Delta\lambda_k}{I_k L_s P_s \; 2d_r \cos \theta_r \sin (\Delta\theta_s)}$$

In terms of $W'(\lambda)$, the streak contribution to reflection n caused by a streak from reflection m is given by

$$I_s{}^m = \frac{I_k L_n P_n 2d_m \cos \theta_n \sin (\Delta\theta_s) \; W'(\lambda)}{L_m P_m \Delta\lambda_k}$$

where W' is evaluated at $\lambda_m/\lambda_k = d_m/d_n$. Canceling common factors, the following equation is obtained

$$I_s{}^m = \left[\frac{I_k L_n P_n d_m \cos \theta_n}{L_m P_m} \right] \left[\frac{I_s L_k P_k}{I_k L_s P_s d_r \cos \theta_r} \right]$$

The quantity in the second brackets, $W(\lambda)$, may conveniently be tabulated vs. λ/λ_k from experimental data.

The process of correcting for streaking consists of subtracting all significant streaking contributions from the characteristic reflection intensity

$$I_k{}^n \text{ (streak corrected)} = I_k{}^n \text{ (uncorrected)} - \sum_m I_s{}^m$$

The reflections to be summed are along a line through the characteristic reflection point and the origin of the reciprocal lattice.

In the fixed-crystal, fixed-counter, divergent source technique, the fixed scan $\Delta\theta_s$ is replaced by a divergent source of fixed angular width $\Delta\theta_f$. If $\Delta\theta_f$ is sufficiently broad so that the count rate is negligible

outside of the angular interval, the situation is completely equivalent to the moving crystal, moving counter method, and the same formulas are applicable.

A streak correction for the wave length range $\lambda_k < \lambda_s \leq 2\lambda_k$ was applied to the 3,4-furandicarboxylic acid intensities, in addition to the usual Lorenz and polarization corrections. No absorption or extinction corrections were made; an exception was the $(\overline{1}10)$ reflection, which was not included in the least squares refinement because its intensity appeared to be reduced by extinction. A counter nonlinearity correction was applied to all crude counting rates.

The streak correction is most important along densely packed radial reciprocal lattice lines; Table 10 illustrates the importance of this correction for the densely packed (00ℓ) reflections. Of the total of 768 reflections, 108 had a significant streak correction.

Table 10. Streak correction data

hk	Counts (uncor.)	Streak counts	F_o (uncor.)	F_o (cor.)	F_c (final model)
002	1,013,560	0	383	382	-355
004	71,500	8,354	143	134	-117
006	133,300	6,884	240	234	228
008	50,240	18,654	172	136	-130
0, 0, 10	47,580	8,233	190	173	-171
0, 0, 12	8,420	6,915	89	37	-16
0, 0, 14	4,460	2,966	72	41	-35
0, 0, 16	1,620	1,126	47	26	21
0, 0, 18	440	453	26	0	7
0, 0, 20	420	141	28	23	20

Treatment of errors and "unobserved" reflections

The estimated error in each intensity measurement was calculated by the formula

$$(\Delta I)^2 = C_T + C_B + (K_T C_T)^2 + (K_B C_B)^2 + (K_S C_S)^2$$

where C_T, C_B, and C_S are the total, background, and streak counts, respectively. In addition to the usual statistical errors, this formula assumes relative errors of K_T, K_B, and K_S in the total, background, and streak counts, respectively. K_T and K_B were assigned values of 0.02 corresponding to a 2% nonstatistical fluctuation in the peak and background counts. K_S was assigned a value of 0.05 corresponding to a 5% error in the streak correction.

When using the counter technique it is unnecessary to distinguish between observed and "unobserved" reflections. However, the usual infinitesimal formula relating the error in the intensity to the error in the structure factor is undefined when the intensity is measured as zero. By using the finite difference method, the following formula may be derived to relate these quantities

$$\Delta F = (Lp)^{-\frac{1}{2}} [-I^{\frac{1}{2}} + (I + \Delta I)^{\frac{1}{2}}]$$

This formula was used for 3,4-furandicarboxylic acid, and all reflections, correspondingly weighted, were included as observed in the refinement of this structure.

Structure Determination

The ($\bar{1}$10) reflection was found to be very intense, and this fact, along with the easy cleavage along ($\bar{1}$10), indicated that the planar 3,4-furandicarboxylic acid molecules were approximately parallel to this plane. In this arrangement, the mirror plane at z = 1/4 of the space group P2$_1$/m must coincide with the mirror plane of the molecule normal to the plane of the molecule. The only remaining degree of freedom is, then, along the ($\bar{1}$10) plane. This parameter was found by examining possible intermolecular hydrogen-bonding configurations between adjacent molecules in the z direction.

Two models were hypothesized, one with a trans intermolecular hydrogen bond and a second with a cis bond, using conventional bond distances and angles. The second model proved correct as indicated by the convergence of the model when subjected to a full matrix least squares treatment. The program of Busing and Levy (14) was used for the refinement. The scattering factors of Berghuis et al. (11) were used for the carbon and oxygen atoms, and those of James and Brindley (21) for the hydrogen atoms.

Refinement using isotropic individual atomic thermal parameters yielded a discrepancy index of 13%. When allowance for anisotropic thermal vibration was made, the discrepancy index decreased to 7%. At this point all hydrogen atoms were included in the model, and both the thermal and positional parameters of the hydrogens were varied. The discrepancy index dropped to 5%. However, the anisotropic thermal parameters of the hydrogen atoms were unsatisfactory.

Several attempts were made to refine a model with statistical hydrogen locations in the hydrogen bonds. It was concluded that the data were insufficient to distinguish between statistical hydrogen positions and symmetric hydrogen positions with a large thermal anisotropy.

For the final model all positional parameters were allowed to vary, along with anisotropic thermal parameters of the heavy atoms. It was necessary to hold the β_{33} thermal parameter of the furan ring hydrogen constant because of the tendency of this parameter to decrease to a negative value. The parameter B_{33} of this atom would be expected to be small since it describes the thermal amplitude nearly parallel to the furan ring C-H bond. The other five anisotropic parameters for this hydrogen were varied, however. The hydrogen-bonded hydrogens were placed symmetrically between the oxygen atoms. A large thermal anisotropy of these hydrogens was assumed in the direction of the hydrogen bonds, and all anisotropic thermal parameters for these hydrogen-bonded hydrogens were held constant.

The final discrepancy index was 4.7%. The quantity $[\Sigma w(F_o-F_c)^2/(m-n)]^{\frac{1}{2}}$ was 1.19, indicating a reasonable assignment of weighting factors. Table 11 lists the final parameters that were obtained. Figure 6 lists the observed and calculated structure factors.

Discussion

Table 12 and Figure 7 show the intramolecular distances and angles and their estimated standard deviations. In calculating the estimated standard deviations the complete variance-covariance matrix was used;

Table 11. Final values of the parameters and their standard deviations. The form of the temperature factor is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}{}^2 - 2\beta_{12}hk - 2\beta_{13}h - 2\beta_{23}k)$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O_1	0.6218	0.4713	0.2500	0.0197	0.0968	0.0057	-0.0153	0.0000	0.0000
σ	.0004	.0007	.0000	.0008	.0028	.0002	.0012	.0000	.0000
C_2	.5000	.3743	.1743	.0221	.0808	.0050	- .0084	.0009	.0015
σ	.0004	.0008	.0002	.0008	.0027	.0002	.0012	.0003	.0005
C_3	.3037	.2188	.1996	.0186	.0595	.0038	- .0034	.0004	.0006
σ	.0004	.0007	.0002	.0007	.0020	.0001	.0009	.0002	.0004
C_4	.1342	.0829	.1335	.0234	.0726	.0044	- .0044	- .0001	- .0017
σ	.0004	.0007	.0002	.0008	.0024	.0001	.0011	.0003	.0005
O_5	- .0214	- .0793	.1617	.0216	.1065	.0046	- .0185	- .0002	- .0015
σ	.0003	.0006	.0001	.0005	.0020	.0001	.0008	.0002	.0004
O_6	.1709	.1318	.0489	.0324	.1414	.0036	- .0256	.0001	.0008
σ	.0003	.0006	.0001	.0007	.0025	.0001	.0010	.0002	.0004

Table 11. (Continued)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
H_7	0.566	0.439	0.115	0.019	0.094	0.004	-0.009	0.004	0.009
σ	.005	.009	.002	.011	.035	.000	.017	.004	.007
H_8	- .046	- .082	.250	.034	.092	.024	.002	.000	.000
σ	.010	.017	.000	.000	.000	.000	.000	.000	.000
H_9	.000	.000	.000	.131	.150	.014	.078	.028	.021
σ	.000	.000	.000	.000	.000	.000	.000	.000	.000

Figure 6.   Observed and calculated structure factors. The first
            column lists the ℓ index; the second and third colums list
            $10F_O$ and $10F_C$

```
 0  0  L    6  20  -19 13  20   20   4  15   18   1  62   63   5  17  -29 12  15  -11 10  40  -38  2  45  -42  2  25  -25
            7  18   17 14  10    7   5  26   26   2  79   78   6  17  -18              11  15  -18  3  21   20  3  16    1  -5  2  L
 2 382 -355  8  10    3              6   7    5   3  43   38   7  19  -16   6  1  L    12  38  -40  4  21  -21  4   4   -6
 3 134 -117  9  23  -17   1  4  L    7   9  -11   4  30   31   8  19  -14              13  11    7  5  27  -28  5  12  -11  0  23   22
 6 234  228 10  26   17              8  36  -36   5  58  -59   9  20   16   0  37   36 14  15   13  6  36   36  6  21   14  1   9   -3
 8 136 -130 11   0   -0   0  13  -15  9  64   61   6  58  -58 10   0    0   1   0   -9 15  33  31. 7   4    0  7  19    5  2  45  -47
10 173 -171              1  20  -10 10  24   19   7  53   55              2   0    2 16   9    3  8  13  -17                3  25  -24
12  37  -16   1  0  L    2   9   -4 11  49  -44   8   0   10   4  4  L    3  20   22              9  12   10 -4  1  L     4   7   20
14  41  -35              3  19   19 12  13   14   9   0   -1              4  18   17 -1  3  L    10  12   -8                5  12   25
16  26   21  0 190  173  4  11   10 13   0    2 10  20  -15   0   8   -9  5  78  -76             11  13   -7  0  21   25  6  14   16
18   0    7  1 210 -199  5  10    1              11  18    0              6  14  -27   0   1    1 12  12  -17  1  60  -61  7  31  -28
20  23   20  2 240  232  6  14   12   2  4  L   12  16  -12   5  0  L    7   0   -5 11  19   16 13   9   -2  2 129 -132  8  28  -26
            3 237 -235  7   0    2                                      7  31   23              3  10   -7  9   0   -1
 0  1  L    4 208 -208  8  33  -32  0  60  -57   3  4  L    0  32  -33   9   0    9  3  37  -35 -2  4  L    4  53   56 10  23   20
            5  80  -76  9  20   18  1   0    9              1  82   80 10   0    6  4  26  -24              5  24   29 11  22   14
 0 321  310  6 121  116              2  40   37  0  10   13  2  41   55 11   7   -2  5  32  -29  0   5   -1  6   0    5 12  18   14
 1 307 -299  7 170 -165  2  0  L    3  25   21  1  47   47  3  74   73              6  17  -10  1  19  -12  7  61  -59
 2 172  169  8   7    2              4  33   28  2   0    3  4  38   19   6  2  L    7   0   -2  2  14   13  8   7   -4  -5  3  L
 3  49  -51  9  21   19  0 123  128  5  15  -14  3  11  -11  5  60  -58              8  43   45  3  11    0  9   7   10
 4 193 -197 10 114 -115  1  92  -98  6  50  -44  4  12   10  6  63  -62  0  19  -26  9   0    9  4   9  -14 10  36   37  0   0   -7
 5 107 -105 11  67  -72  2 170 -169  7  12    9  5  10  -14  7  59   60  1  23   26 10  33  -33  5   0   -2 11  19   22  1   6   -5
 6 150  147 12  27  -30  3 158 -159  8  16   18  6  10   -3  8  30   35  2  16   16 11  47  -44  6   0   -3 12  32   32  2  10   -0
 7 110 -107 13  91   93  4 182 -178              7   3    6  9  25   24  3  16  -19 12   7   -4  7   0   -8 13  14  -18  3  20   18
 8  56  -53 14  36   33  5 196 -197  3  0  L    4  0  L   10  55  -56  4  26  -12 13  50   45  8  20   15 14   7    1  4  16   10
 9  30   25 15  23   28  6 194  194              4  0  L   11   0  -13  5  47  -41 14   5    9  9  11   13 15   0    6  5  16  -16
10  83  -81 16  28  -22  7  80   60  0  69  -67  0  21  -17 12   0   12  6   7  -10                               6   0    2
11  53  -46 17  15   -4  8  15   16  1 179  178  1  40   41 13  17  -21  7   0  -12 -1  4  L    -3  1  L    -4  2  L    7   0    2
12  83  -60 18   5   14  9 145 -146  2 216 -218  2  39  -41 14  17   -6  8  23   18                                        8  10  -12
13  53   51             10  40  -44  3  90  -91  3 109  110              1   0   -1  1  59   62  1   0    7              9  12    3
14  39   14   1  1  L   11  20   24  4  68   65  4  46  -44   5  1  L    7  0  L    2   0   -5  2  62  -63  2  17  -17 -6  1  L
15  46   42             12 116  119  5   0    8  5  16  -12              1   0  -10  3   9  -12  3  90   92  3  47   48
16  22   11  0 205  211 13  36  -42  6  29    8  6 116  116  0  35   34  0   0   -5  4 104 -107  4  18  -20  0  15  -17
17  24   12  1  30   18 14  18  -24  7  47   49  7  60   59  1 170  168  1  21   -5  4  14  -17  5  10   22  5  32  -31  1  63  -62
19   7    8  2 157 -158 15  46   45  8  35   33  8  92  -91  2  64   65  2  15   12  5  14   -8  6 138  140  6  47   43  2  42   35
19  18   16  3 181 -186 16  22  -23  9  32  -13  9  67   69  3  15  -14  3  17   15  6  16    9  7  13  -19  7  14    6  3  30  -27
            4 118 -115 17   0   -7 10  61   63 10  40   41  4  22  -11  4  10   -9  7  14   19  8  36  -33  8  25  -26  4   0   -2
 0  2  L    5 264 -263 18  23   22 11  35  -33 11  70  -69  5  79  -81  5  58  -50  8   4   11  9  83   84  9  29   31  5  57   54
            6  89   92             12  49   50 12  45   46  6  18   18  6  17   -5  9  19  -20  9  83   84  9  29   31  5  57   54
 0  84   81  7  82   82   2  1  L   13  29   13  0   3    7  7  53   57  7   0    2 10   0  -13 10   0    8 10  19   18  6  17  -13
 1  67   67  8  89   90             14  19   17 14   0  -14  8  55  -54  8   0    5             11  36  -38 11  25  -23  7  53  -46
 2  38  -27  9 116 -117  1 198 -202 15   0   -5 15   0    6  9   7   10              -2  1  L   13  15   -2 13   4    6  9  11    4
 3 114 -115 10  93  -98  1 189  185 16  21  -18 16   7  -18 10  17  -11   7  1  L               13  15   -2 13   4    6  9  11    4
 4  45  -42 11  27  -29  2 151 -151 17  13   -9              11  14  -16              0  99   99 14  10   -7 14   0    1 10  25  -26
 5 129 -128 12 106  108  3 181 -184              4  1  L   12  26  -25  0  14   -2  1  26   27 15  25  -27              11   0   -2
 6   0    0 13  86   88   4   7  -14              0  52  -55 13   0    0  0  17   21  2  50   55 16  27  -24 -4  3  L
 7  27   28 14  26  -28  5  35   34  0  24  -30  1  93   92   5  2  L    2   0   -5  3 190  195                        -6  2  L
 8  86   86 15  30   17  6  62   60  1  71   70  2  52   52              3  17  -17  4  88  -89 -3  2  L    0  12    5
 9  34  -31 16  18  -12  7  12   12  2 115 -112  3  94   95  0  69   70  4  15   -9  5  30   29              1   0    7  0  30  -13
10  80  -78 17  10  -13  8  26   27  3 152  155  4  77   79  1  17   16  5  35  -29  6  34   33  0  41   40  2   0   -2  1   0    0
11  61  -59 18  19   15  9   5  -25  4   6  -11  5   6   -1  2   3  -13  7   0   -7  8  83   83  1  12   11  3  20   21  2   8    7
12  45   41             10  75   79  5   6   -1  6  87  -91  3   0    6              8  55   56  2   7   -8  4   7   -7  3  11  -16
13  84   43   1  2  L   11  21  -26  6  89  -86  7  29   31  4  41   41 -1  1  L   10  99 -107  4  70  -23  6  11    5  5   0   -1
14  18   -7             12  45   47  6  99   99  7  29   31  4  41   41             11  51   51  5  18    7  7  16  -14  6  84    1
15  12   15  0 148  146 13  29   28  7 161  163  8  14   37  5  57  -61             12  15   26  6   0    6  8   0    7  7  17  -21
16   0    5  1  59   61 14  22   28  8  78  -83  9  77   79  6  41  -36  0 827  895 12  15   26  6   0    6  8   0    7  7  17  -21
17   0    3  2  29  -30 15  13    9  9  20   24 10  57  -59  7  18  -18 -1 359  361 13  92  -92  7   0    2  9  32   27  8   0    1
19   4    6  3 122 -120 16  25  -26 10  80   80 11  44  -44  8   0   -0  2 160 -167 14   8    6  8  35   38 10  29  -21  9  37  -12
            4  65  -47 17   5  -11 12  45   44 13  19  -22 10   0   -1  3  60  -60 15   0   -8  9  36   34 11   0   -5
 0  4  L    5  11   -0 18  16  -11 12  45   44 13  19  -22 10   0   -1  4  95   99 16  17  -16 10  60  -58              -6  3  L
            6  76   69             13  14   17 14  15  -13 11  11    5  5  14  -20 17   0    1 11  11   13 -4  4  L
 1  47  -41  7  15   18   2  2  L   15  11  -11              6 164  164              1  11   11              0  10    7
 3   6    1  8  13   17             16  12  -12   4  2  L    5  1  L   13  47  -44  0   9  -12  1  0   11
 4  40  -43 10  48  -46  1  79   78              0  25  -30  9  15   16  0 199  205 15   8   -0  2  17   14  3   8  -11
 6  18  -16 11   0   -0  2 121  125   4  1  L    0  45  -45  1  0  113 -114  1 219  226              3  10    2  4   0    1
 7  18   16 12  29   33  3  78   42              1 119  140  3  32   26 11  21  -24  2  28   -4 -3  3  L    4   0   -6
 7  11  -12 13  11   14  4  60   58  0  75   74  2 107  107  4   0   -6 13   8   12  4  63  -63  0  10   11  5  13  -12 -7  1  L
 8  16   17 14  17   17  5  66   46  1  59   60  4   0   -6 13   8   12  4  63  -63  0  10   11
10  30   28 15  26   21  7 145  142  2  31   35  5   0    7  5  43  -42 14  19  -16 15  22  -22  6  67   66  2  20   21  0  67   61
12   1    1             16   0   -3  8  66   60  3  93  -96  6  14  -14 15  22  -22  6  67   66  2  20   21  1  11  -11
13   2   21   1  1  L    9  26   16  5  46   45  7  83   86  7  13  -11 11  13    7  6   27  62  3   0   -4  0  11   -8  2  29  -25
14  11  -12             10  50   50  7  74   74  8  34  -29  6  0  L   17  17    4  8  10  -30  4  29  -25  1  11  -12  3   0   -0
15  24   15  2 -24  11  50   50  7  74   74  8  34  -29  6  0  L   10  38  -36  6   9  9    3  46  -43  5  16   15
16  15    2  3  61  -61 14  26    9  95  100 11  10   -8  1 108  108              11  12  -10  7  26   32  4   5  -17  6  18   11
            4  41   41 -2 14    0 10  36  -17 12  10  -28  4  1  L   -5   0  -5  0 251  260 13   0   12  8  13   18  7   8    4
            6  61   60  0 11  57  -69 13   0   -6  4  0  L   -5   0  -5  0 251  260 13   0   12  8  13   18  7   8    4
            6  41  -45 21 16   18  7 12  28   25              4   0  -23  1 135 -140 14  19  -10  7  10  18 -7  2  L
            9  30  -41  3 38   39 16   0    2 12  15  -14 10  17   -2  1  40  -34
 3  27   18 14  7  60   64  2  3  L   14  19  -14              6  30   26  4  77  -81             10  17   -2  1  40  -34
 1  27   23 11   0   -4  5 52   51  2  0  -10  9   8   16  7  26  -24  0 131  135  0  52   53 13   9    4  4  10  -10
            9  22  10  46  41  1  0  10  3  3  L    2   0  -10  9   8   16  7  26  -24  0 131  135  0  52   53 13   9    4  4  10  -10
           11  16  18                              3  12  -12 10  13  -10  8  16  -38
```

Table 12. Intramolecular distances and angles and their estimated standard deviations

| Atoms	Distance (uncor.), A	Distance (cor.), A	Furan[10], A	Atoms	Angle	Furan[10]
O_1-C_2	1.356 ± .003	1.361	1.362 ± .001	$C_2-O_1-C_2'$	107.2 ± 0.3°	106.6 ± 0.1°
C_2-C_3	1.346 ± .003	1.351	1.361 ± .001	$O_1-C_2-C_3$	110.8 ± 0.2	110.7 ± .1
C_3-C_3'	1.454 ± .005	1.462	1.431 ± .002	$O_1-C_2-H_7$	115.7 ± 1.8	115.9 ± .1
C_3-C_4	1.472 ± .003	1.478		$C_3-C_2-H_7$	133.6 ± 1.8	133.4 ± .1
C_4-O_5	1.262 ± .003	1.267		$C_2-C_3-C_3'$	105.7 ± 0.2	106.1 ± .1
C_4-O_6	1.251 ± .003	1.254		$C_2-C_3-C_4$	124.0 ± .2	125.9 ± .1[a]
O_5-O_5'	2.544 ± .004	2.555		$C_4-C_3-C_3'$	130.3 ± .2	128.0 ± .1[a]
O_6-O_6'	2.652 ± .004	2.639		$C_3-C_4-O_5$	120.7 ± .2	
C_2-H_7	0.97 ± .03		1.075 ± .002	$C_3-C_4-O_6$	117.7 ± .2	
				$O_5-C_4-O_6$	121.6 ± .2	
				$C_4-O_5-O_5'$	108.9 ± .2	
				$C_4-O_5-H_8$	110.1 ± 2.6	
				$C_4-O_6-H_9$	109.5 ± 0.2	

[a]Angle to hydrogen atom.
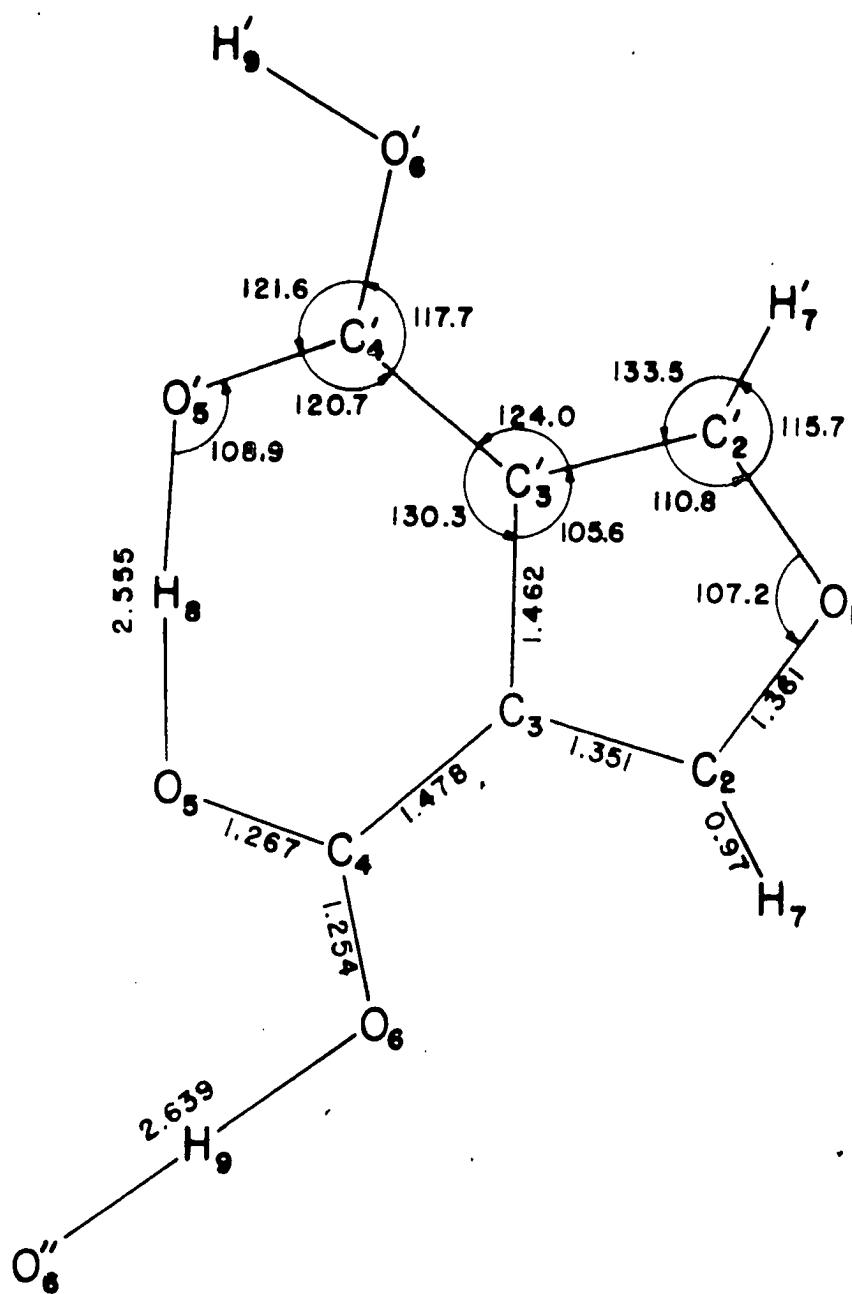
Figure 7. Intramolecular distances and angles, corrected for rigid body libration

these calculations were made with the program of Busing and Levy (15).
The third column of the table gives distances corrected for rigid body
libration as explained below; this correction is negligible for the
angles. For comparison, Table 12 also shows the distances and angles
found by Bak et al. (22) in his careful microwave structure determination
of furan itself.

The ring C-O distance of 1.361 A is very close to other observed
aromatic C-O distances; in phoroglucinol (23), 1.36 $\pm$ 0.01, and in
salicylic acid (24), 1.36 $\pm$ 0.01 A. The ring C-H distance of 0.97 $\pm$
0.03 A has not been corrected for thermal motion, and it would be expected
that the thermal correction for this bond length would be large. The
thermal parameters for hydrogen are not known with sufficient accuracy to
permit the thermal correction for this bond length.

The ring double bond distance of 1.351 A is close to the r_g value of
1.361 A found by Bak in furan itself. The ring single bond distance of
1.462 A appears to be significantly longer than the r_g value of 1.431 A
found in furan. This difference in the single bond length is easily
explained as the result of the nonbonded repulsion of the two carboxyl
groups. Bartell (25) has recently re-evaluated the effect of nonbonded
interactions in determining bond lengths. The nonbonded repulsion of the
carboxyl groups also increases the C_4-C_3-C_3' bond angle from 128.0 to
130.3°. Indeed, even the slightly shorter value of the double bond length
might be explained as the result of loss of conjugation caused by stretch-
ing the ring single bond.

The ring-carboxyl single bond is of length 1.478 A. There is

considerable discussion in the literature as to the normal value of the

trigonal-trigonal bond length type.[1] The single bond in 1,3-butadiene

is reported as 1.483 ± 0.010 by electron diffraction (26), and as 1.476

± 010 A by infrared-Raman spectroscopy (27). A microwave investigation

of acrolein yielded 1.472 A as the trigonal-trigonal C-C distance (28).

On the other hand, a very careful investigation of 1,3,5,7-

cyclooctatetraene by electron diffraction yielded 1.462 ± 0.001 for the

single bond length (29). If the cyclooctatetraene value is rejected as

abnormal, the ring-carboxyl distance in this structure is very close to

the average (1.477 A) of the above three quoted distances for butadiene

and acrolein.

The two carboxyl C-O distances of 1.267 and 1.254 A differ by only

0.013 A, but this difference should be significant if the estimated

standard deviations of 0.003 A in the individual distances are correct.

The longer C-O distance corresponds to the shorter hydrogen bond and vice

versa.

The intramolecular hydrogen bond is of length 2.555 A. The small

observed departure from collinearity is not significant. The C-O-H bond

angle is very nearly tetrahedral. The molecules are joined into chains in

the c-lattice direction by intermolecular hydrogen bonds of length 2.639 A

(Figure 8). These bonds are collinear by symmetry, and again the observed

C-O-H bond angle is nearly tetrahedral. Both hydrogens in the hydrogen

bonds are in crystallographic special positions, the intramolecular bond

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[1]See, for example, "An Epistelogue on Carbon Bonds", in _Tetrahedron_
_17_, No. 3/4 (1962).

Figure 8. The structure projected onto the ring least squares plane
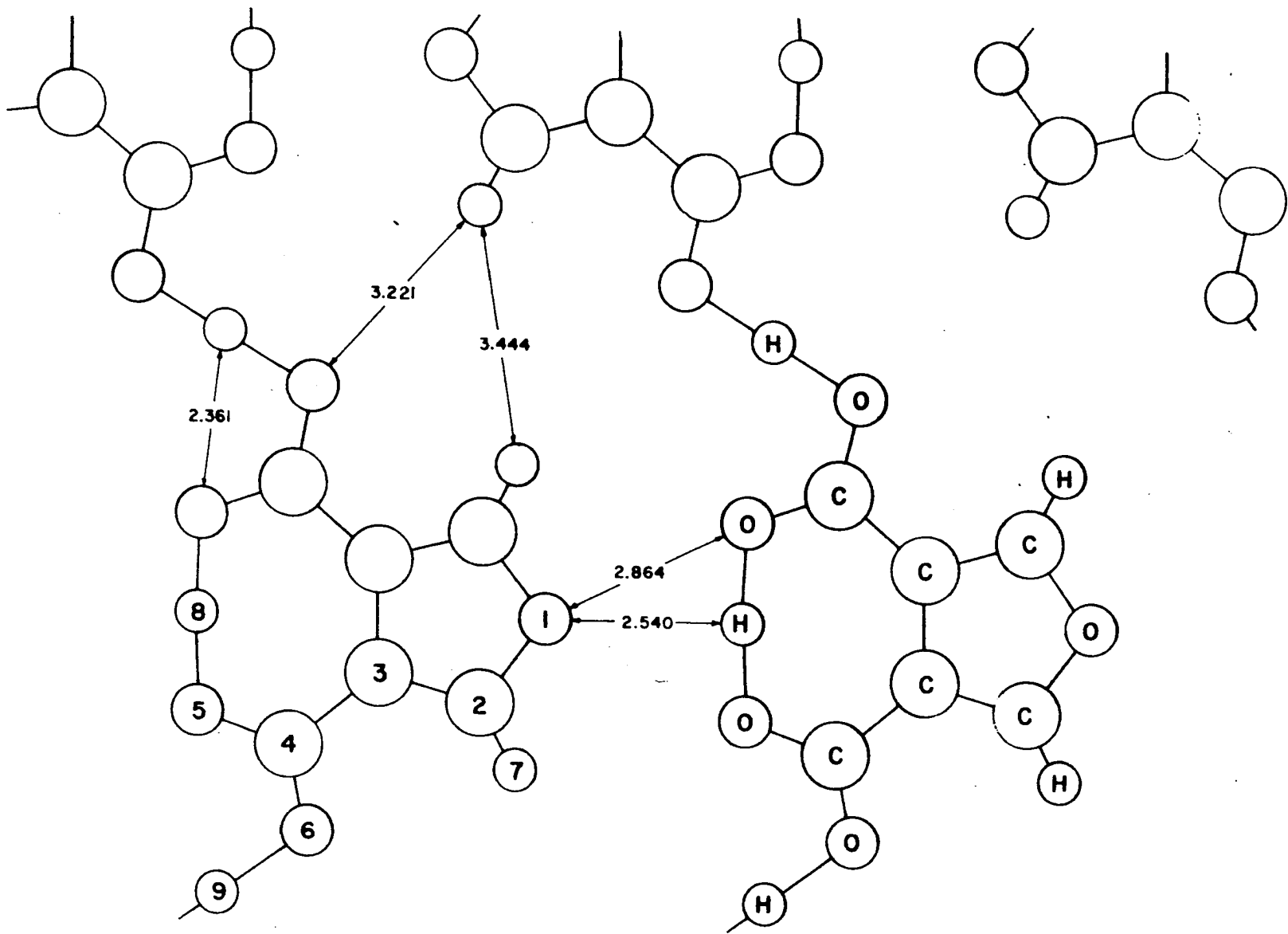
being across a mirror, and the intermolecular bond being across a center of symmetry.

The furan ring is accurately planar; the equation of the least squares plane and atomic distances from the plane are given in Table 13. The carboxyl oxygen atoms are significantly out of the ring plane; the twist angle of the carboxyl group relative to the ring plane is 3.8°. The twist of the carboxyl group, and also the slight displacement of the carboxyl carbon, is such as to move O_5, the intramolecular hydrogen bonded oxygen, closer to the furan ring oxygen in the diagonally adjacent unit cell (see closest intermolecular approaches discussed below).

Table 13. Distances from the ring least squares plane in A
(The equation of the plane is - 0.4402X + 0.8980Y + 0.0749 = 0 with cartesian axes X and Z parallel to unit cell axes a and c.)

Atom	Distance	Atom	Distance
O_1	0.0005	O_6	0.062
C_2	- .0004	H_7	.04
C_3	.0002	H_8	- .08
C_4	- .004	H_9	.08
O_5	- .082	$O_1{}^a$	- .692

[a]Furan oxygen in diagonally adjacent unit cell; this is the stepping distance.

Table 14 lists the intermolecular distances less than 3.5 A, uncorrected for rigid body libration. The limitingly short O-H nonbonded distance of 2.361 A between atom 51000 and atom 91000 appears important

Table 14. Nearest nonbonded neighbor distances less than 3.5 A

(The atoms are identified by a five digit code; the first digit is the atom number, the second the symmetry transformation applied, and the third, fourth, and fifth the number of cell translations a, b, and c, respectively. The numbers of the symmetry transformations are (1) x, y, z; (2) x, y, ½-z; (3) -x, -y, -z; (4) -x, -y, ½+z.)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
11000	31000	2.224	31000	42000	2.655	51000	42000	3.184
	71000	1.978		52000	3.059		63000	3.140
	51100	3.201		72000	3.195			
	81100	2.924		51010	3.433	61000	71000	2.769
	31010	3.499		81010	3.477		81000	3.263
	51110	2.864					43000	3.289
	81110	2.540	41000	71000	2.885		53000	3.140
				81000	2.077		91010	3.465
21000	41000	2.489		91000	2.105		73110	3.221
	61000	2.807		32000	2.655			
	22000	2.181		42000	3.359	71000	22000	3.070
	32000	2.232		52000	3.184		32000	3.195
	72000	3.070		63000	3.289		51100	3.186
	51100	3.311		51010	3.322		51110	2.978
	81100	3.463					81110	3.470
	31010	3.387	51000	11$\bar{1}\bar{1}$0	2.864		63110	3.221
	51110	3.359		21$\bar{1}\bar{1}$0	3.359		73110	3.444
				71$\bar{1}\bar{1}$0	2.978			

Table 14. (Continued)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
31000	110$\bar{1}$0	3.499		310$\bar{1}$0	3.433	81000	11$\bar{1}\bar{1}$0	2.540
	210$\bar{1}$0	3.387		410$\bar{1}$0	3.322		71$\bar{1}$10	3.470
	51000	2.379		11$\bar{1}$00	3.201		310$\bar{1}$0	3.477
	61000	2.333		21$\bar{1}$00	3.311		11$\bar{1}$00	2.924
	71000	2.133		71$\bar{1}$00	3.186		21$\bar{1}$00	3.463
	81000	2.453		61000	2.193			
	91000	3.489		91000	2.361	91000	610$\bar{1}$0	3.465
	22000	2.232		3200	3.059		63010	3.465

in determining the c-lattice constant (see Table 14 for explanation of atom code). There are also very close nonbonded approaches between atom 11000 (the furan ring oxygen) and atoms 51110 and 81110 of the intramolecular hydrogen-bonding system in the diagonally adjacent unit cell. On the other hand, the distances between atoms 61000 and 73110, and 71000 and 73110, are larger than expected, resulting in a small hole in the structure. The molecules are not quite in the $(\bar{1}10)$ crystallographic plane. This leads to stepping distance of 0.692 A between molecules, as may be seen from Table 15. The perpendicular distance between furan ring planes is 3.371 A.

Analysis of Thermal Motion

The orientation and magnitudes of the principal axes of thermal vibration for the individual atoms are given in Table 15 and are shown stereographically in Figure 9. The surface described by the r.m.s. vector is not an ellipsoid, but is a surface of the fourth order.[1] To avoid confusion, it is suggested that this surface be referred to as a "thermaloid."

The thermal vibrations of the individual atoms are generally larger normal to the molecular plane and are generally near a minimum in the direction of a covalent bond. The thermaloids for the two hydrogen-bonded oxygen atoms, in particular, show that the observed thermal motion in the direction of the C-O bonds is small. This fact seems to rule out a

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[1]See, for example, Waser, J., Acta Crystallographica 8, 731 (1955).

Table 15. Angle θ(I) (degrees) between principal thermal axes R and axes I of a cartesian coordinate system defined by the least squares ring plane

(The X'-axis is in the direction parallel to the XY plane defined by the least squares plane; the Y'-axis is perpendicular to the molecular plane.)

| Atom	R	R.m.s. amplitude (A)	θ(X')	θ(Y')	θ(Z)
O_1	1	0.166 ± .004	178 ± 1	88 ± 1	90 ± 0
	2	.247 ± .004	90 ± 0	90 ± 0	180 ± 0
	3	.276 ± .004	88 ± 1	2 ± 1	90 ± 0
C_2	1	.183 ± .004	164 ± 4	85 ± 3	150 ± 4
	2	.232 ± .004	74 ± 4	81 ± 10	161 ± 6
	3	.249 ± .004	87 ± 4	11 ± 9	80 ± 10
C_3	1	.176 ± .003	164 ± 6	84 ± 4	104 ± 6
	2	.201 ± .003	75 ± 6	86 ± 18	165 ± 8
	3	.210 ± .004	85 ± 6	7 ± 10	85 ± 17
C_4	1	.195 ± .004	156 ± 9	77 ± 5	70 ± 8
	2	.213 ± .004	113 ± 9	108 ± 8	150 ± 8
	3	.236 ± .004	95 ± 5	158 ± 5	69 ± 7
O_5	1	.169 ± .003	171 ± 2	87 ± 1	82 ± 2
	2	.220 ± .003	98 ± 2	94 ± 2	171 ± 2
	3	.293 ± .003	87 ± 1	5 ± 1	95 ± 2
O_6	1	.193 ± .003	75 ± 9	93 ± 1	16 ± 9
	2	.207 ± .003	16 ± 8	95 ± 1	106 ± 9
	3	.341 ± .003	84 ± 1	6 ± 1	89 ± 1
H_7	1	.10 ± .09	43 ± 16	97 ± 19	48 ± 13
	2	.23 ± .05	53 ± 19	55 ± 36	124 ± 32
	3	.28 ± .05	108 ± 29	36 ± 36	60 ± 23
H_8	1	.25 ± .00	0 ± 0	90 ± 0	90 ± 0
	2	.25 ± .00	90 ± 0	0 ± 0	90 ± 0
	3	.50 ± .00	90 ± 0	90 ± 0	0 ± 0
H_9	1	.25 ± .00	122 ± 0	90 ± 0	32 ± 0
	2	.25 ± .00	90 ± 0	0 ± 0	90 ± 0
	3	.60 ± .00	32 ± 0	90 ± 0	52 ± 0

Figure 9. Thermal stereograms for the individual atoms. The plane of
the paper is the least squares ring plane in the same
orientation as Figures 7 and 8. The directions of the
principal axes of the thermaloids are shown sterographi-
cally. The root mean square amplitude is shown for each
axis in A
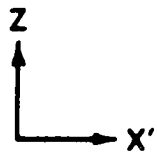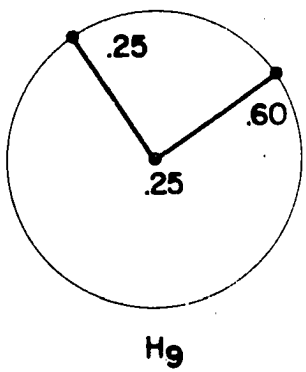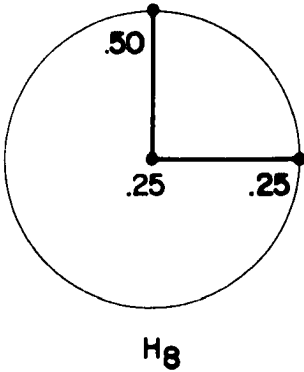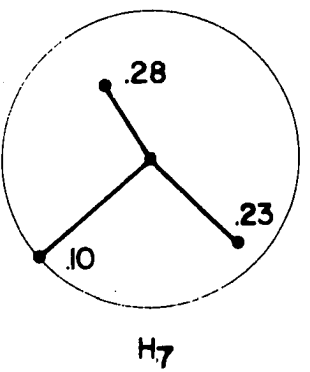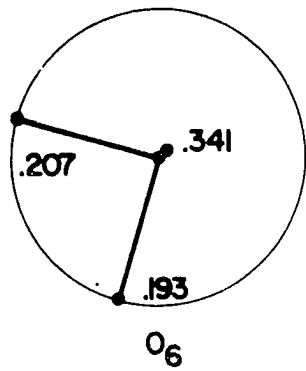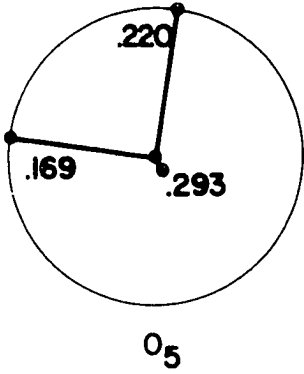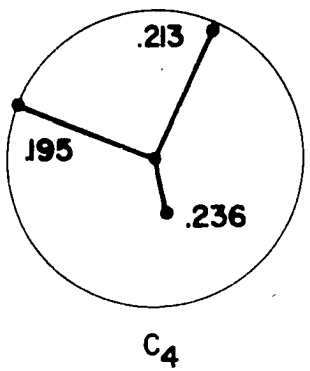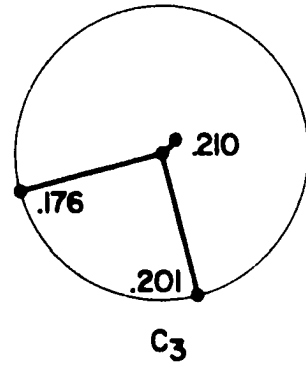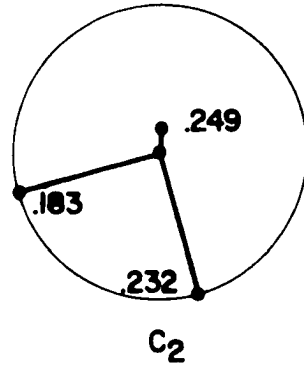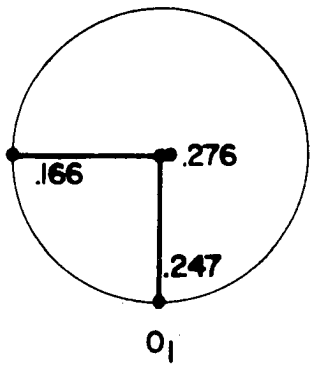
statistical combination of C-O and C=O in the carboxyl groups (see additional discussion below). The crystal structures of bis(m-bromobenzoyl)methane (30) and bis(m-chlorobenzoyl)methane (31), which have hydrogen-bonded enolic rings, have similarly small amplitudes of vibration in the direction of their C-O bonds and are also believed to be nonstatistical structures.

Because of the strong intramolecular hydrogen bond, it would be expected that the entire molecule could reasonably be approximated as a rigid body, and the individual atomic vibrations could be expressed as rigid body translations and librations by the method of Cruickshank (32). Such an analysis was carried out, using the program UCLATO1.[1] The analysis was quite successful, with over 90% of the magnitudes, on the average, of the anisotropic thermal parameters β_{ij} being expressible as rigid body translation and libration. Table 16 gives the results of the rigid body analysis.

The rigid body translations are not markedly anisotropic. The largest amplitude, 0.205 A, is in the direction of the hydrogen-bonded chain. The next largest amplitude, 0.184 A, is very roughly perpendicular to the molecular plane. The smallest amplitude, 0.170 A, is roughly in the molecular plane and perpendicular to the hydrogen-bonded chain.

The smallest rigid body librational axis, 2.6°, is very nearly perpendicular to the molecular plane. The other two librational axes, of

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[1]Gantzel, P., Coulter, C., and Trueblood, K. California Institute of Technology, Pasadena, California. IBM 709 or 7090 program UCLATO1. Private communication. 1963.

Table 16. Results of rigid body thermal analysis

The translational tensor T and its estimated standard deviation

0.0316	- 0.0025	0.0000	0.0014	0.0016	0.0000
	0.0308	.0000		0.0021	.0000
		.0422			.0012

Principal axes of T (A) and their direction cosines relative to the cartesian coordinate system defined in Table 13

0.205	0.000	0.000	1.000
.184	.758	- .652	0.000
.170	.652	.758	0.000

The librational tensor ω and its estimated standard deviation (sq. radians)

0.0076	0.0031	0.0000	0.0004	0.0003	0.0000
	0.0038	.0000		0.0003	.0000
		.0079			.0007

Principal axes of ω and their direction cosines (degrees)

5.5	-0.872	-0.489	0.000
5.1	.000	.000	1.000
2.6	- .489	.872	0.000

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amplitudes 5.1 and 5.5°, are very nearly in the molecular plane and parallel to the hydrogen-bonded chain, respectively. The smaller libration around the axis perpendicular to the molecular plane is consistent with the tight packing along the hydrogen-bonded chains discussed under

closest intermolecular approaches above.

The rigid body libration causes a shift in the apparent atomic centers toward the center of rotation (here assumed to be the center of mass of the molecule with all atoms equally weighted). Corrected atomic positions were obtained by the method of Cruickshank (33), and all intramolecular distances and angles were recalculated (see Table 12). The magnitude of the librational correction for the intramolecular distances varied from 0.003 to 0.013 A.

Discussion

Both hydrogen bonds in this structure are at critical distances where it cannot be said with certainty that the hydrogens should be centered in a symmetrical single potential well, or distributed over a double potential well (34), and, as has been noted (30, 31), this question cannot be settled using ordinary methods of X-ray diffraction, and probably not by neutron diffraction (35).

One of the significant features of this structure determination is that it demonstrates that with careful (but not excessively time-consuming) attention to gathering and treatment of the X-ray data, and sufficient computer capacity, structures are obtainable where bond distances are reliable to about 0.01 A. (The difficulties in attaining such accuracies have been pointed out by Cruickshank (36). This makes possible the discrimination between single and double potential wells for hydrogen bonds by the presence or absence of the abnormal isotope effect (37) as

suggested by Rundle[1].

[1]Rundle, R. E., paper to be published in Journal de Physique et Radium as part of the International Symposium on Neutron Diffraction, Grenoble, France. 1963.

SUMMARY AND CONCLUSIONS

The crystal structure of palladium dimethylglyoxime has been deter-
mined, and the proportional counter intensity data have been refined by
isotropic least squares analysis. The palladium dimethylglyoxime molecule
has a significantly longer hydrogen bonded O-O distance than the
isostructural nickel compound. The palladium compound also appears to be
less symmetrical than the nickel compound. These differences would be the
expected result if the nickel dimethylglyoxime molecule possessed a
symmetrical hydrogen bond and the palladium compound an unsymmetrical
hydrogen bond.

The crystal structure of bis(m-bromobenzoyl)methane has been deter-
mined, and the three dimensional scintillation counter data refined by
anisotropic least squares. The molecule is nearly planar, with a maximum
deviation of 0.12 A from the least squares plane, and is tilted in the
unit cell $\pm$ 29.9° from the (010) plane. The molecule has a short intra-
molecular hydrogen bonded distance of 2.464 $\pm$ 0.015 A, but the thermal
parameters suggest an anomaly. Symmetry requires complete equivalence of
the two C-O groups and the intervening C-C bonds of the enol ring, and the
thermal parameters support the interpretation that this equivalence is
real rather than statistical.

The crystal structure of 3,4-furandicarboxylic acid has been deter-
mined, and the three dimensional scintillation counter data have been
refined by anisotropic least squares analysis. The furan ring is planar,
with a crystallographic symmetry plane normal to the ring plane and
passing through the ring oxygen atom. The carboxyl groups are slightly

tilted and rotated 3.8° from the ring plane. An intramolecular hydrogen bond of length 2.555 A joins the two carboxyl groups. The molecules are joined into chains by an intermolecular hydrogen bond of length 2.639 A. The hydrogens in these bonds must lie on mirror planes and centers of symmetry, respectively, or must be disposed symmetrically about these symmetry elements, either statistically or in double wells. Thermal parameters seem to eliminate statistical averaging. The abnormal isotope effect (Robertson-Ubbelohde effect) may prove useful in distinguishing between single and double well distributions.

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