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The physical and optical properties of carbodiimides

Philip Harvey Mogul
Iowa State University

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THE PHYSICAL AND OPTICAL PROPERTIES

OF CARBODIIMIDES

by

Philip Harvey Mogul

A Dissertation Submitted to the

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In Charge of Major Work

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Dean of Graduate College

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INTRODUCTION

Carbodiimides were synthesized for the first time in the latter part of the nineteenth century (1,2,3,4,). They have not been found in nature. These compounds belong in the same class as allenes, ketenes, isocyanates and keteneimines, all of which contain a twinned or cumulative double bond system. Molecular fragments which demonstrate the differences between these five groups of compounds and illustrate the cumulative double bond in these molecules are shown in Figure 1.

Aliphatic carbodiimides are colorless or very slightly colored distillable liquids with a characteristic odor. The aromatic carbodiimides are generally crystalline compounds which decompose or become partly polymerized on heating or prolonged storage. An example of a relatively stable carbodiimide is the N,N'-dicyclohexyl compound which is widely used in laboratory investigations of living systems (5). This compound is fairly stable and can be kept without significant polymerization for several months. In general, the stability of carbodiimides increases with increasing chain length and branching of the side-chains (6). For example, N,N'-diethylcarbodiimide polymerizes after a few days, but the N,N'-diisopropyl or N,N'-dicyclohexyl compounds are stable when stored for several months (7). Unsaturated

(a) $\diagup\!\!\!\!\diagdown C = C = C \diagdown\!\!\!\!\diagup$

(b) $\diagup\!\!\!\!\diagdown C = C = C = C \diagdown\!\!\!\!\diagup$

(c) $\diagup\!\!\!\!\diagdown C = C = O$

(d) $-N = C = O$

(f) $-N = C = N-$
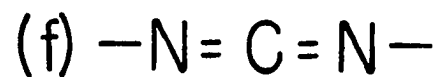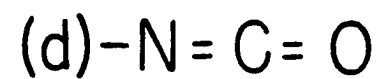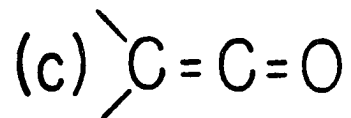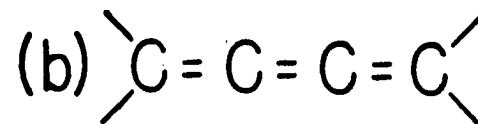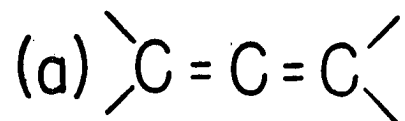
Figure 1.   Cumulative double bond systems.

a.   Allene
b.   Cumulene
c.   Ketene

d.   Isocyanate
f.   Carbodiimide

dialkenecarbodiimides with an unbranched chain (diallyl- and allyl-carbodiimides) are stable as monomers only when a polymerization inhibitor has been added (4).

The aromatic carbodiimides differ considerably in their stability (8). For example, N,N'-di-p-iodophenylcarbodiimide polymerizes very rapidly while the parent compound, N,N'-diphenylcarbodiimide, a mobile liquid when freshly distilled, becomes a solid paste upon standing for several days (8). The longest period of stability thus far observed for a carbodiimide was for the N,N'-di-p-dimethylaminophenyl compound which appeared to remain unchanged for over three years (8).

The decomposition and polymerization products of carbodiimides are basic, but their composition and structure have not been sufficiently studied. However, it was observed that N,N'-diphenyl and N,N'-di-o-tolycarbodiimide polymerization products exist in dimeric and trimeric form (8). These polymers are illustrated in Figure 2.

The chemical properties of carbodiimides are primarily determined by their unsaturation, and therefore by their tendency to enter into addition reactions. This (reactivity) refers in particular to reactions with compounds having an active hydrogen atom.

    a. <u>Reactions with weak acids</u>. Carbodiimides react with hydrogen sulfide to form symmetrical-dialkyl

$$ArN \text{—} C = NAr$$
$$\mathrm{\,|\qquad\quad |}$$
$$ArN{=}C \text{—} NAr$$

$$NAr$$
$$\mathrm{\|}$$
$$C$$

$$ArN \qquad NAr$$

$$ArN{=}C \qquad C{=}NAr$$

$$NAr$$
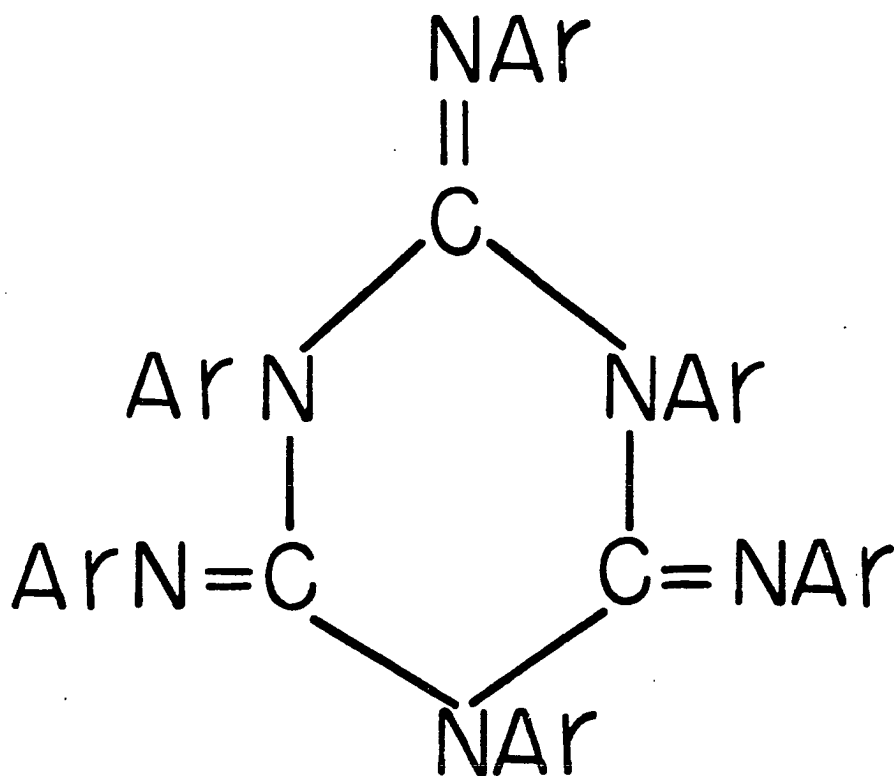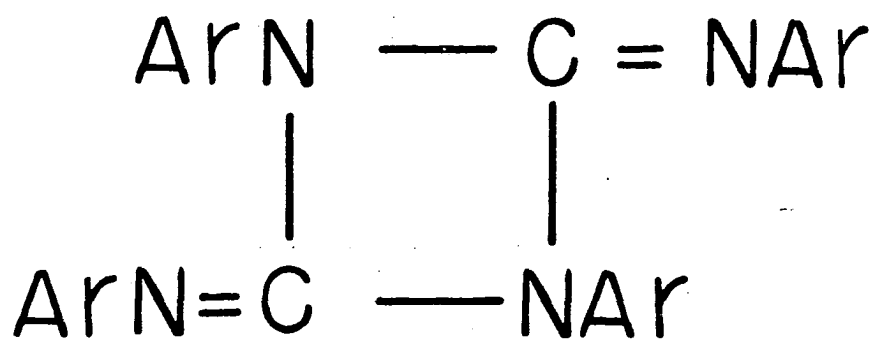
Figure 2.   Polymers of aromatic carbodiimides

(aryl)-thioureas (2)

RN = C = NR + HSH → RNHCSNHR.
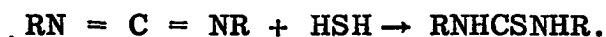
b. <u>Reactions with phenols</u>. When carbodiimides are heated with phenols, crystalline ethers of pseudoureas are formed (9).

RN = C = NR + ArOH → RNHC(=NR)OAr.

c. <u>Reactions with carboxylic acids</u>. Carbodiimides react with carboxylic acids to form acyl ureas or acid anhydrides, depending on the reaction conditions (10).

$$RN = C = NR + R'COOH \nearrow \atop \searrow \begin{matrix} RNHCONHR + (R'CO)_2O \\ \\ R'CONRCONHR \end{matrix}$$
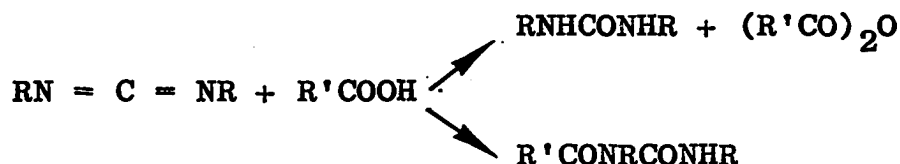
Dicarboxylic acids react analogously with carbodiimides (11). In fact, the reaction of oxalic acid with carbodiimides is used for the identification and quantitative determination of these compounds (12).

The chemical properties of the carbodiimides given above demonstrate that carbodiimides are similar to the other classes of compounds with cumulative double bond systems, in particular to those of the isocyanates. However, under ordinary conditions, carbodiimides react less vigorously than isocyanates with acids, alcohols, and amines (13).

Since a relatively large text would have to be written to explain the varied and numerous processes in which

carbodiimides are involved, the following list was constructed
to illustrate some of their more important uses:

    a. The β-lactam ring in penicillinoic acid was
first closed to form penicillin by means of
carbodiimides (14).

    b. Carbodiimides are used in the synthesis of
nucleotides, poly-nucleotides, and coenzymes (15).

    c. Carbodiimides inhibit the autocatalytic process
caused by the formation of carboxylic compounds in
polyurethanes. This catalytic process causes the
plastic to age (16).

    d. Carbodiimides can be used as anti-shrink
additives in the treatment of textiles (17).

    e. Water-soluble carbodiimides alone or in
combination with CH_2O or $(CH_2O)_2$ impart to photo-
graphic gelatin emulsions freedom from fogging
during storage, increase the photographic
speed, improve storage stability, etc. (18).

    f. Some carbodiimides are found to be more
toxic to malignant than to normal cells (19).

    g. Carbodiimides, in conjunction with other
organic compounds, are used with success as
cathode depolarizers (20).

There has been considerable speculation in the
literature concerning structure models for carbodiimides.

In 1929, Vorlander (21) suggested a linear model from purely theoretical considerations. Three years later, Bergmann and Schutz (22), utilizing the proposal of Vorlander, attributed the rather large dipole moments they observed for N,N'-diphenyl and 4,4'-dimethyl-diphenylcarbodiimide, which were 1.89 and 1.96 D respectively, to a large finite group moment in the NCN molecular fragment. Schneider (23), on the other hand favored an asymmetric structure based upon a linear NCN chain with substituent groups oriented in planes different from each other. In Schneider's model which is illustrated in Figure 3, the NCN chain is assumed to be located along the Y axis. The bond to one substituent group, R_2, is assumed to lie in the (-Y, -Z) plane, whereas the bond to the other substituent group, R_1 lies in the (-X, +Y) plane. When Schneider investigated p,p'-dichlorophenylcarbodiimide, he found that this compound possessed a zero moment. Schneider explained this dipole moment value by equating the aromatic carbon-nitrogen bond moment to the aromatic carbon-chlorine moment, which he assumed were acting in opposite directions. He calculated an independent value for the carbon-nitrogen moment from the observed moment for N,N'-diphenylcarbodiimide and his proposed structure. For an assumed C-N=C bond angle of 121 degrees, Schneider obtained an aromatic carbon-nitrogen bond moment of 1.17 D which exactly equaled the aromatic carbon-chlorine bond moment for chlorobenzene. On
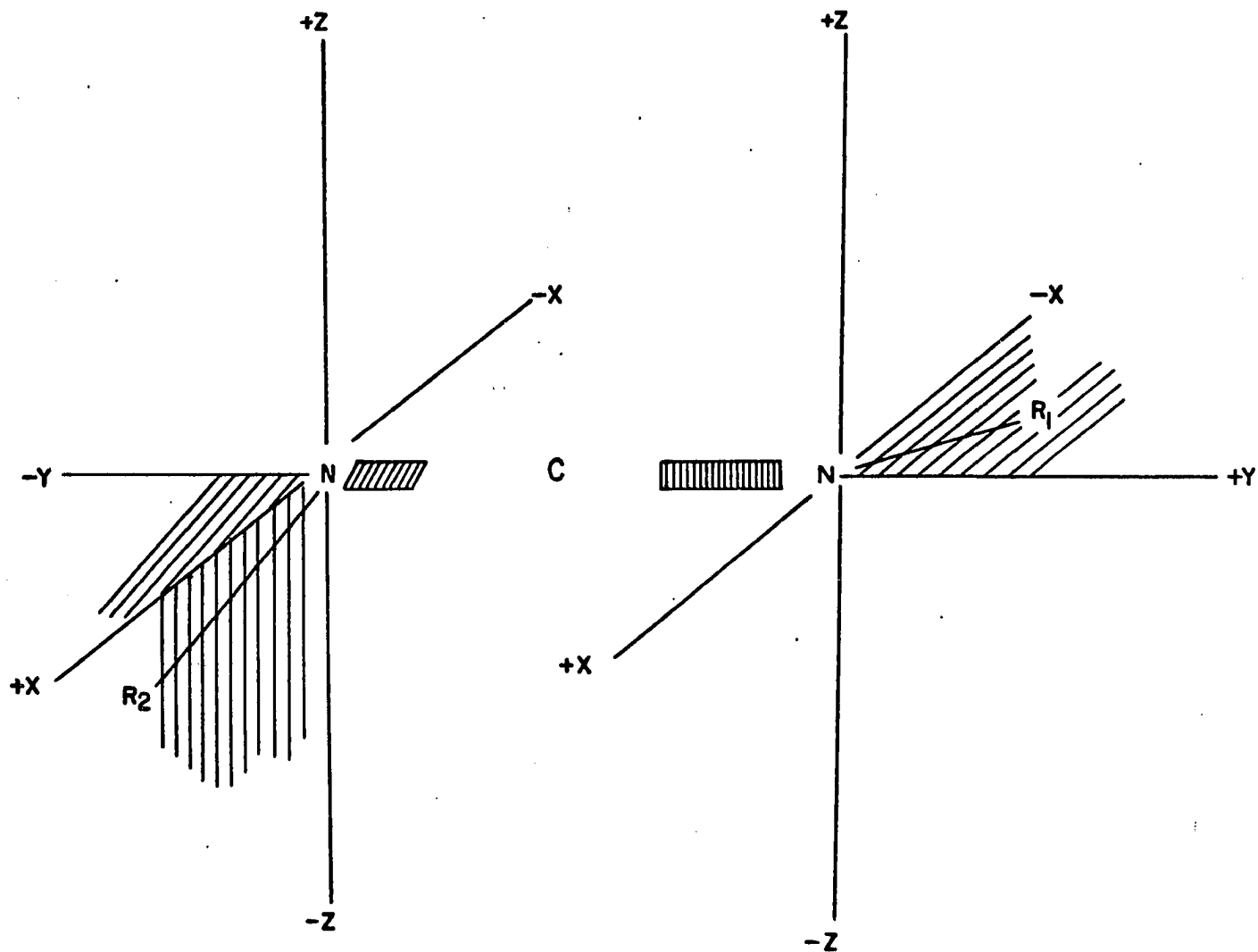
Figure 3. Asymmetric carbodiimide structure proposed by Schneider (23).

this basis, he concluded that the structure he proposed was reasonably correct. A two-dimensional x-ray investigation of bis-p-di-methylaminophenylcarbodiimide by Daly and Wheatley (24) supported the asymmetric figure proposed by Schneider. Diagrammatically, the x-ray model is represented in Figure 4. Although angles cannot be evaluated exactly from this x-ray study, it was apparent that the angular value assumed by Schneider for the RNC structural unit was incorrect. Feichtmayr and Wurstlin (25) concluded that the dipole moments of para and meta substituted diphenyl carbodiimides agreed with an "allene" structure, i.e., the RNC structural unit is in the same plane. Thus they disagreed with the structural model proposed by both Schneider and Daly and Wheatley. Feichtmayr and Wurstlin's model is illustrated in Figure 5.

If the model suggested by either Schneider or Feichtmayr and Wurstlin is correct, then one must assume that the lone pair of electrons associated with the two nitrogen atoms should be in a bonding configuration. This implies that these compounds should easily form charge-transfer complexes. Complexes of this type have not been reported thus far in the literature and early probing experiments by the author revealed no evidence of charge-transfer formation between iodine (I_2) and N-methyl, N'-tert.-butyl, N,N'-diethyl, N,N'-di-isopropyl and N,N'-di-tert.-butylcarbodiimide. These observations raised doubt as to the validity of the models
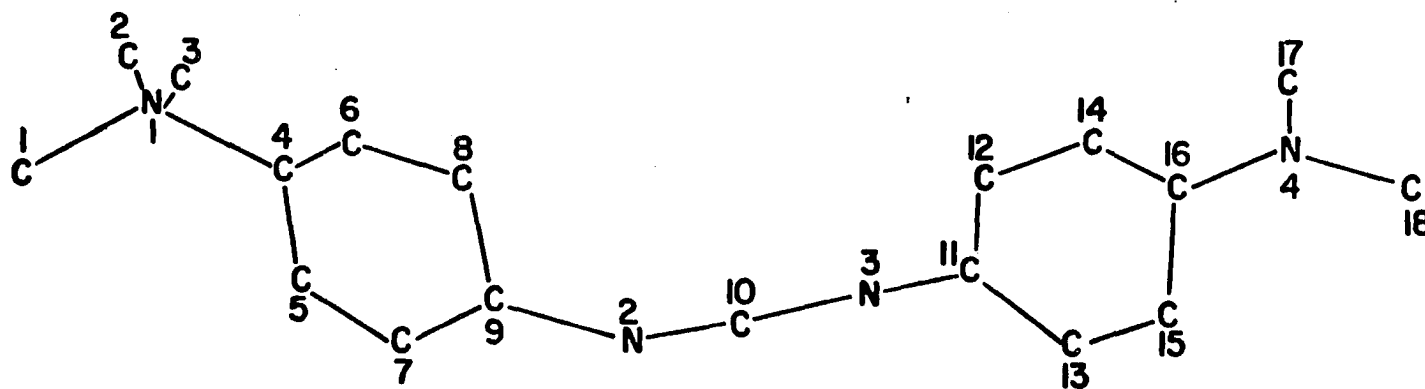
Figure 4.   Asymmetric x-ray structure as determined by Daly and Wheatley (24).
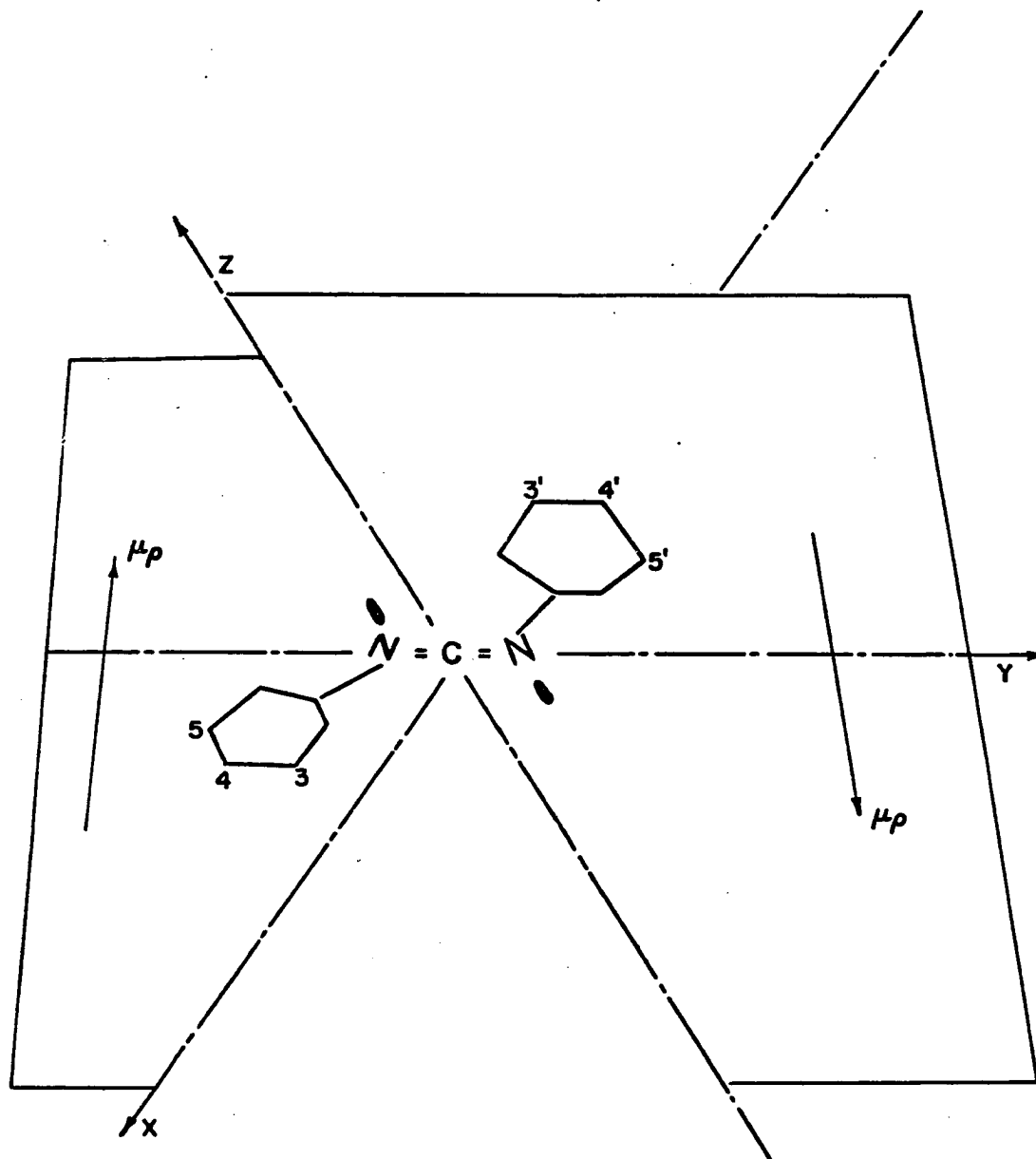
Figure 5.   Asymmetric carbodiimide structure proposed by
            Flichtmayr and Wurstlin (25)

proposed by Schneider and Feichtmayr and Wurstlin.

Among the early chemical speculations on these compounds, repeated mention was made of the possible tautomeric equilibrium between carbodiimide and cyanamide and many investigators (26, 27, 28, 29, 30, 31) have considered the possibility of a tautomeric equilibrium between the cyanamide and carbodiimide configurations

$$H_2N - C = N \rightleftarrows HN = C = NH$$
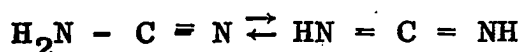
Such an equilibrium has been discounted by the nuclear magnetic resonance studies of Ray, Piette and Hollis (32) who found only a single signal for the nitrogen-14 (N^{14}) resonance of N,N'-dicyclohexylcarbodiimide. An unsymmetrical cyanamide structure would give two lines.

Fragmentary infrared observations of disubstituted carbodiimides were first reported by Khorana (33) who indicated that these compounds had an intense character-istic absorption band near 2150 cm^{-1}. In another study of the 2100 cm^{-1} spectral region, Meakins and Moss (34) not only confirmed the findings of Khorana, but expanded the range of the characteristic vibration for carbodiimides to frequencies between 2150 and 2100 cm^{-1}. In addition, they assigned these frequencies to the NCN asymmetrical stretching mode. Meakins and Moss also obtained an approximate value of 1500 for the extinction coefficient of NCN groups. Rao (35), like Khorana and Meakins and Moss, made fragmentary infrared

observations on carbodiimides and assigned the intense absorption bands occurring in the 2150 to 2100 cm^{-1} region to the NCN asymmetrical stretching vibration. Khorana, Rao, Meakin and Moss also observed that aliphatic carbodiimides gave rise to a single peak between 2140 and 2125 cm^{-1} for the asymmetric stretching mode of the NCN system, whereas the aromatic compounds exhibit two bands. These investigators suggested that the doublet observed for the phenyl derivatives was probably due to Fermi resonance with an overtone or combination tone.

Kahovec and Kohlraush (27) concluded from Raman spectroscopic observations on a series of nitrogen compounds that a tautomeric equilibrium existed between the cyanamide and a carbodiimide structure, as discussed above. The equilibrium is represented by:

$$H_2N - C = N \rightleftarrows HN = C = NH.$$
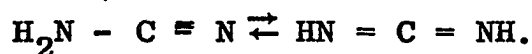
The conclusions of Kahovec and Kohlrauch were apparently invalidated by the nuclear magnetic resonance work of Ray, Piette and Hollis (32) documented earlier. The Raman spectrum of N,N'-diisopropylcarbodiimide was recorded by Kahovec and Kohlrauch but no interpretation was given. Their spectrum did not possess bands in the 2150 to 2100 cm^{-1} region. Since a strong absorption in the infrared spectrum in this region was later assigned to the fundamental NCN asymmetrical stretching mode, the absence of a Raman transition

suggests the existence of symmetry elements within carbodiimide molecules.

A few scattered observations of the ultraviolet spectra of these molecules have been reported. Franssen (36) reported an absorption band at 2599 Å for N,N'-diisopropylcarbodiimide, but Behringer and Meier (37) found only characteristic absorption bands for aliphatic and alicyclic compounds in the region 2120 to 2130 Å. This suggests that Franssen observed the benzene impurity transition at 2600 Å. Benzene was used in the preparation of N,N'-dipropylcarbodiimide. Experiments in the laboratory by the author revealed no evidence of absorption bands for aliphatic carbodiimides between 2120 and 2130 Å. These observations raise doubt as to the validity of the results reported by Behringer and Meier.

Optical rotary dispersion observations in all but one investigation failed to demonstrate the ability of carbodiimide molecules to rotate plane polarized radiation. Schlogl and Mechtler (38) showed that optical antipodes of N,N'-diferrocenylcarbodiimide exist as suggested by Roll and Adams (26).

With the exception of dipole moment measurements documented earlier and the single density and heat of combustion value measured by Salley and Gray (39) for N,N'-diisopropylcarbodiimide, physical properties such as surface tension, viscosity, heats of vaporization, etc.

have not been reported for any compounds in this class. It is
thus apparent that the physical properties and the vibrational
spectra of these compounds have not been adequately studied.
In addition to the paucity of these basic data, the large
dipole moments observed for these compounds raises the basic
question of what inter- or intramolecular phenomena cause
these high values. This thesis is therefore concerned with:
(a) the observation of basic data on the physical properties
and spectra of these compounds; and (b) interpretation of
these data in terms of inter- and intramolecular forces.

PHYSICAL CONSTANTS

Synthesis of Alkyl Carbodiimides

The alkyl carbodiimides in this study were synthesized by reacting the proper thioureas with freshly prepared mercuric oxide in a water-diethyl ether mixture (40). This reaction is illustrated by:

$$RNHCSNHR' + HgO \rightarrow RNCNR' + HgS + H_2O$$
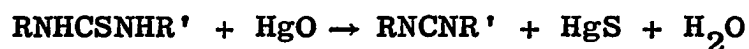
where R and R' represent alkyl groups. When the reaction was complete, the mixture was filtered to remove the black mercuric sulfide. The water and ether fractions were separated by means of a separatory funnel and the water layer was washed twice more with fresh portions of diethyl ether. The washings were combined with the first ether fraction and the total amount was distilled at atmospheric conditions. This distillation removed most of the diethyl ether from the crude alkyl carbodiimide. Solid calcium chloride was added to the fraction containing the alkyl carbodiimide. This inorganic material was left in contact with the carbodiimide for about 24 hours during which time the small quantity of water intermixed with the organic liquid was absorbed. The hydrated calcium chloride was removed by filtration. Then the alkyl carbodiimide was purified by repeated distillations at reduced pressure.

N,N'-dimethylcarbodiimide could not be synthesized by any of the existing chemical procedures. This was stated by Sidgwick (41) in his text on nitrogen chemistry. Similarly repeated attempts by the author to obtain the N,N'-dimethyl compound, using up-to-date chemical techniques and apparatus, also met with failure.

Molecular Weights by the Freezing Point Depression Method

The molecular weights of N,N'-diisopropyl and N,N'-di-tert.-butylcarbodiimide (between 0.5 and 0.01 molal) were determined by the freezing point method (42). The solvent used was spectroscopic grade cyclohexane, which has a freezing point constant of 20.5°K/molal. The molecular weight was calculated from the freezing point depression by the relationship:

$$M = \frac{g_2}{g_1} \cdot \frac{K_f}{\Delta T} \cdot 10^3$$

where g_2 and g_1 are the grams of solute and solvent respectively, K_f is the freezing point constant of the solvent and ΔT is the freezing point temperature difference between the pure solvent and the solution. The results of these measurements are summarized in Table 1. The measured molecular weights are very close to the theoretical values for the non-associated molecules, indicating a negligible amount of intermolecular attraction in solution.

Density

The standard pycnometer method was used to determine the density of three typical carbodiimides. Distilled water

Table 1. Molecular weight of carbodiimides

Compound	Molecular Weight Theoretical	Weight Measured	Percent Difference
N,N'-diisopropylcarbodiimide	126	120	5% low
N,N'-di-tert.-butylcarbodiimide	154	161	4% high
	154	158	2.5% high
N,N'-di-o-tolycarbodiimide	214	221	3% high

was employed to determine the volume of the pycnometer. The
results of the density measurements are summarized in
Table 2. Salley and Gray (39) reported a density of

Table 2. Density of the carbodiimides

Compound	Density at 25°C
N,N'-diisopropylcarbodiimide	0.807 g/ml
N,N'-di-tert.-butylcarbodiimide	0.796 g/ml
N,N'-di.-o-tolycarbodiimide	1.063 g/ml

0.909 g/ml for N,N'-diisopropylcarbodiimide, which is some-
what higher than the 0.807 g/ml value reported here. Repeated
determinations agreed with the latter value. It appears, then
that the density reported by Salley and Gray is in error.
The density trend observed for the two aliphatic carbodiimides
suggest a rigid sphere model, which implies negligible
intermolecular forces.

Surface Tension by the Ring Method

The duNouy tensiometer (43), provides a convenient means of evaluating the surface tension of a liquid. Using the standard procedures (44), the surface tension for N,N'-diisopropyl, N,N'-di-tert.-butyl and N,N'-di-o-tolylcarbodiimide were found to be 23.9 ± 0.96, 23.5 ± 0.94 and 29.6 ± 1.5 dynes per cm respectively at 25°C.

Vapor Pressure Measurements

The Ramsay-Young apparatus (42), illustrated in Figure 6, provides an excellent way to obtain vapor pressure measurements as a function of temperature. When this information is combined with the Clausius relationship (45), referred to as the Clausius-Clapeyron equation, a linear expression of the form $\log_{10} P = -\frac{A}{T} + C$ is developed. The constants A and C were evaluated from the pressure-temperature data used in conjunction with a least squares procedure (46) and with an IBM-7074 computer. The heat of vaporization ΔH_v was evaluated from the constant A by the relationship $A = \frac{\Delta H_v}{2.303R}$ where R is the gas constant. Exact agreement between experimental results and the derived linear relationship $\log_{10} P = -\frac{A}{T} + C$ was not observed for the entire pressure-temperature range. The deviation from linearity is demonstrated by the $\log_{10} P$ versus 1/T plots illustrated in Figures 7, 8 and 9. This apparent deviation
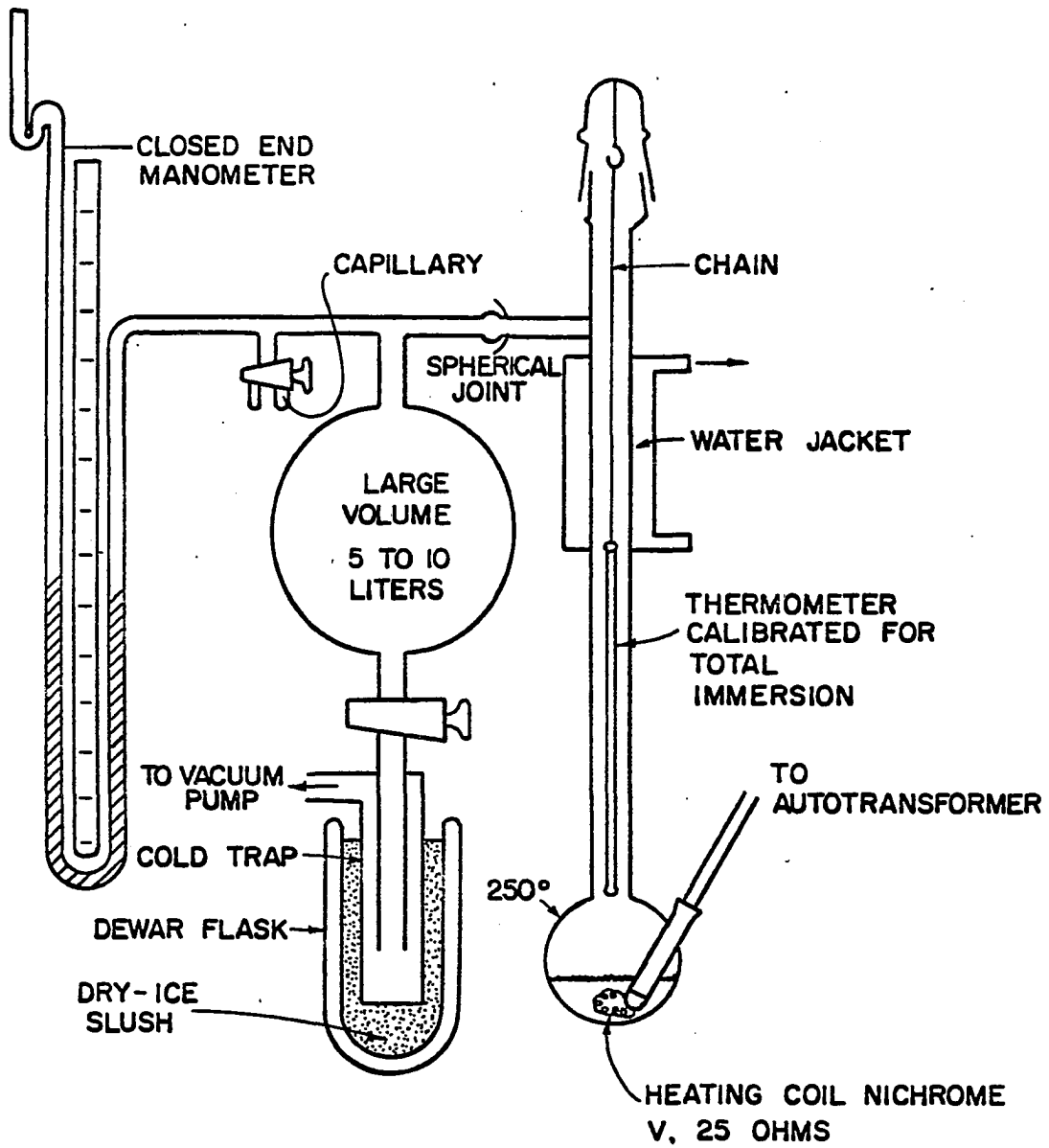
Figure 6. Ramsay-Young apparatus
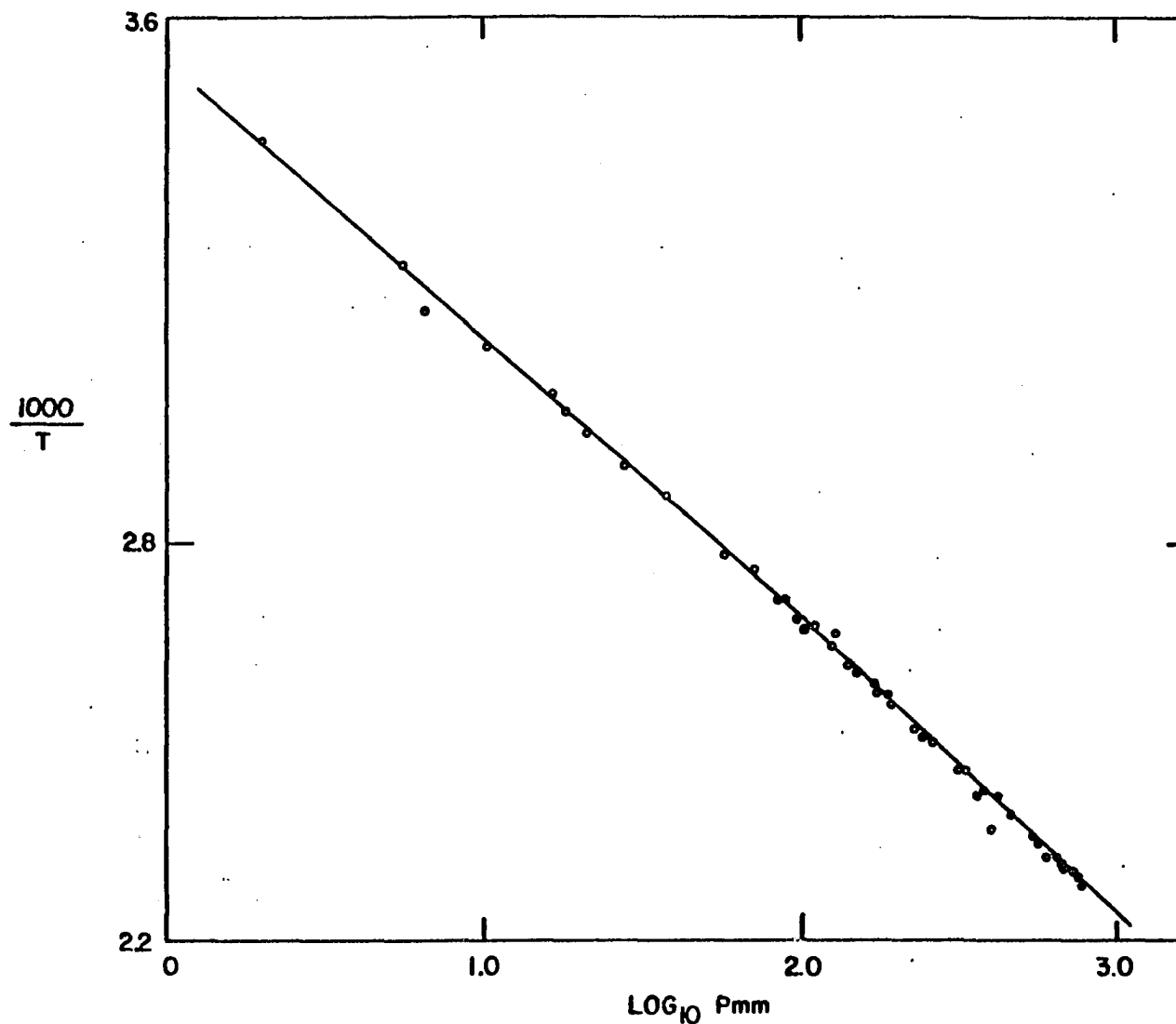
Figure 7. $Log_{10}P$ versus $1/T$ for the vapor pressure of N,N'-di-tert.-butylcarbodiimide
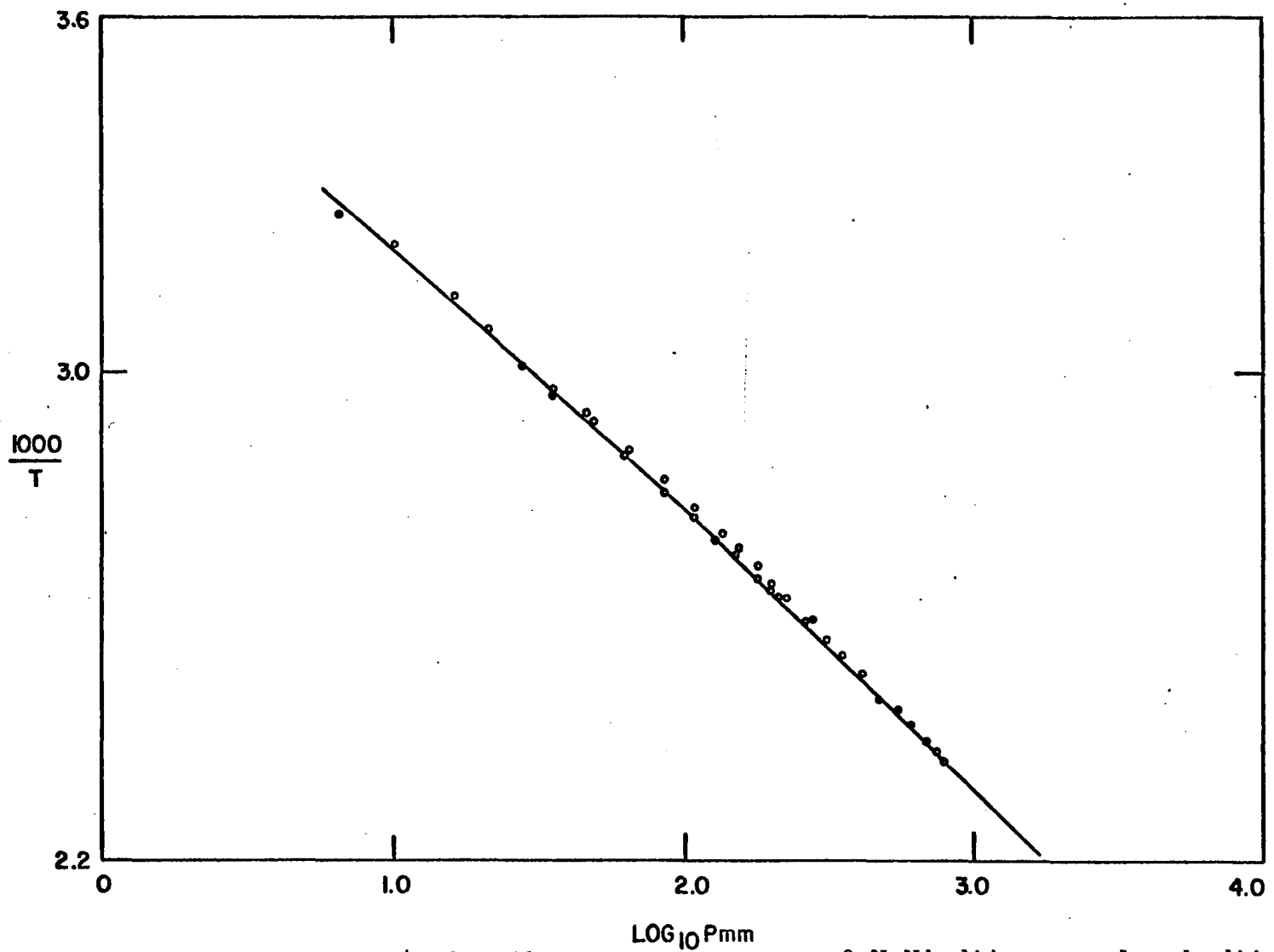
Figure 8. $Log_{10}P$ versus $1/T$ for the vapor pressure of N,N'-diisopropylcarbodiimide

22
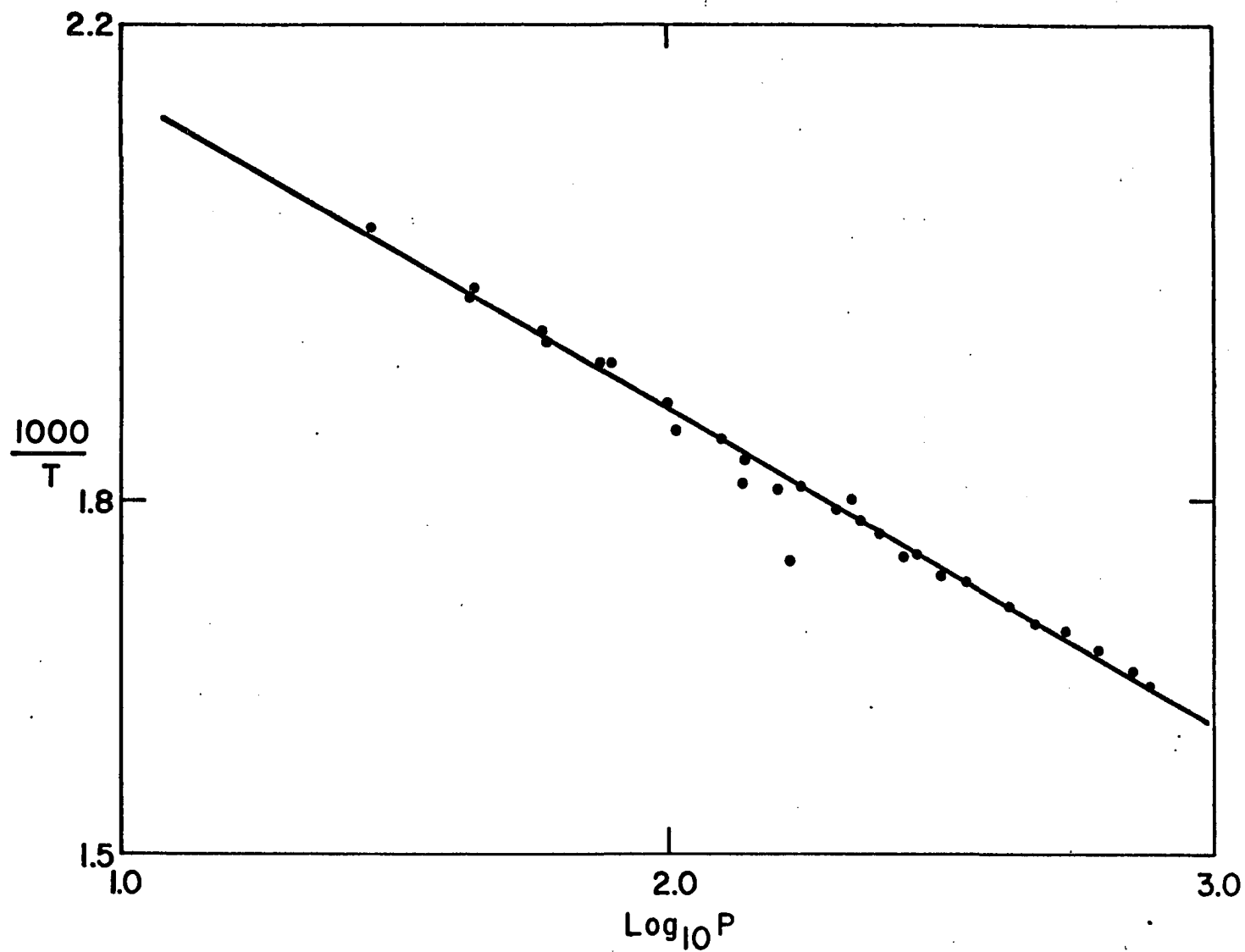
Figure 9. $\text{Log}_{10}P$ versus $1/T$ for the vapor pressure of N,N'-di-o-tolylcarbodiimide

from the linear function is not unexpected for two reasons:
first, the ideal gas laws have been assumed in the deviation;
and second, the heat of vaporization is not constant over an
appreciable temperature range. However, as illustrated
by the $\log_{10}P$ versus $1/T(°K)$ plots in Figures 7, 8, and 9, there
are regions between 10 and 760 torr where this equation is
applicable. Five equations of state, two each for N,N'-
diisopropyl and N,N'-di-tert.-butylcarbodiimide and one for
N,N'-di-o-tolycarbodiimide, and the heats of vaporization
are summarized in Table 3. The normal boiling points for
N,N'-di-isopropyl, N,N'-di-tert.-butyl and N,N'-di-o-
tolylcarbodiimide, as obtained from the $\log_{10}P$ versus $1/T$
plots, were 421, 438 and 612°K respectively.

According to Trouton's rule (45), the molar heat of
vaporization divided by the absolute boiling temperature at
760 torr is between 21 and 23 calories per mole per degree
for non-associated liquids. For the heats of vaporization
indicated in Table 3, the values calculated for N,N'-
diisopropyl, N,N'-di-tert.-butyl and N,N'-di-o-tolylcarbodi-
imde are 22.5, 22.7 and 20.6 calories per mole degree
respectively. Thus, according to this rule, these compounds
in their liquid state are not appreciably associated. The
infrared spectroscopic results to be discussed later
reinforce these conclusions.

Table 3. Vapor pressure data

Compound	Equation of state $\log_{10}P = \frac{A}{T} + C$	Pressure range in mm of Hg	Mean absolute deviation	Heat of vaporization
N,N'-dissopropyl-carbodiimide	$\log_{10}P = \frac{2360.24}{T} + 8.57$	10 to 200 torr	1.67×10^{-2}	10.80 ± 0.5 Kcal/mole
	$\log_{10}P = \frac{2064.73}{T} + 7.78$	200 to 760 torr	6.8×10^{-3}	9.45 ± 0.5 Kcal/mole
N,N'-di-tert.-butyl-carbodiimide	$\log_{10}P = \frac{2386.11}{T} + 8.41$	10 to 108 torr	1.12×10^{-2}	10.92 ± 0.5 Kcal/mole
	$\log_{10}P = \frac{2170.27}{T} + 7.83$	108 to 760 torr	1.52×10^{-2}	9.93 ± 0.5 Kcal/mole
N,N'-di-o-tolyl-carbodiimide	$\log_{10}P = \frac{2730}{T} + 7.53$	30 to 760 torr		12.6 ± 0.5 Kcal/mole

In 1890, Guldberg's relationship (45) stated an empirical rule that the absolute critical temperature of a substance is about one and one-half times its absolute boiling point at 760 torr. From this rule, N,N'-diisopropyl, N,N'-di-tert.-butyl and N,N'-di-o-tolylcarbodiimide yielded critical temperature values of 358, 384 and 645°C. Critical temperatures can also be evaluated by using surface tension and density parameters in conjunction with the Ramsay-Shields relationship (47). This equation is mathematically represented by:

$$\gamma \left(\frac{m}{\rho}\right)^{2/3} = K(t_c - t - 6)$$

where γ is the surface tension, m is the molecular weight, ρ is the density, t_c is the critical temperature, t is the temperature at which the surface tension and density are measured, and K is the temperature coefficient of the molar surface energy. According to Ramsay and Shields, K, the coefficient of the molar surface energy, had the same value, namely 2.12, for all normal nonassociated liquids. The critical temperature values obtained from the Ramsay-Shields expression and Guldberg's relationship are in Table 4. From Table 4, it is apparent that there is a substantial difference between the critical temperatures evaluated by Guldberg's and the Ramsay-Shields relationships for the aromatic compound. However, the difference between these values probably occurred because the shape and orientation

Table 4.   Critical temperatures

	Guldberg's Rule	Ramsay-Shields Relationship
N,N'-diisopropyl-carbodiimide	358±11°C	357 ± 18°C
N,N'-di-tert.-butyl-carbodiimide	384±12°C	402 ± 20°C
N,N'-di-o-tolylcarbo-diimide	645±19°C	523 ± 26°C

of the aromatic molecules were affecting the temperature

coefficient of the molar surface energy.   This shape and

orientation concept (48) is highly theoretical and apparently

has not been studied in any detail.

Dipole Moments

As discussed on page 7 to 9 of this thesis, the dipole

moments of carbodiimides have been extensively studied and

interpreted, but not in an unequivocal manner.   Since a

number of values have already been reported, only one

measurement was made on N,N'-diisopropylcarbodiimide to

check the literature values.   This measurement was made by

the Guggenheim method (49).   This method has the advantage

that precise values of solution densities are not required.

The pertinent data for this measurement are summarized in

Table 5 and the graphical solution is found on page 30 .

The measured value of 2.04 ± 0.04 D agrees well with the

Table 5.   Data used with the Guggenheim dipole moment method

Data	1	2	3	4	5
Concentration $\times 10^5$ moles/ml	1.052	2.224	3.801	5.604	6.891
n	1.42413	1.42456	1.42513	1.42578	1.42643
n^2	2.02815	2.02937	2.03099	2.03285	2.03470
capacitance of cell empty	40.7867	40.7822	40.7822	40.7822	40.7837
capacitance of cell full	32.2413	32.1771	32.1011	32.0123	31.9586
ΔC $C_{empty} - C_{full}$	8.5454	8.6051	8.6811	8.7699	8.8251
C_o cell constant (40.5708-32.2004) empty - full	8.3704	8.3704	8.3704	8.3704	8.3704
$\Delta C/\Delta C_o$	1.0209	1.0290	1.0371	1.0477	1.0543
	2.03621	2.04342	2.05266	2.06342	2.07012
$(\epsilon - n^2)$	0.00806	0.01405	0.02167	0.03057	0.03542
$(\epsilon + 2)(n^2 + 2)$	16.2585	16.2924	16.3363	16.3872	16.4217
$\dfrac{(\epsilon - n^2)}{(\epsilon + 2)(n^2 + 2)}$ $\times 10^4$	4.957	8.623	13.264	18.564	21.569

Volume of solution = 25 ml
Solvent - cyclohexane
ϵ cyclohexane = 2.015
T = 25°C

value of 2.08 D reported by Birkofer, Ritter and Richter (50), Schneider (23) and Feichtmayr and Wurstlin (25). The consideration of the high dipole moment value generally observed for these compounds in terms of intermolecular forces will be deferred until after the results of the ultraviolet and vibrational analysis have been presented.
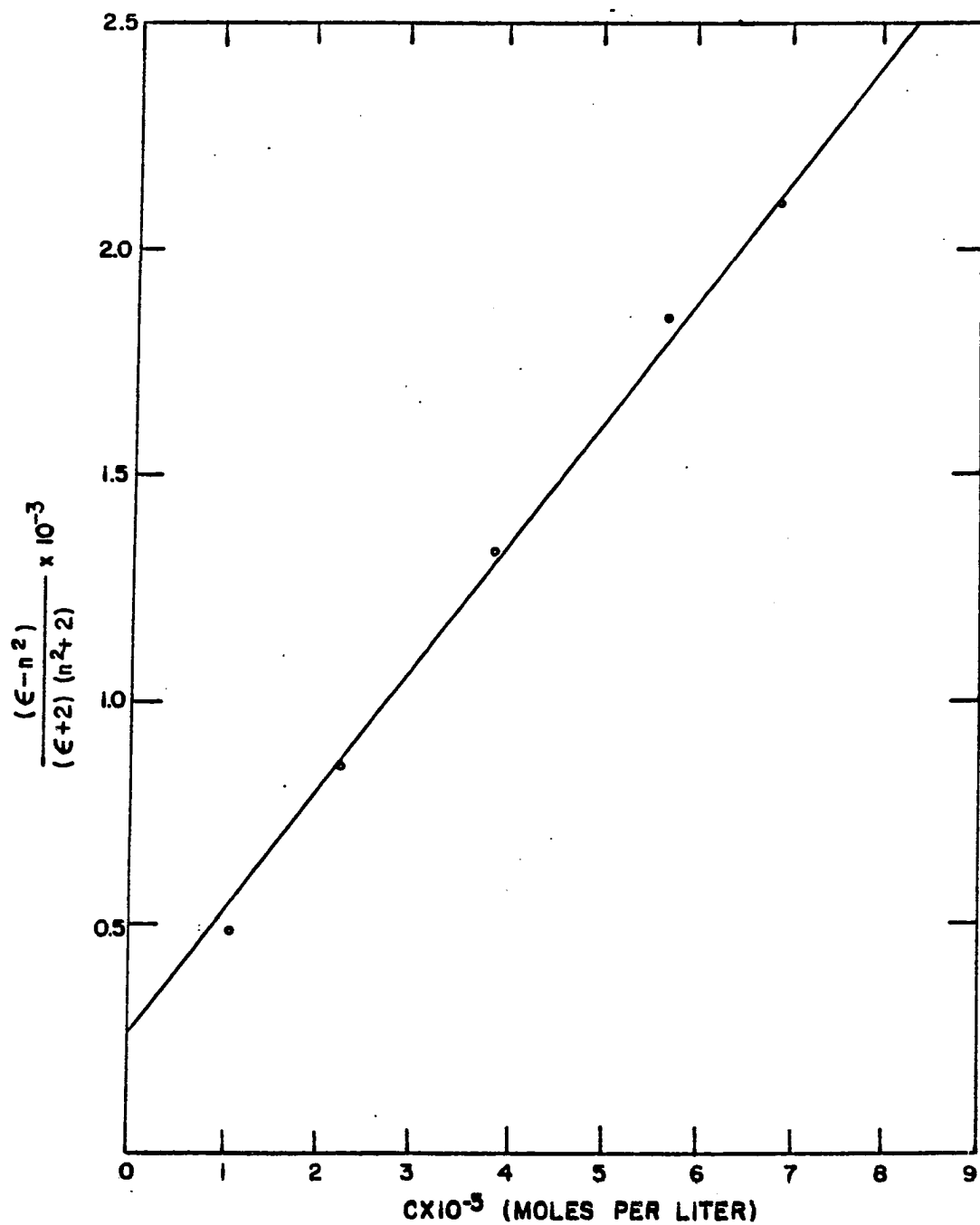
Figure 10. The dielectric constant and refractive index relationship versus molar concentration of N,N'-diisopropylcarbodiimide

ULTRAVIOLET AND VISIBLE SPECTRA

Molecules will absorb radiation in the ultraviolet and visible regions as a result of excitation of the outer or valence electrons, from the ground to high electronic states. The interpretation of these electronic spectra is very difficult for molecules containing more than three or four nuclei, except where some simplification results from a high degree of symmetry, as, for example in benzene and in linear molecules. However, a systematic approach is possible, both experimentally and theoretically, if the electronic transition are regarded in complex molecules as localized in certain chemical groups or bonds.

It has long been recognized that series of related molecules which all contain a particular group often have absorption spectra of similar appearance and intensity in a particular region of the spectrum. For example, in the 3500-4000Å region, nitrous acid HONO and aliphatic nitrites of the form RONO exhibit a system of weak absorption bands which are ascribed to the -ONO group. Olefins, which contain the ethylenic $C = C$ group, show characteristic strong absorption in the 1500-2000Å region. Such groups are commonly called chromophores, a term introduced by O. N. Witt in 1876 (45) to describe groups which determine the colors of series of synthetic dyestuffs molecules.

The types of electronic transitions observed in the
ultraviolet and visible region are denoted by letter
combinations $N \to V$, $N \to R$ and $N \to T$ (45). An $N \to V$ transi-
tion is pictured as a partial transfer of a σ-electron pair
to one of the constituent atoms in a bond, causing a
momentary increase in the ionic character, e.g., $CH \to \overset{-+}{CH}$,
of this bond. The two strong bands observed for benzene
near 1800 and 2000Å are good examples of an $N \to V$ transition.
When substituents such as CH_3 and CH_3CH_2, are directly
attached to the benzenoid system, the 1800 and 2000Å bands
are observed at higher wavelength values. The red shift can
be described as moving a negative charge into the ring thereby
lowering the energy required to excite an electron. The
second, termed an $N \to R$ or Rydberg transition, represents the
progressive removal of a σ-electron from both constituent
atoms of a bond, resulting in complete ejection of an electron
from the molecule forming a positive ion, e.g. $C\text{-}C \to \overset{+}{C \cdot C}$,
where the dot designates the remaining electron. π-electrons
undergo the same types of transitions as σ-electrons, but
because the concentration of electron density in the π-system
is lateral to the axis, rather than in the axis of the bond,
the displacement of π-electrons occurs more readily than σ-
electrons. There is also another transition associated with
the π-electrons which is designated an $N \to T$ transition. The
spectra resulting from this type of electron excitation are

usually weak and are assigned to forbidden transitions. An example of forbidden transitions are the weak bands observed for benzene between 2500 and 3000Å.

The electronic spectra between 2000 and 8000Å of aliphatic and aromatic carbodiimides were obtained in a cyclohexane solution using a Cary-14 spectrophotometer. Table 6 summarizes the observations made.

Table 6. Ultraviolet and visible absorption bands of alkyl and aromatic carbodiimides and alkyl carbodiimides with iodine

Compound	Absorption Bands
N,N'-diethylcarbodiimide	none
N,N'-diisopropylcarbodiimide	none
N,N'-di-tert.-butylcarbodiimide	none
N-methyl, N'-tert.-butylcarbodiimide	none
N,N'-diphenylcarbodiimide	2500 and 2425Å
N,N'-di-o-tolylcarbodiimide	2444Å
N,N'-bis(2,6 diethylphenyl) carbodiimide	2500Å
Iodine in cyclohexane	5220Å
N,N'-diethylcarbodiimide + iodine	5220Å
N,N'-diisopropylcarbodiimide + iodine	5220Å
N,N'-di-tert.-butylcarbodiimide + iodine	5220Å
N-methyl, N'-tert.-butylcarbodiimide + iodine	5220Å

The absence of absorption bands for the aliphatic carbodiimides reported in Table 6 indicates that electronic transitions in these compounds must occur in the region below 2000Å. This information contradicts the observations of Franssen (36), Behringer and Meier (37) documented earlier.

The red shift of the aromatic compounds relative to N,N'-diphenylcarbodiimide is indicative of alkyl substitution on the benzene ring (51). It is not apparent, however, why the N,N'-diphenylcarbodiimide band splits into two components. A similar band splitting effect is observed for trans-azoxybenzene (52) where two (or possibly three) bands occur at 2380, 2310 (and possibly 2270Å).

Iodine in cyclohexane absorbs at 5220Å. Since no other bands appear when iodine is added separately to each alkyl carbodiimide, complexation does not appear to occur. This result is surprising because compounds possessing nitrogen atoms usually form weak molecular compounds with a molecule such as iodine. When these complexation results are correlated with the nuclear magnetic resonance (32) and physical constant studies, there is very strong indication that the nitrogen lone pair exists in a non-bonding configuration.

When attempts were made to interpret the non-bonded configuration proposal in terms of the electronic structure of molecules, two approaches were used. These were the

valence bond and molecular orbital methods.

A classical valence-bond representation is demonstrated in Figure 11. From this picture, it is obvious that the R groups are perpendicular to the planes containing the nitrogen atoms. Also, from this valence bond representation, the two planes containing an N=C unit are observed to be perpendicular to each other. While the x-ray information of Daly and Wheatley (24) is not consistent with this structure, a molecular configuration of this type does agree with the ultraviolet observations since the lone pair is located in a configuration which would not form a molecular complex with iodine. Moreover, the structural proposals used by Schneider (23), Feichtmayr and Wurstlin (25), documented earlier, appear to be unlikely because the nitrogen lone pair in their models are in a configuration which has a high probability of bonding with molecular iodine.

Molecular orbital concepts seem to be utilized with more success than valence bond procedures for organic compounds. However, molecular orbital theory is still rudimentary and it appears that molecular systems lacking a high degree of symmetry cannot be described with any certainty. The carbodiimides studied in this investigation appear to lack this high degree of symmetry.

Figure 11.   Valence bond model for carbodiimides without hybridized orbitals

INFRARED AND RAMAN SPECTRA

Infrared Spectra

The vibrational spectra of polyatomic molecules, obtained either by infrared or Raman methods, may be interpreted through mathematical analysis, in terms of internal structural parameters and force constants relating the interactions between bonded and nonbonded pairs of atoms. However, as molecular complexity increases the difficulties pertaining to the mathematical analysis become so great as to render this method useless. An alternate and very useful approach involves the interpretation of the vibrational spectra in terms of group frequencies. This investigation is primarily concerned with the group frequency approach. Therefore, a clear insight is necessary concerning the origin and limitations of group frequencies.

Group Frequencies

When infrared spectra are observed for a number of compounds, it is found that subgroups common to all the molecules absorb within the same limited range of frequencies, irrespective of the molecule in which the subgroup is present. This limited range of frequencies designated for a specific group of nuclei is called a group frequency (53). The essential constancy of group frequencies results from the

constancy of the bond force constants from molecule to molecule. An example of the relatively constant spectral regions for group frequencies is observed for the carbonyl group. The limited frequency range listed for the CO stretching vibration is 1950 to 1600 cm^{-1}. Group frequencies for organic and inorganic molecules have been summarized in the form of very useful identification charts (54,55,56).

The concept of group frequencies depends upon the assumption that the vibrations occurring for a particular group are relatively independent of the molecule in which the group is present. When a group includes relatively light atoms such as hydrogen (OH, NH, CH, CH_2, etc.) or relatively heavy ones such as halogens (CCl, CBr, CI, etc.), the concept of an isolated vibration can be justified (since these atomic groups absorb over a narrow range of frequencies regardless of the rest of the molecule). Vibrations of groups having multiple bonds (C $\equiv$ C, C $\equiv$ N, C = C, C = O, etc.) can also be relatively independent of the remaining portion of the molecule if the groups do not belong to a conjugated system. In many cases it is not possible to localize the vibration to a pair of atoms, but it is often possible to consider a large set of atoms as a group. An example of this is the phenyl ring. No absorption resulting from the stretching of individual carbon-carbon bonds is observed but many vibrations characteristic of the entire

ring skeleton are found. These arise from simultaneous motion
of most or all of the atoms in the ring. Examples of group
frequencies in terms of XY_2 and XY_3 molecules are illustrated
in Figure 12.

The major limitation of the group frequency concept
arises from interaction of vibrations. The phenyl group is
one case, but fortunately with characteristic results. Inter-
action can be expected when the masses and force constants in
the system are similar. The system -C-C-N, for example,
does not possess vibrations characteristic purely of C-N
or C-C bonds but does have vibrations involving simultaneous
motion of all the atoms.

It was stated previously that group frequencies occur
not at specific and characteristic points, but within a
limited spectral region. The factors which cause the frequency
to vary from molecule to molecule and which therefore produce
a small change in the force constant are of interest. The
first of these factors is the inductive effect of the groups
connected to the system under consideration. The character-
istic group frequency changes depend on the electronegativity
of the atoms connected to the nuclei involved in the absorp-
tion. Since substituents may change the electron density
within a bond, the force constant of the bond may vary,
resulting in a different absorption frequency. Conjugation
of multiple bonds, such as an alternation between single

Figure 12. Group frequencies of XY_2 and XY_3 molecules

Top row: Stretching vibrations: (a) XY_2
symmetrical stretching; XY_2 asymmetrical
stretching; (c) XY_3 symmetrical stretching;
and XY_3 asymmetrical stretching

Bottom row: Bending (deformation) vibrations:
(a) XY_2 in-plane deformation or scissoring;
(b) XY_2 out-of-plane deformation or twisting;
(c) XY_2 out-of-plane deformation or wagging;
(d) XY_2 rocking: (e) XY_3 symmetrical deformation;
and (f) XY_3 asymmetrical deformation. The +
and – signs represent motion above and below
the plane of the paper, respectively.
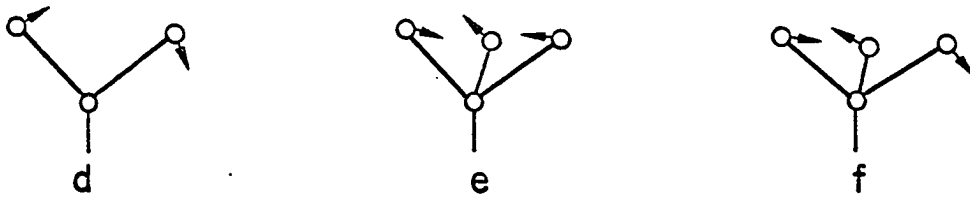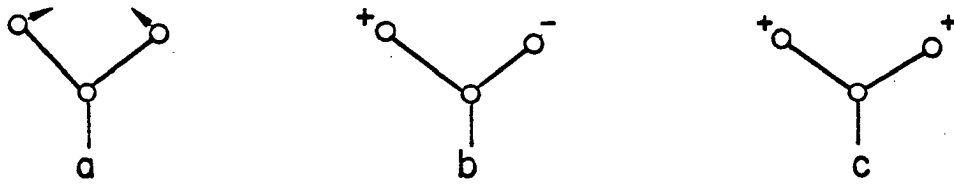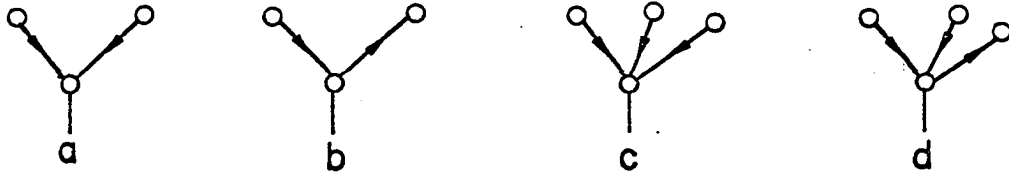
and multiple bonds, also affects the frequency within a system.
Resonance tends to decrease the electron density in the
multiple bonds causing their absorptions to shift to lower
frequencies. Strain is yet another intramolecular parameter
which affects shifts within the characteristic frequency range.
An example of intermolecular strain is found in cyclic ketones
where bond angles may be deformed from their normal values.
However, broad generalizations cannot be made because the
subject has not been studied sufficiently. Association is a
major cause of frequency shifts. The frequency of the stretch-
ing vibrations usually shifts to lower frequencies because
the electron density of the bond is decreased by association.
Bending vibrations in general are observed to be displaced
to higher frequencies by association. This is due to the
fact that more work is required to move an atom from the
position stabilized by the two bonding system.

Raman Spectra

Another way in which a molecule can interact with
light is by a type of inelastic scattering. Here, the light
radiation can give up part of its energy to raise the
molecule from one eigenstate to another, and to be scattered
with a lower frequency;

$$h\upsilon_o = h\upsilon_{molec} + h\upsilon_{ac},$$

where υ_o and υ_{ac} denote the frequencies of incident and

scattered light. The term $h\nu_{molec}$ is the difference between certain molecular energies. This kind of inelastic scattering was first predicted by Smekal in 1923 and first observed experimentally by Raman in 1928. The technique for observing this inelastic scattering is usually referred to as the Raman effect or Raman scattering.

Raman scattering is observed to be weak for most conditions. Because of the weak nature of the radiation, it is necessary to use a very intense light source for ν_o and usually liquid phase samples so as to concentrate many molecules into the scattering volume.

Probably the greatest utility of the Raman spectrum lies in the fact that it obeys selection rules different from the infrared spectrum. The selection rules for the Raman effect depend upon the molecular polarizability, in contrast to the selection rules for the infrared, which depend upon the dipole moment. A fundamental vibration is allowed in the Raman spectrum if the molecular polarizability changes during vibration.

The selection rules always allow the totally symmetric modes to appear in the Raman spectrum. For highly symmetric molecules, the Raman spectrum can furnish vibrational frequencies that are absent from the infrared spectrum.

The combination of both the Raman and infrared spectrum can be a powerful tool in the determination of structure.

VIBRATIONAL SPECTRA OF THE CARBODIIMIDES

The carbodiimides utilized in this infrared and Raman investigation were liquids at room temperature. The compounds were vacuum distilled immediately before their vibrational spectra were obtained because, as indicated previously, carbodiimides have a marked tendency to polymerize. Moreover, sulfur compounds could not be used as solvents because they appeared to accelerate the chemical decomposition of carbodiimides.

Spectroscopic Procedures

Infrared spectra between 4000 and 33 cm^{-1} were obtained by using the Beckman IR-7 and IR-11 spectrophotometers. The IR-7 is a prism-grating spectrophotometer, equipped with sodium chloride and cesium iodide interchanges, and covers the spectral region between 4000 and 200 cm^{-1}. The IR-11 grating-filter spectrophotometer was used in the range between 700 and 33 cm^{-1}. The wavelength accuracy of the IR-7 is estimated to be ± 3 cm^{-1} above 2000 cm^{-1} and ± 2 cm^{-1} below this value. Similarly, the wavelength accuracy of the IR-11 is estimated to be ± 2 cm^{-1}.

Standard techniques and cells (57) were used to obtain spectra of solid, liquid and vapor state samples. The cell window materials used with the IR-7 were potassium bromide

and cesium iodide, while polyethylene window material was utilized with the IR-11. The spectra at low and elevated temperatures were obtained using an LTJ-1 cell (Limit Research Corporation). Temperature measurements were made by using an iron-constantan thermocouple.

Although standard cells were utilized, their metallic portions, which came into contact with the sample had to be replaced with nonmetallic material. The metal parts tended to accelerate polymerization of the carbodiimides.

Raman spectra between 3000 and 100 cm^{-1} were obtained with a Cary-81 spectrophotometer using laser excitation. The wave number accuracy of the bands were estimated to be ± 2 cm^{-1}. These spectra were obtained by W. Renken at Cary instruments, a division of Varian.

In the region of 3000-2800 cm^{-1} there is good correlation between the Raman and infrared frequencies; whereas, in the region of 1500-100 cm^{-1}, occasional discrepancies appear between the frequencies obtained from the two spectroscopic methods. When H. Sloane of Applied Physics Corporation, subsidiary of Varian, was consulted in regard to this matter (58), he reported that Raman spectra obtained from an instrument utilizing a high intensity laser source occasionally gave frequencies 5 to 25 cm^{-1} higher than the infrared but that the reason for this discrepancy is unknown.

W. Renken "hand scanned" the spectral region between 2600 and 1600 cm^{-1} and found no Raman lines. Recordings in this frequency range were not made, in order to minimize ultraviolet decomposition of the samples.

Characteristic Group Frequencies of Carbodiimides

The Raman and infrared spectra of the aliphatic carbodiimides are shown in Figures 13 through 15, while the infrared spectra of the aromatic compounds and N,N'-dicyclohexylcarbodiimide appear in Figures 16 and 17. Assignments for the fundamental vibrations of the alkyl carbodiimides appear in Figure 18. The combination and overtone bands of the alkyl carbodiimides appear in Table 7. Although the infrared bands of the N,N'-dicyclohexyl and the aromatic compounds were not interpreted because of the highly complex nature of their spectra, their spectrograms were included to give a more complete infrared representation of the carbodiimides.

Vibrational Degrees of Freedom

Carbodiimides, having a C_1 symmetry should theoretically possess 3N-6 vibrational degrees of freedom, where N is the number of atoms in the molecule. However, this rule apparently does not apply as expected, since approximately one-half to two-thirds of the fundamental vibrations are observed. This can be explained by the following: (1) the twinned nature of the
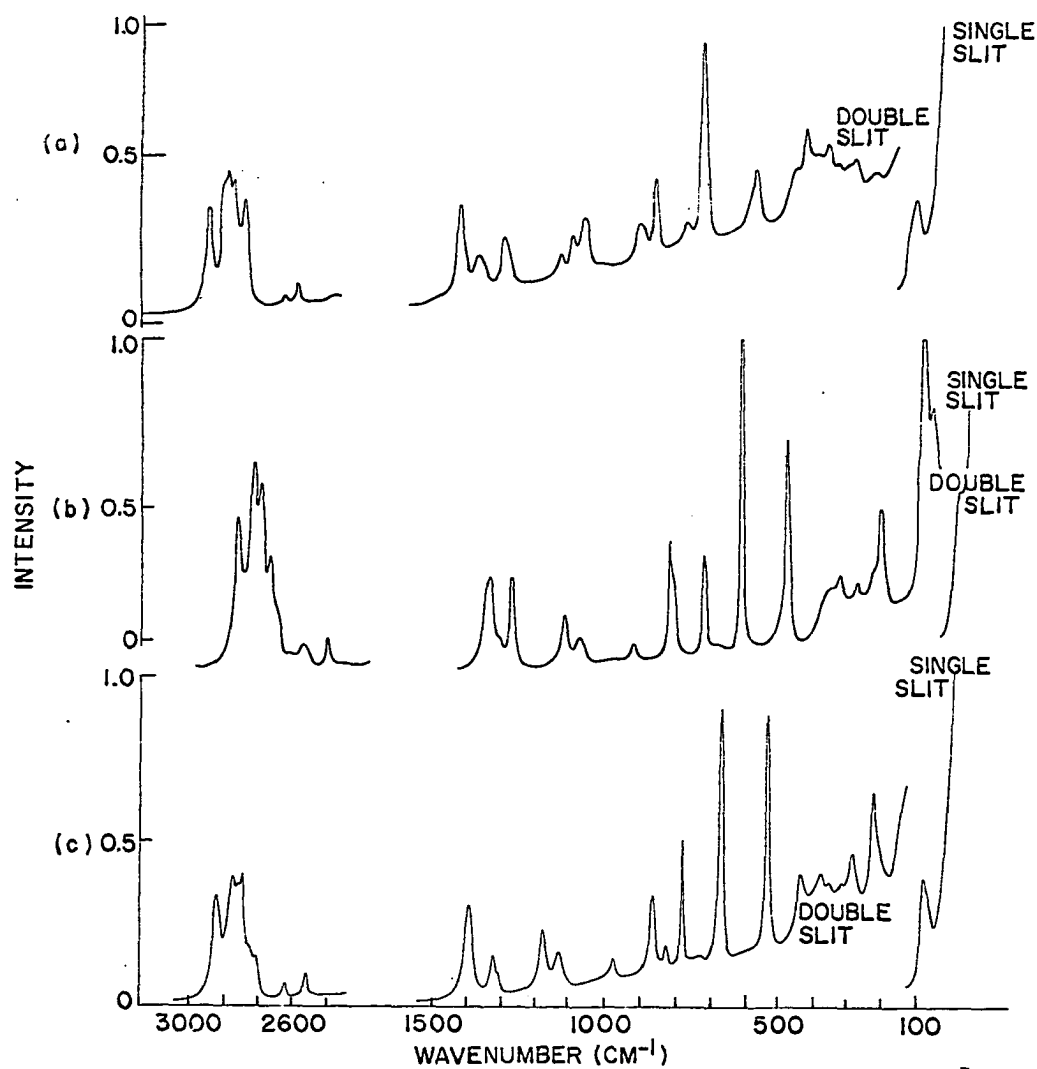
Figure 13. Raman spectra between 100 and 3000 cm^{-1} for the alkyl carbodiimides

(a) N-methyl, N'-tert.-butylcarbodiimide
(b) N,N'-diisopropylcarbodiimide
(c) N,N'-di-tert.-butylcarbodiimide

Figure 14. Infrared spectra between 40 and 600 cm^{-1}
for the alkyl carbodiimides

(a) N-methyl, N'-tert.-butylcarbodiimide

(b) N,N'-diethylcarbodiimide

(c) N,N'-diisopropylcarbodiimide

(d) N,N'-di-tert.-butylcarbodiimide
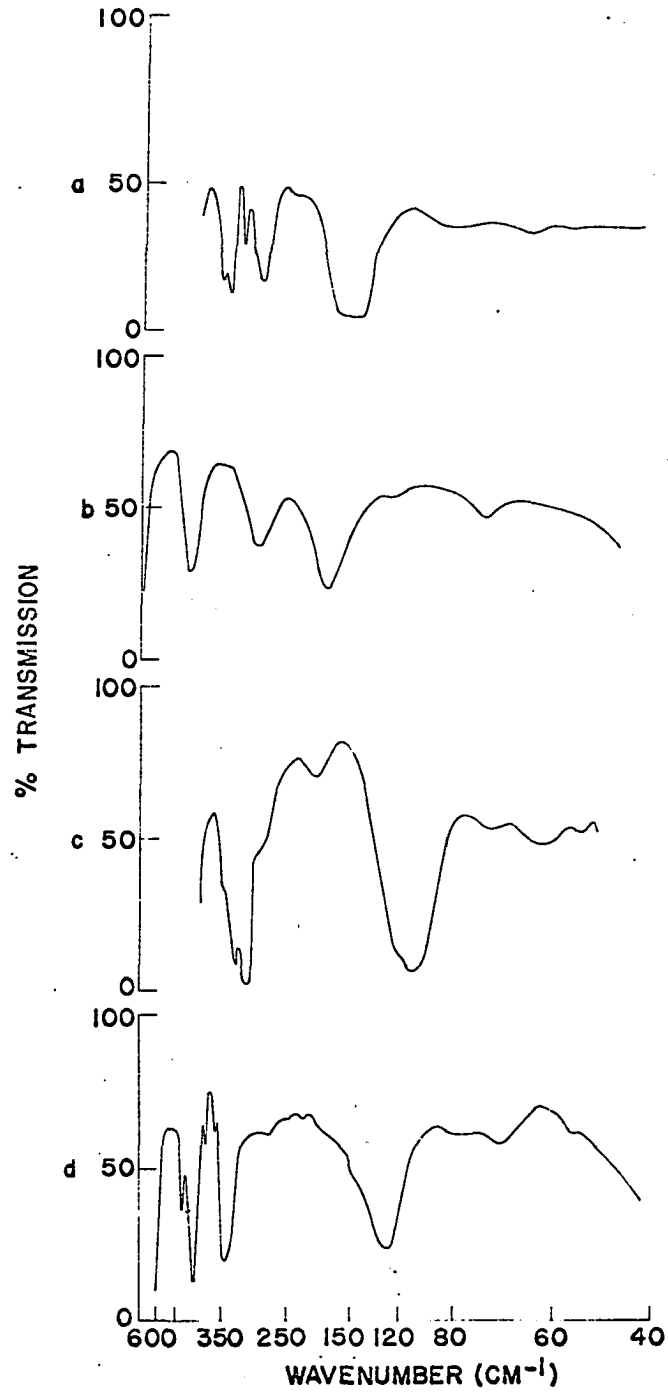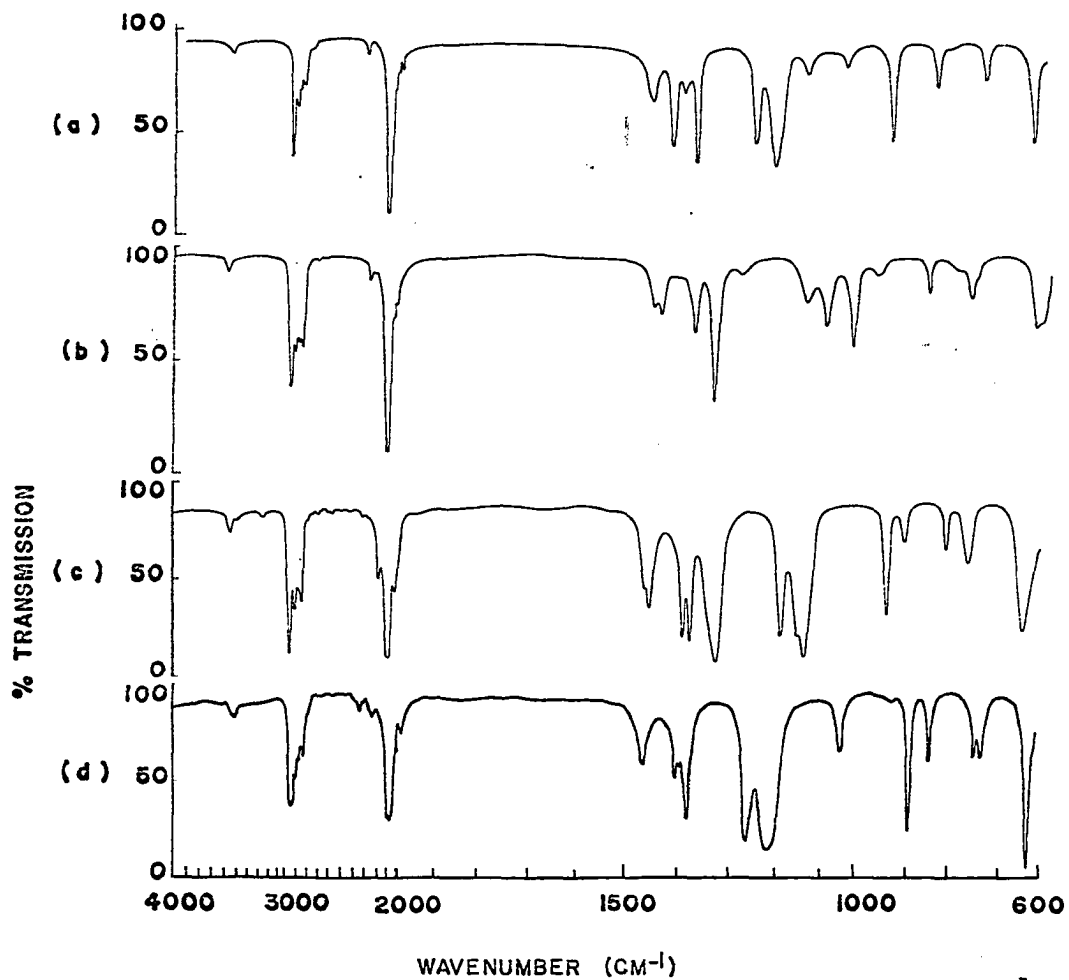
Figure 15. Infrared spectra between 600 and 4000 cm^{-1} for the alkyl carbodiimides

    (a) N-methyl, N'-tert.-butylcarbodiimide
    (b) N,N'-diethylcarbodiimide
    (c) N,N'-diisopropylcarbodiimide
    (d) N,N'-di-tert.-butylcarbodiimide

Figure 16. Infrared spectra between 40 and 600 cm^{-1} for

      (a) N,N'-dicyclohexylcarbodiimide

      (b) N,N'-bis(2,6 diethylphenyl)carbodiimide

      (c) N,N'-di-o-tolylcarbodiimidiide

      (d) N,N'-diphenylcarbodiimide

Figure 17. Infrared spectra between 600-4000 cm^{-1} of

(a) N,N'-dicyclohexylcarbodiimide
(b) N,N'-bis(2,6 diethylphenyl) carbodiimide
(c) N,N'-di-o-tolylcarbodiimide
(d) N,N'-diphenylcarbodiimide

Figure 18.   Assignments for the fundamental modes of
             alkyl carbodiimides

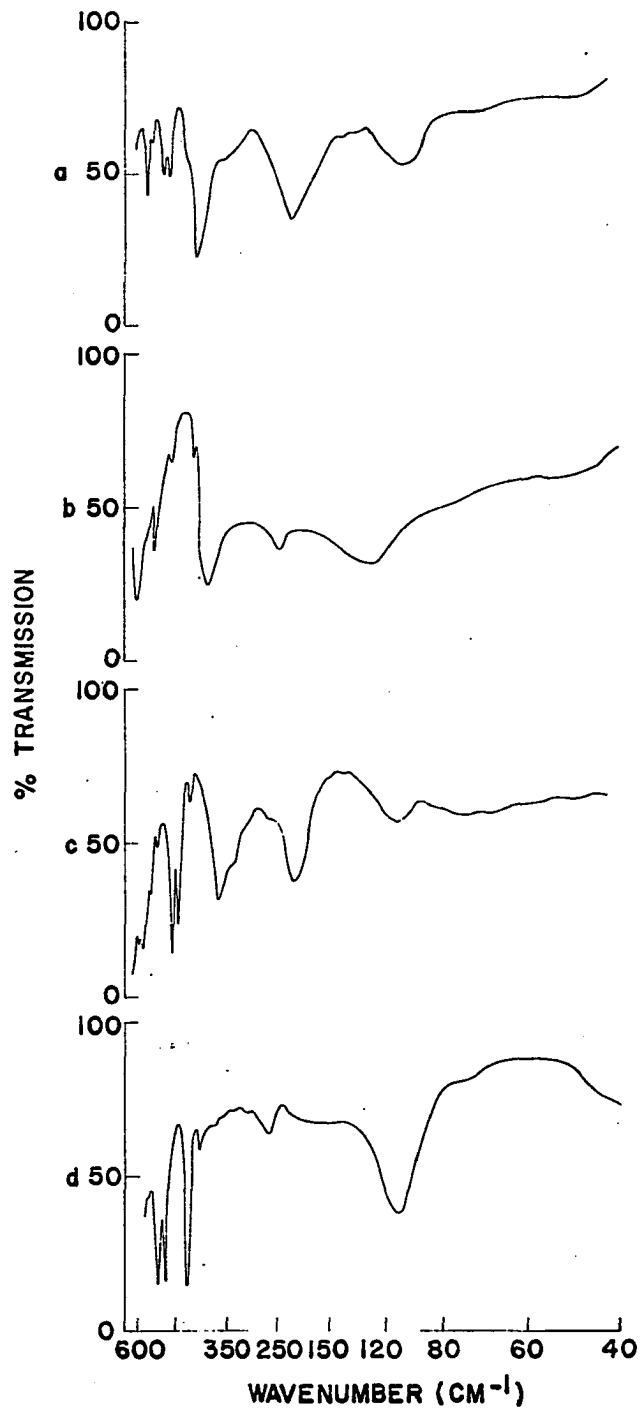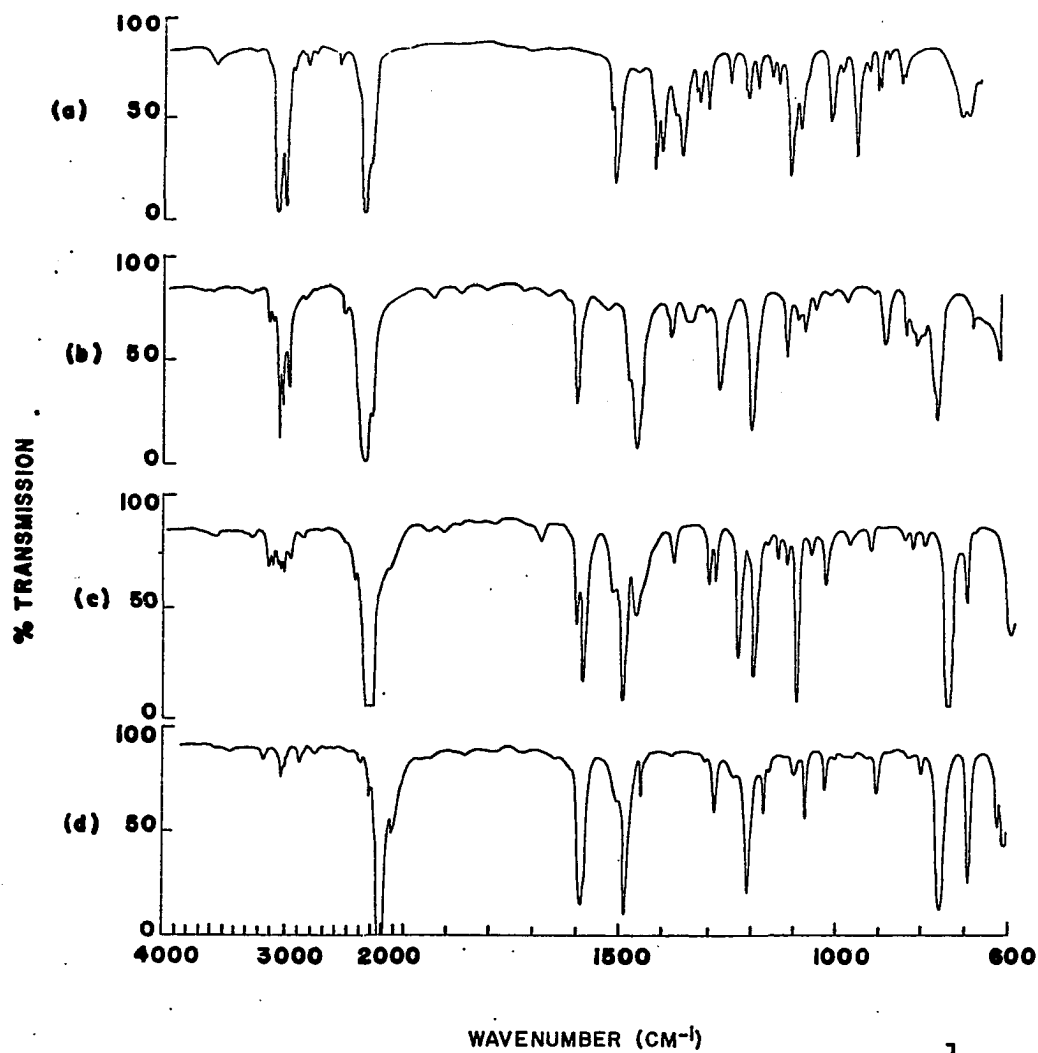| N-methyl, N'-tert.-butyl Infrared cm⁻¹	Iᵃ	Raman cm⁻¹	Iᵃ	N,N'-di-tert.-butyl Infrared cm⁻¹	Iᵃ	Raman cm⁻¹	Iᵃ	N,N'-diisopropyl Infrared cm⁻¹	Iᵃ	Raman cm⁻¹	Iᵃ	N,N'-diethyl Infrared cm⁻¹	Iᵃ	Assignment
2978	ms	2976	s	2980	ms	2978	ms	2972	ms	2978	ms	2976	ms	$\nu_{as}(CH_3)$
2936	mw	2924	w	2935	w	2931	w	2931	mw	2931	m	-	-	$\nu_{as}(CH_3)$
-	-	2905	w	2910	vw	2904	w	-	-	-	-	-	-	$\nu_{as}(CH_3)$
2881	w	2875	mw	2872	mw	2864	vw	2874	w	2886	w	2879	vw	$\nu_s(CH_3)$
-	-	-	-	-	-	-	-	-	-	-	-	2879	vw	$\nu_s(CH_2)$
2130	vs	-	-	2136	vs	-	-	2116	vs	-	-	2128	vs	$\nu_{as}(NCN)$
-	-	1457	s	-	-	1453	ms	-	-	1454	ms	-	-	$\nu_s(NCN)$
1462	m	1457	s	-	-	-	-	-	-	-	-	-	-	t-butyl $\delta_{as}(CH_3)$
-	-	-	-	1463	s	1453	ms	1465	sh	-	-	1470	w	$\delta_{as}(CH_3)$
-	-	-	-	-	-	-	-	1455	m	1454	ms	-	-	$\delta_{as}(CH_3)$
-	-	-	-	-	-	-	-	-	-	-	-	1452	m	CH_2 scissor
1420	s	-	-	-	-	-	-	-	-	-	-	-	-	methyl $\delta_{as}(CH_3)$
1394	mw	1404	mw	-	-	-	-	-	-	-	-	-	-	t-butyl $\delta_s(CH_3)$
1367	s	-	-	-	-	-	-	-	-	-	-	-	-	t-butyl $\delta_s(CH_3)$
-	-	-	-	1391	m	-	-	1383	m	1390	ms	1378	s	$\delta_s(CH_3)$
-	-	-	-	1384	w	1383	m	1367	m	-	-	-	-	$\delta_s(CH_3)$
-	-	-	-	1367	s	-	-	-	-	-	-	-	-	$\delta_s(CH_3)$
-	-	-	-	-	-	-	-	-	-	-	-	1335	vs	CH_2 wag
-	-	1330	-	-	-	-	-	-	-	-	-	-	-	methyl $\delta_s(CH_3)$
-	-	-	-	-	-	-	-	1310	s	-	-	-	-	$\delta(CH)$
-	-	-	-	-	-	-	-	-	-	-	-	1277	w	CH_2 twist
1237	ms	-	-	1236	s	1239	m	-	-	1239	-	-	-	$\nu(C-C)$
1192	s	-	-	2190	s	1194	mw	-	-	1194	-	-	-	$\gamma(CH_3)$
-	-	1167	w	-	-	-	-	1167	ms	-	-	-	-	$\gamma(CH_3)$
1121	mw	1135	w	-	-	-	-	-	-	-	-	-	-	methyl $\gamma(CH_3)$
-	-	1100	m	-	-	-	-	-	-	-	-	-	-	methyl $\gamma(CH_3)$
-	-	-	-	-	-	-	-	-	-	-	-	1134	m	$\gamma(CH_3)$
-	-	-	-	-	-	-	-	1115	m	-	-	-	-	$\nu(C-C)$
-	-	-	-	-	-	-	-	-	-	-	-	1090	ms	$\gamma(CH_3)$
1034	mw	-	-	1034	m	1037	w	-	-	1039	w	-	-	$\gamma(CH_3)$
-	-	-	-	-	-	-	-	-	-	-	-	977	mw	$\nu(C-C)$
935	s	940	m	922	w	926	mm	933	s	939	ms	-	-	$\delta(NCN)$
-	-	895	ms	885	vs	884	w	894	m	-	-	-	-	A(NCN)
-	-	-	-	-	-	-	-	-	-	-	-	867	m	$\delta(NCN)$
837	ms	-	-	838	ms	840	s	804	m	840	ms	-	-	$\nu(C-C)$
-	-	-	-	-	-	-	-	-	-	-	-	775	m	$\nu(C_\alpha-N)$
-	-	-	-	-	-	-	-	756	ms	735	vs	-	-	$\nu(C_\alpha-N)$
732	ms	758	vs	-	-	-	-	-	-	-	-	-	-	t-butyl $\nu(C_q-N)$
-	-	-	-	727	m	729	vs	-	-	-	-	-	-	$\nu(C_\alpha-N)$
627	s	-	-	626	vs	-	-	637	s	-	-	632	ms	$\delta(CNC)$
596	w	610	ms	-	-	594	vs	-	-	600	m	-	-	$\delta(CNC)$
-	-	-	-	498	w	504	mw	-	-	-	-	-	-	$\delta(C-C)$
472	vvw	-	-	-	-	-	-	-	-	-	-	-	-	$\delta(C-C)$
441	vw	458	m	457	m	446	m	458	mw	458	w	-	-	$\delta(C-C)$
394	w	400	mw	414	w	420	vw	431	mw	414	w	409	mw	$\delta(CCN)$
-	-	-	-	378	vw	382	vw	-	-	-	-	-	-	$\delta(CCN)$
-	-	-	-	-	-	-	-	362	vw	-	-	-	-	$\delta(C-C)$
-	-	-	-	344	mw	350	mw	-	-	-	-	-	-	$\delta(C-C)$
-	-	-	-	-	-	-	-	330	w	-	-	-	-	$\delta(C-C)$
320	w	319	w	-	-	-	-	-	-	-	-	-	-	$\delta(C-C)$
281	vw	284	m	284	w	289	ms	-	-	-	-	-	-	0 → 2
266	vvw	-	-	-	-	-	-	-	-	-	-	267	mw	0 → 2
258	vvw	260	w	-	-	-	-	-	-	-	-	-	-	methyl 0 → 2
-	-	-	-	-	-	-	-	209	vs	-	-	-	-	0 → 2
188	w	-	-	-	-	-	-	182	w	-	-	-	-	torsional 0 → 1
-	-	-	-	-	-	-	-	-	-	-	-	160	w	0 → 1
-	-	144	m	-	-	146	m	139	w	-	-	-	-	0 → 1
-	-	-	-	128	w	-	-	-	-	-	-	-	-	0 → 1

ᵃThe following notation was used to describe the relative intensities of the infrared absorption bands and Raman lines.

vs very strong
s   strong
ms moderate to strong
m   moderate
mw moderate to weak
w   weak
vw very weak
vvw very, very weak
sh appears as a shoulder to a stronger band

Table 7. Assignments for the combination bands in alkyl carbodiimides (cm^{-1})

a	b	c	d	e
–	3486	–	3530	$\upsilon_s(CH_3) + \delta(CNC)$
3508	–	3500	–	$\upsilon_{as}(NCN) + \delta_s(CH_3)$
–	3460	–	–	$\upsilon_s(CH_3) + \delta(CNC)$
–	–	3434	–	$\upsilon_{as}(CH_3) + \delta(C\text{-}C)$
–	3314	–	–	$\upsilon_{as}(CH_3) + \delta(CCN)$
–	3194	–	–	$\upsilon_{as}(CH_3) + \Gamma(CH_3)$
–	–	–	3108	$\upsilon_{as}(NCN) + \upsilon(C\text{-}C)$
–	–	–	2903	$\upsilon_{as}(NCN) + \upsilon(C_\alpha - N)$
2792	–	–	–	$\upsilon_s(NCN) + \delta_s(CH_3)$
–	2781	2790	–	$2X\delta_s(CH_3)$
2762	2752	–	–	$\delta_s(CH_3) + \delta_s(CH_3)$
–	–	–	2732	$\delta_{as}(CH_3) + \upsilon(C - C)$
2725	–	–	–	$\delta_s(CH_3) + \delta_s(CH_3)$
–	2720	2720	–	$2X\delta_s(CH_3)$
–	–	–	2664	$2X[CH_2\ wagg]$
–	–	2648	–	$\upsilon_s(NCN) + \gamma(CH_3)$
–	2624	–	–	$\delta_s(CH_3) + \upsilon(C - C)$
–	–	2602	–	$\upsilon_s(NCN) + \gamma(CH_3)$
–	2478	–	–	$2X\upsilon(C - C)$
–	–	–	2444	$\delta_{as}(CH_3) + \upsilon(C - C)$

[a] N-methyl, N'-tert.-butyl

[b] N,N'-di-tert.-butyl

[c] N,N'-diisopropyl

[d] N,N'-diethyl

[e] Assignment

Table 7.   continued

_a	_b	_c	_d	_e
–	–	2430	–	$\upsilon(C - C) + \gamma(CH_3)$
–	2396	–	–	$\delta_s(CH_3) + \gamma(CH_3)$
–	2372	–	–	$2\times\gamma(CH_3)$
–	–	2331	–	$\upsilon_s(NCN) + \delta(NCN)$
2320	–	–	–	$\gamma(CH_3) + \gamma(CH_3)$
–	–	–	2278	$\upsilon_{as}(NCN) + \Gamma(CH_3)$
–	2262	–	–	$\upsilon(C - C) + \gamma(CH_3)$
–	–	–	2244	$\delta_{as}(CH_3) + \upsilon(C_\alpha - N)$
–	–	2200	–	$\gamma(CH_3) + \gamma(CH_3)$
–	2110	–	–	$\gamma(CH_3) + \delta(NCN)$
–	–	–	2072	$[CH_2 \text{ scissor}] + \delta(CNC)$
–	–	2055	–	$\upsilon_s(NCN) + \delta(CNC)$
–	–	–	2046	$[CH_2 \text{ twist}] + \upsilon(C_\alpha - N)$
2017	–	–	–	$\gamma(CH_3) + \upsilon(C - C)$
–	2014	–	–	$\delta_s(CH_3) + \delta(NCN)$
806	–	–	–	$\delta(CNC) + \Gamma(CH_3)$

carbodiimide molecules as illustrated by the alkyl groups;
(2) degeneracy of specific vibrations; (3) some absorption
bands cannot be detected because of low intensity.

(1) Carbodiimide molecules analyzed in this study,
with the exception of the N-methyl, N'-tert.-butyl compound,
possess the same substituent alkyl groups on either side of
the NCN molecular fragment. Since the group frequencies of
the alkyl groups in the symmetric molecules are identical,
absorption bands characteristic of single alkyl substituents
occur. For the unsymmetrical carbodiimide the vibrations of
the methyl and the methyl units in the tert.-butyl group
between 3000-2800 cm^{-1} are nearly identical and therefore
not resolved. In the remaining spectral regions, the vibra-
tions of the methyl and tert.-butyl groups can be distin-
guished and readily assigned.

(2) It frequently happens that two or more energy states
of a molecule have numerically the same value of the energy.
If this is the case, and if the atoms connected by the
identical forces have equivalent masses, two (or more) of
the 3N-6 fundamentals will have the same frequency and will
be observed as a single absorption band in the infrared
spectrum of the molecule. This is known as degeneracy.
For the alkyl carbodiimides this type of degeneracy is
illustrated by the CCN deformation modes in the N-methyl,
N'-tert.-butyl, N,N'-diisopropyl, and N,N'-di-tert.-butyl
compounds.

Degenerate vibrations will occur in any molecule having an axis of threefold or greater symmetry (examples: the symmetry axis of ammonia, the axis perpendicular to the benzene ring at its center, and the parallel axis of a linear molecule). Although carbodiimides do not possess a threefold or greater axis of symmetry, the methyl groups that make up the alkyl substituents do have such symmetry elements and have one or more pairs of degenerate vibrations.

(3) This point is self-evident.

NCN Modes

All of the infrared spectra show a very intense band between 2160 and 2100 cm^{-1} which can be readily assigned to the asymmetrical stretching vibration of the NCN group (59). When Kahovec and Kohlrausch (27) obtained the Raman spectrum of N,N'-diisopropylcarbodiimide, they observed that the spectral region between 1500 and 2600 cm^{-1} was void of lines.

For coupled vibrations, the symmetrical stretching band usually appears at about one half the asymmetrical stretching frequency value (53,59,60). By applying this rule to the carbodiimides, the NCN symmetrical stretching vibration should occur near 1100 cm^{-1}. However, Pump (61) and Ebsworth (62) assigned the strong Raman lines at 1516 and

1496 cm^{-1} to the NCN symmetrical stretching vibration in
N,N'-trimethylsilyl and N,N'-silylcarbodiimide respectively.
Figure 13 shows strong Raman lines in this frequency range,
but it is well known that the asymmetric methyl deformation
mode also falls in this region. Nevertheless, the NCN
symmetrical stretching vibrations for alkyl carbodiimides
are assigned to the 1460-1450 cm^{-1} region based upon the
Raman data of the organo-metallic compounds and the fact
that the Raman lines observed for the aliphatic compounds
between 1200 and 1000 cm^{-1} are readily assigned to methyl
rocking and C-C stretching vibrations. The assignment of
the symmetrical NCN modes are further supported by the
1450-1400 cm^{-1} spectral region designated for the NCO
symmetric stretching vibrations in the analogous and
structurally similar isocyanate molecules (63).

The fact that the NCN symmetrical stretching modes were
difficult to assign for the alkyl carbodiimides is attributed
to an accidental degeneracy. This effect is caused by two
different vibrational modes occurring in different symmetry
classes (57) at or very near the same frequency. Instead of
the modes coupling, causing frequencies which appear at
higher and lower values than either of the unmixed funda-
mentals, only one vibration is observed.

The Raman and infrared spectra of the alkyl carbodiimides
demonstrate that the principle of mutual exclusion is

operating for the symmetric and asymmetric NCN vibrations. The principle simply states that vibrations symmetric with respect to the center of symmetry are Raman and not infrared active, whereas the vibrations asymmetric with respect to the center of symmetry are infrared but not Raman active. Because vibrations of submolecular groups tend to act independently of the remaining parts in the molecule, the symmetry indicated by the mutual exclusion principle is localized within the NCN molecular fragment.

C_α-N Vibrations

The C_α-N stretching vibrations generally give rise to bands in the region between 1200 and 600 cm^{-1}. This rather extensive range is attributed to the labile nature of the nitrogen valence electrons.

The C_α-N modes were assigned after a thorough analysis and comparison with the analogous alkyl isocyanates. Table 8 contains the C_α-N frequencies assigned to both aliphatic isocyanates and carbodiimides.

From Table 8 it is observed that the C_α-N stretching vibration of the methyl group in N-methyl, N'-tert.-butyl carbodiimide was not assigned. This occurred because a suitable frequency was not observed for this compound. However, by plotting the C_α-N stretching vibrations versus the molecular weight of the alkyl substituents (in grams per mole) a straight line is generated. This relationship is

Table 8. Assigned C_α-N stretching vibrations for alkyl
isocyanates and carbodiimides

Carbodiimides		Isocyanates	
Compound	Vibration (cm^{-1})	Compound	Vibration (cm^{-1})
N,N'-diethyl	775	ethyl	794
N,N'-diisopropyl	756.5, 735	isopropyl	753
N,N'-di-tert.-butyl	742, 728	tert.-butyl	?
N-methyl, N'-tert.-butyl	732 (t-butyl)		

shown in Figure 19. When the function in Figure 19 is
extrapolated, the C_α-N stretching vibration for the methyl
group is estimated to fall near 795 cm^{-1}.

To substantiate the C_α^--N stretching vibration
assignments in Table 8, a graph was constructed by plotting
these modes against known C_α-X stretching frequencies, where
X represents Cl, Br, S, and N. The functions obtained from
such a graph should be straight lines, if the unknown modes
are the proper C_α-N stretching vibrations (63). Linear
relationships were observed when the C_α-N stretching frequen-
cies assigned to the alkyl carbodiimides are plotted versus
the C_α-X stretching modes. Figure 20 illustrates this
relationship.

CNC and CCN Deformation Modes

In the 600 cm^{-1} region, Raman and infrared modes were
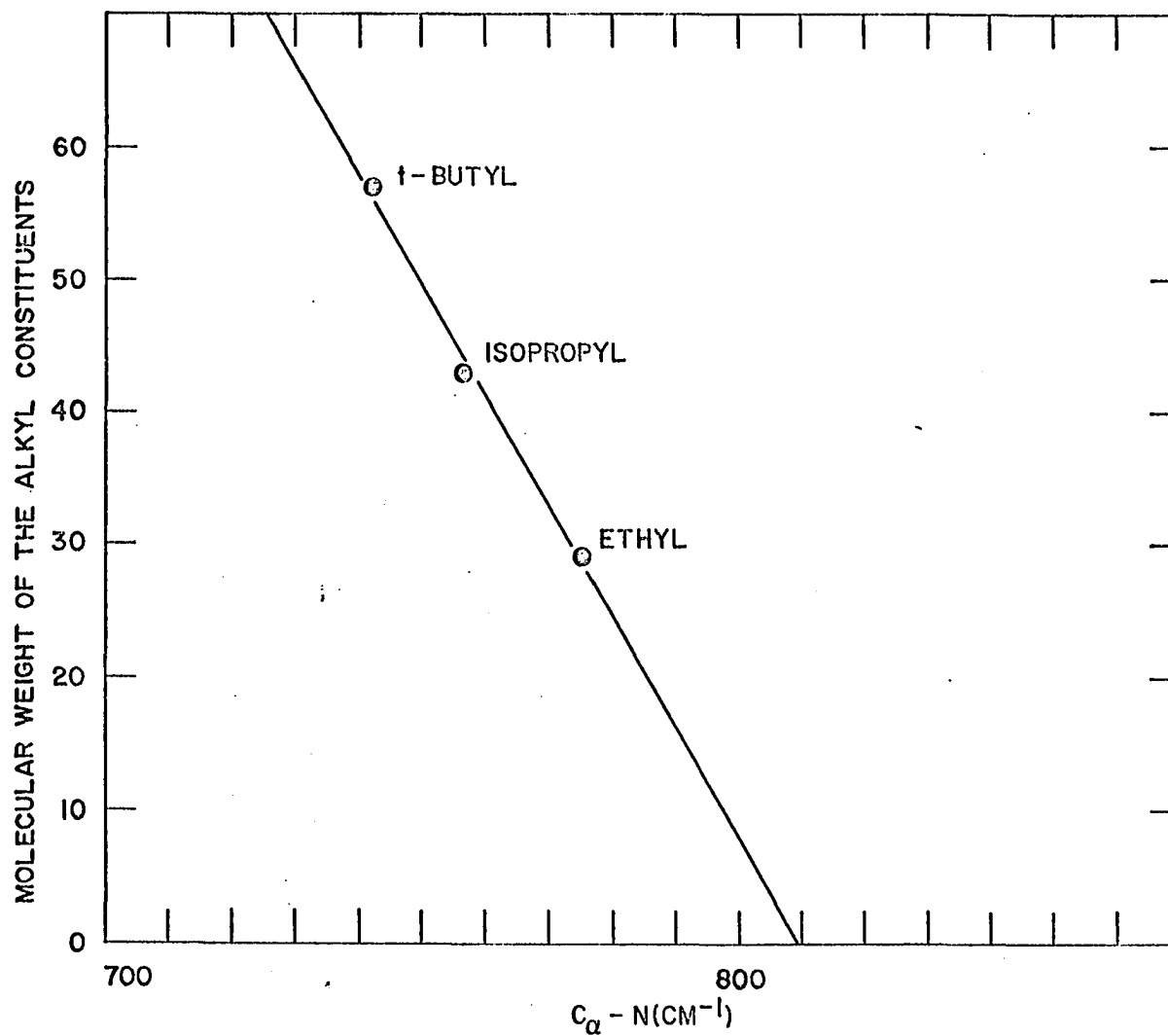
Figure 19.   Molecular weight of the alkyl constituents in the carbodiimides plotted versus their C_α-N (cm^{-1}) stretching vibrations
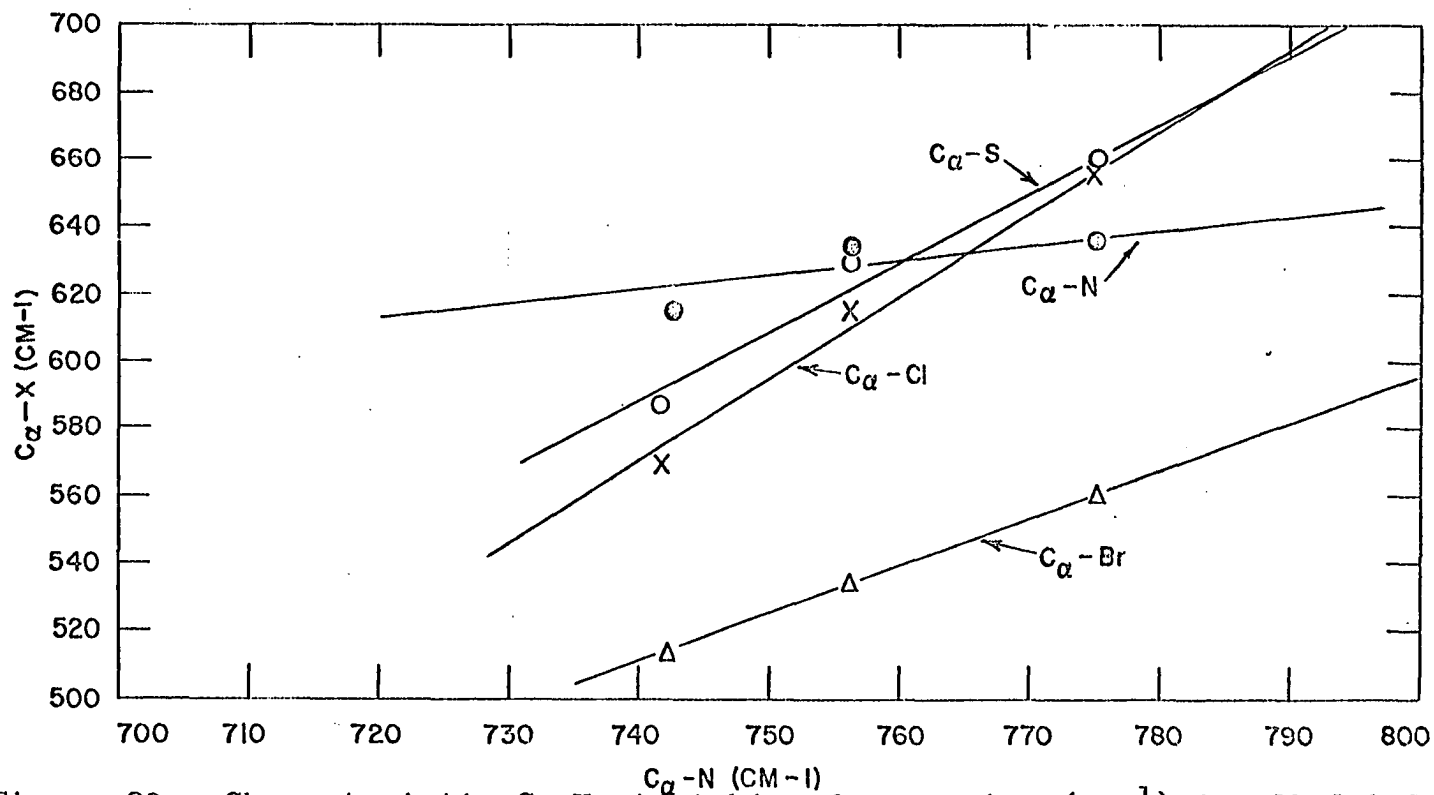
Figure 20. Characteristic C_α-X stretching frequencies (cm^{-1}) in alkyl halides, thiols and isocyanates plotted versus the C_α-N stretching frequencies (cm^{-1}) in alkyl carbodiimides

observed at 600 ± 10 and 630 ± 5 cm^{-1} respectively. The Raman mode was also active in N-methyl, N'-tert.-butyl-carbodiimide. These frequencies can be assigned to C-C, CCN or CNC deformation vibrations. However, because the force constant associated with the CNC deformation mode is expected to be larger than the other two, the CNC deformation modes are assigned to this spectral region.

The assignments of the CCN deformation vibrations for the alkyl carbodiimides were based upon a comparison with Hirschmann's infrared study of the analogous and structurally similar aliphatic isocyanates and isothiocyanate molecules (63). These vibrations are found between 480 and 380 cm^{-1}. Table 9 contains these assignments.

Alkyl Group Vibrations

In the following section, each alkyl carbodiimide is analyzed separately for the vibrational modes associated with the alkyl groups. The first compound considered is N-methyl, N'-tert.-butylcarbodiimide followed in order by the N,N'-diethyl, N,N'-diisopropyl and N,N'-di-tert.-butyl derivatives.

Table 9.   CCN dèformation modes of alkyl carbodiimides, isothiocyanates and isocyanates

Carbodiimides		Isothiocyanates		Isocyanates	
Compound	(cm^{-1})	Compound	(cm^{-1})	Compound	(cm^{-1})
N-methyl, N'-tert.-butyl	441, 396				
N,N'-diethyl	409	ethyl	448, 382	ethyl	417, 397
N,N'-diisopropyl	421, 400	isopropyl	459, 335	isopropyl	460, 352
N,N'-di-tert.-butyl	417, 380	tert.-butyl	336	tert.-butyl	?

N-METHYL, N'-TERT.-BUTYLCARBODIIMIDE

N-methyl, N'-tert.-butylcarbodiimide has C_1 molecular symmetry. Although only 46 vibrations are observed, a 24 atom asymmetrical molecule such as N-methyl, N'-tert.-butylcarbodiimide should have 66 vibrational degrees of freedom.

Methyl Stretching and Deformation Modes

Stretching and deformation vibrations for the methyl group can be easily assigned (64). The methyl asymmetric stretching frequencies $\upsilon_{as}(CH_3)$ are observed at 2979 and 2936, while the symmetric stretching mode $\upsilon_s(CH_3)$ is found at 2881 cm^{-1} in the infrared spectrum of the liquid phase. The frequencies at 1465.5 and 1420 cm^{-1} are assigned to the asymmetric methyl deformation vibrations $\delta_{as}(CH_3)$ which are in agreement with those reported by Hirschmann (63) and Sheppard and Simpson (65). The symmetrical deformation modes $\delta_s(CH_3)$ of the t-butyl group assigned at 1420, 1394.5 and 1367.5 cm^{-1} are observed where they are expected (65). A band for the $\delta_s(CH_3)$ of an isolated methyl group is not observed by infrared procedures. However, the Raman spectrum of this compound reveals a band at 1330 cm^{-1}, which is assigned to the isolated symmetrical methyl deformation.

The two bands observed by Raman methods occurring at 1457 and 1404 cm^{-1} are assigned to an asymmetric methyl deformation and a symmetric deformation respectively. Both of these frequencies are linked to the t-butyl group (66).

C-C Stretching and Methyl Rocking Modes

Both of these modes generally occur in the 1300-650 cm^{-1} region (67). To identify the C-C vibrations, recourse was taken to a useful correlation of the C-C stretching mode frequencies in alkyl hydrocarbons, halides, isocyanates and isothiocyanates (68). It is seen in Figure 21 that frequencies assigned to the C-C stretching vibrations in alkyl carbodiimides follow the same behavior pattern. Confirmation of these assignments is evident in the Raman spectra. The rocking vibrations ascribed to the methyl group are assigned to the infrared band of 1121 cm^{-1} and the Raman frequencies of 1135 and 1100 cm^{-1}. These assignments are based upon an analogous and structurally similar molecule methyl isothiocyanate (63). In the infrared vapor state spectrum, the isothiocyanate frequencies of 1126 and 1107 cm^{-1} were observed and assigned to methyl rocking modes. Furthermore, Mantica and Zerbic, (69) in their study of methyl azide, assigned the 1140 cm^{-1} band to a methyl rocking mode, while Hirschmann (63) assigned this vibration in methyl isocyanate to 1132 cm^{-1}. Similarly the 1034.5 band is assigned to a methyl rocking vibration based upon tert.-butylisothiocyanate(63).
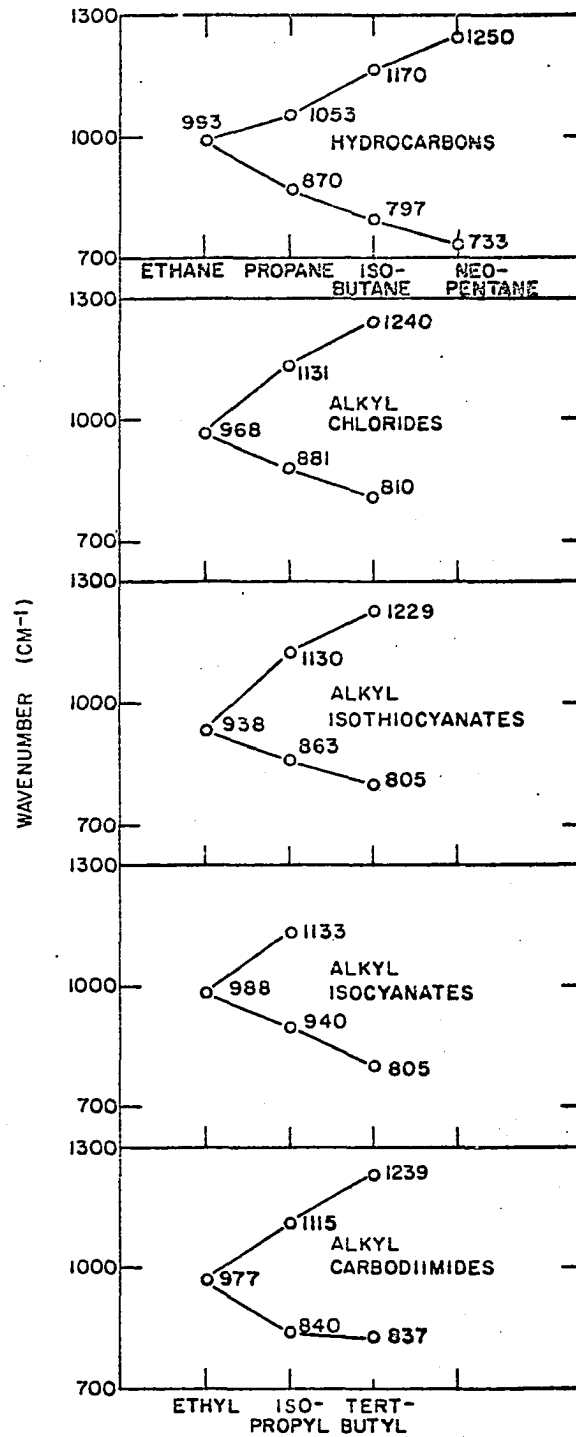
Figure 21. Correlation of C-C stretching frequencies

The 1192.5 band assigned to a methyl rocking vibration could also be designated a C-C vibration associated with the t-butyl group. However, the latter assignment would be inconsistent because a band at 1194 cm^{-1} appears in N,N'-di-isopropylcarbodiimide. Skeletal vibrations associated with the isopropyl group occur between 1170 and 1140 cm^{-1} (65). The Raman line observed at 1167 cm^{-1} is designated as a methyl rocking vibration. This frequency is in general agreement (63,70,71,72) with the 1175 cm^{-1} band assigned to the methyl rocking vibration of methyl isothiocyanate. Also, the relatively weak intensity of this Raman line is indicative of a methyl rocking vibration. The skeletal vibrations in this region are usually prominent (65).

Alkyl Deformation Modes

The frequencies assigned to the alkyl deformation modes in alkyl carbodiimides occurring between 500 and 260 cm^{-1} were based upon Raman data by Edsall (73,74,75,76) and infrared vibrations of primary and secondary amines assigned by Ebsworth and Sheppard (77). As expected, the frequencies assigned to the alkyl deformation modes of the carbodiimides showed moderate Raman intensities (77).

Methyl Torsional Modes

Using an analogy with methylamine, Cortoulas and Werner (70) assigned the methyl torsional vibration to a frequency

of 270 cm^{-1}. In a more recent investigation, Fateley and
Miller (78) assigned the bands between 280 and 100 cm^{-1} to
either a $0 \rightarrow 1$ or $0 \rightarrow 2$ methyl torsional transitions. The
assignments proposed by Fateley and Miller were substantiated
by a microwave study of methyl formate. In this microwave
investigation, Curl (79) obtained a potential barrier of
1190 ± 40 calories per mole for methyl formate. When
Fateley and Miller assigned a frequency of 130 cm^{-1} in methyl
formate to a $0 \rightarrow 1$ transition, a potential barrier of 1164
calories per mole was obtained. This value was in good
agreement with Curl's result. Similarly, in a microwave
study of gaseous acetaldehyde, Kilb, Lin and Wilson (80)
obtained a potential barrier of 1168 ± 30 calories per mole.
When Fateley and Miller assigned the 150 cm^{-1} band in
acetaldehyde to a $0 \rightarrow 1$ methyl torsional transition, a
potential barrier of 1180 calories per mole was evaluated.
Again, this was in good agreement with the microwave result.
Based upon the $0 \rightarrow 1$ methyl torsional transition in acetalde-
hyde, Fateley and Miller attributed the weak bands between
280 and 257 cm^{-1} to $0 \rightarrow 2$ transitions. Because of the
correlation between the infrared and microwave results, the
methyl torsional modes in carbodiimides were based upon
the work of Fateley and Miller.

Overtone and Combination Modes

Table 7 contains proposed assignments for overtone and combination modes of N-methyl, N'-tert.-butyl-carbodiimide.

N,N'-DIETHYLCARBODIIMIDE

N,N'-diethylcarbodiimide has C_1 molecular symmetry. Although only 24 bands are observed, a 17-atom asymmetrical molecule such as N,N'-diethylcarbodiimide should have 45 vibrational degrees of freedom. Assignments are given in Figure 18 for the fundamental vibrations.

Most of the vibrations characteristic of the ethyl group are readily assigned and are in agreement with Sheppard and Simpson (65). The CH_2 scissoring and methyl asymmetric deformation vibrations in the 1460 cm^{-1} region tend to be close in frequency (57). However, if the CH_2 group is adjacent to a double bond, as is the case with alkyl carbodiimides, the CH_2 scissoring frequency tends to decrease. Therefore, the band at 1470 cm^{-1} is designated the asymmetric methyl deformation mode, while the 1452.5 cm^{-1} band is assigned to the CH_2 scissoring vibration. Furthermore, the vibration at 1452.5 cm^{-1} is absent in the N-methyl, N'-tert.-butyl compound which emphasizes these assignments.

The weak CH_2 rocking mode was not observed; it may have been degenerate with the C_α-N stretching vibration.

Table 7 contains the proposed assignments for the overtone and combination bands of N,N'-diethylcarbodiimide.

N,N'-DIISOPROPYLCARBODIIMIDE

Assignments for 41 of the 63 theoretically available normal vibrations are presented in Figure 18.

A majority of the assignments for vibrations internal to the isopropyl group are in agreement with those proposed by Sheppard (81) and need no further comment. The band representing the CH deformation mode usually absorbs weakly in the range of 1360-1330 cm^{-1} (82). In N,N'-diisopropyl-carbodiimide this vibration is strong and occurs at 1310 cm^{-1}. The lack of this frequency in either of the N-methyl, N'-tert.-butyl or N,N'-di-tert.-butylcarbodiimide supports the assignment of the CH deformation mode.

Assignments for combination and overtone bands of N,N'-diisopropylcarbodiimide appear in Table 7.

N,N'-DI-TERT.-BUTYLCARBODIIMIDE

For a tert.-butyl functional group, a high degree of coupling of the group vibrations results from the presence of three equivalent methyl groups. For example, a vibration such as $v_s(CH_3)$, from one of the methyl units, can couple with the same vibration in the other two methyl units in two ways: (1) The methyl group can couple in phase to form a single vibrational mode. (2) Two methyl groups move in phase while the third methyl unit moves out of phase. This latter mode, as expected, is doubly degenerate.

Of the 81 normal vibrations theoretically possible for N,N'-di-tert.-butylcarbodiimide, only 65 are observed by Raman and infrared procedures. With the exception of the CC stretching and methyl rocking vibrations discussed separately, the assignments shown in Figure 18 are compatible with those of Sheppard (66) for tert.-butyl halides. Since there is little new information in this analysis, any further discussion would be redundant.

Assignments for combination and overtone bands of N,N'-di-tert.-butylcarbodiimide appear in Table 7.

SOLUTION AND SOLID STATE SPECTRA

Solution spectra (~0.02 M) of N,N'-diethyl, N,N'-diisopropyl and N,N'-di-tert.-butylcarbodiimide did not contribute additional information to the analysis of the vibrational modes. However, the very small band shifts (1-4 cm^{-1}) observed for the solution spectra supported the conclusion of the physical property studies; namely molecular weight in solution, density and surface tension. In addition, the solid state spectra, aside from very small frequency shifts and variation in the intensity of the absorption bands, did not contribute to the vibrational analysis of these compounds.

VAPOR STATE SPECTRA

Although the solution and solid state spectra did
not show significant band shifts, some of the vapor phase
absorption bands were observed at different frequencies.
The most significant frequency shift occurred for the NCN
asymmetrical mode ($\sim$40 cm^{-1}). These liquid-to-vapor-phase
frequency changes were attributed to the removal of the
perturbating influence caused by the intermolecular forces.
A high resolution study of the vapor phase spectra revealed
no detail. If the high resolution study had revealed fine
structure (the splitting of bands into evenly spaced
components), moments of inertia could have been evaluated
from the spacing of the fine structure bands. From these
moments of interia interatomic distances and bond angles
could be calculated. Since the high resolution information
was lacking, it was not possible to estimate the CNC bond
angle in these molecules.

SUGGESTIONS FOR FUTURE WORK

Thus far, no information appears to be available concerning the structural evaluation of disubstituted carbodiimides by means of microwave spectra, electron diffraction and three dimensional x-ray methods. Each study should constitute a separate problem because of the intricacies of the experimental procedures. When bond distances and angles have been obtained by these structural methods, a rigorous group theory and normal coordinate study should be attempted to establish selection rules pertaining to a carbodiimide model.

SUMMARY

The evidence obtained by measuring specifically selected physical parameters, such as molecular weight in solution, density, surface tension and heat of vaporization, demonstrated that aliphatic, phenyl and alkylphenyl carbodiimides have intermolecular potentials usually referred to as van der Waals forces. Moreover, Trouton's and Guldberg's relationships further demonstrated the nearly ideal liquid state character of the carbodiimides. In addition, when the pressure – temperature information is used with the Clausius expression, equations of state of the general form $\log_{10}P = -\frac{A}{T} + C$ were obtained.

An ultraviolet investigation of the alkyl, phenyl and alkylphenyl carbodiimides demonstrated that absorption bands of the NCN group occur below 2000Å. Earlier reports by Behringer, Meier and Franssen that absorption bands for alkyl carbodiimides occur near 2130 and 2600Å disagree with this observation. Also, a molecular complex is not observed between the aliphatic compounds and iodine cyclohexane.

Most of the characteristic alkyl group vibrational frequencies attributed to the Raman and infrared spectra of carbodiimides were accounted for without much difficulty.

The C_α-N stretching vibrations were assigned after a thorough analysis of the 1200-600 cm^{-1} region and comparison with the analogous alkyl isocyanates. The C-C stretching vibrations in alkyl carbodiimides follow the same behavior pattern shown by alkyl hydrocarbons, halides, isocyanates and isothiocyanates. In addition, the NCN symmetrical stretching mode appears near 1460 cm^{-1} and is accidentally degenerate with the asymmetric methyl deformation vibration.

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APPENDIX 1: OBSERVED INFRARED ABSORPTION
FREQUENCIES FOR ONE ALICYCLIC AND THREE AROMATIC
CARBODIIMIDES

The following notation was used to describe the relative intensities of the infrared absorption bands and Raman lines.

vs very strong

s   strong

ms moderate to strong

m   moderate

mw moderate to weak

w   weak

vw very weak

vvw very, very weak

sh appears as a shoulder to a stronger band.

Table 10. Observed infrared absorption frequencies (cm^{-1})
for the liquid N,N'-dicyclohexylcarbodiimide

Liquid State
100 (w)
203 (w)
254.5 (m)
456 (w)
477.5 (w)
520 (vw)
542.5 (m)
629 (mw)
646 (mw)
779.5 (vw)
786.5 (mw)
817.5 (mw)
836 (mw)
842.5 (mw)
863 (mw)
891 (s)
927.5 (mw)
953 (ms)
1024.5 (m)
1046 (s)
1074.5 (m)
1090.5 (m)
1124 (m)
1145 (m)
1150 (sh)
1190.5 (m)
1240 (ms)
1260 (m)
1268 (w)
1299 (s)
1316 (vw)
1347 (ms)
1359.5 (s)
1401 (w)
1450.5 (vs)
1463.5 (vw)
2065 (vw)
2121 (vs)
2587 (vw)
2657 (vvw)
2795 (vvw)
2854.5 (s)
2932 (s)
3148 (vw)
3472 (m)

Table   11.   Observed infrared absorption frequencies (cm^{-1})
for the liquid N,N'-diphenylcarbodiimide

Liquid State

107 (m)
243.5 (vw)
357.5 (vw)
405 (mw)
490 (m)
519 (s)
602.5 (s)
621.5 (m)
689 (vs)
754.5 (vs)
801 (mw)
829.5 (w)
875 (vw)
904 (s)
929 (vw)
972 (vw)
1003.5 (vw)
1026.5 (s)
1071.5 (s)
1098.5 (m)
1125.5 (vw)
1155.5 (w)
1168.5 (ms)
1203.5 (vs)
1238 (vw)
1284.5 (s)
1306 (w)
1385.5 (vw)
1452.5 (ms)
1487.5 (vs)
1510.5 (vw)
1590 (vs)
1804 (vw)
1864.5 (w)
1943.5 (vw)
1962.5 (vw)
2034 (m)
2106 (w)
2142 (vs)
2238 (w)
2320 (w)
2752 (m)

Table 11 . continued

Liquid State
2896 (m)
3028 (vw)
3064 (m)
3229 (m)
3550 (vw)
3660 (vn)

Table 12 . Observed infrared absorption frequencies (cm^{-1}) for the liquid N,N'-di-o-tolylcarbodiimide

Liquid State
102 (w)
199 (m)
317 (m)
382.5 (m)
422.5 (w)
442 (w)
490 (vvw)
505 (w)
527.5 (vw)
558.5 (vvw)
572.5 (vvw)
612 (mw)
713 (ms)
754.5 (vs)
810.5 (mw)
839 (mw)
856 (mw)
935.5 (m)
986.5 (mw)
1042 (m)
1076.5 (vs)
1110 (vs)
1134 (m)
1158 (w)
1185.5 (s)
1222 (s)
1279.5 (ms)
1293.5 (ms)
1378.5 (ms)
1458.5 (s)
1487 (vs)

Table 12.   continued

Liquid State
1515 (vw)
1580.5 (s)
1598 (ms)
1685? (mw)
1906.5 (w)
1944.5 (w)
2118 (w)
2148 (vs)
2266 (w)
2574 (vw)
2750 (w)
2866 (mw)
2926 (mw)
2951 (mw)
2979 (w)
3028 (mw)
3070 (mw)
3220 (vw)
3560 (vw)

Table   13.   Observed infrared absorption frequencies (cm^{-1}) for the liquid N,N'-bis(2,6-diethylphenyl) carbodiimide

Liquid State
128.5 (w)
234 (vw)
343.5 (w)
385 (vvw)
467.5 (vvw)
520 (m)
577.5 (m)
605 (m)
751 (s)
797 (mw)
823.5 (mw)
873 (ms)
899 (w)
961 (mw)
997.5 (w)
1035.5 (m)
1059.5 (m)
1077.5 (mw)

Table 13. Continued

Liquid State
1104 (ms)
1184 (vs)
1261 (s)
1291 (w)
1331 (m)
1374 (m)
1450 (vs)
1470 (vw)
1521 (w)
1587.5 (s)
1795 (w)
1858 (w)
1921.5 (mw)
2106 (vw)
2168 (vs)
2364 (w)
2730 (vw)
2876 (ms)
2935 (ms)
2969 (s)
3022 (w)
3058 (w)
3230 (vw)
3590? (vw)
3688? (vw)