Table VIII. Data for Preparative Scale Solvolyses

Nosylate	Solvent	Distillate yield, %	Pot residue yield, %
2-Chloro-1-propyl[a]	$CF_3COOH-NaOCOCF_3$		
4-Chloro-1-pentyl	HOAc–NaOAC	65	1.1
4-Chloro-1-pentyl	HOAc	66	0.8
4-Chloro-1-pentyl	HCOOH–NaOCOH	54	0.6
4-Chloro-1-pentyl	$CF_3COOH-NaOCOCF_3$	57	4.9
5-Chloro-1-hexyl	$CF_3COOH-NaOCOCF_3$	42	23

[a] Carried out by F. J. Slama.

The identification of the two major products from 5-chloro-1-hexyl nosylate was confirmed by collecting the compounds contained in each peak separately by preparative gas chromatography (6-ft DC-550 column, 120°) and comparing the nmr spectra of the collected material with those of authentic samples. The spectra were identical.

Sealed Tube Solvolyses. An approximately 0.1 *M* (**1-hexyl** and **5-bromo-1-hexyl nosylates**) or 0.4 *M* (**6-chloro-1-heptyl nosylate**) buffered solution was prepared by weighing out the appropriate quantity of crystalline nosylate, together with a 25–50% *M* excess of vacuum-dried sodium trifluoroacetate, into a Dry Ice chilled ampoule or nmr tube, adding the appropriate quantity of redistilled trifluoroacetic acid by pipet, flushing with dry nitrogen, and sealing. The container was then totally immersed in a 60.0° water bath for 7–8 half-lives (1-hexyl and 5-bromo-1-hexyl nosylates) or 1.8 half-lives (6-chloro-1-heptyl nosylate). Subsequent product work-up and analysis varied with the compound as follows.

For **1-hexyl nosylate** the products were worked up quantitatively into a dry ether solution (by the method used for the reference trifluoroacetates) and analyzed by glc (4.0 μl injections, 6-ft TCEP column with 8-in. base forecolumn,[28] programmed temperature of 70–100°). The product composition and yield (96%) were determined by comparison of the resulting chromatogram with chromatograms of the products from an identical work-up of an authentic mixture of 1-hexyl, 2-hexyl, and 3-hexyl trifluoroacetates.

For **5-bromo-1-hexyl nosylate** the reaction mixture was evaporated to one-quarter its original volume and an nmr spectrum was taken. Relative amounts of primary and secondary bromides were estimated by comparing the integral at δ 3.43 (t, $-CH_2Br$) with twice the integral at 4.02 (m, $-CHBr-$). The relative amounts of primary and secondary trifluoroacetates were estimated in a similar manner using the integrals at δ 4.50 (t, $-CH_2OCOCF_3$) and 5.20 (m, $-CH-OCOCF_3-$). The relative amounts of 6-bromo-2-hexyl and 6-bromo-3-hexyl trifluoroacetates were estimated from the integrals at δ 1.44 (d, CH_3CHBr-) and 1.00 (t, CH_3CH_2Br-).

For **6-chloro-1-heptyl nosylate** an nmr spectrum was taken on the contents of the still-sealed tube, using an external TMS capillary as reference. (Peaks were observed having δ values 1–2, 3.59 (t, primary chloride), 4.05 (secondary chloride), 4.35 (t, unreacted nosylate), 4.52 (t, primary trifluoroacetate), and 5.27 (secondary trifluoroacetate)). The relative areas were divided by 1, 2, or 11 (peak at δ 1–2) depending on the number of hydrogens contributing to the peak, to obtain the relative molarities 13.6, 2.35, 7.75, 1.25, 3, and 4.5, respectively. Compounds differing from **6**, **7**, **8**, and **9** (this paper) only by the presence of an additional methylene group may be envisioned as the sources of these signals. The areas do not show full internal consistency, but the ratio of primary chlorides to all compounds, 2.35/13.6 = 0.173, should be relatively free of interference due to unanticipated components. (The presence of 12, not 11, upfield hydrogens in compounds analogous to **9** is not a serious problem.)

Trifluoroacetolysis of 4-Chloro-1-butyl-*1*-d_2 Nosylate.[29] An approximate 0.1 *M* buffered solution of the nosylate in redistilled trifluoroacetic acid containing a molar excess of vacuum-dried sodium trifluoroacetate was prepared and allowed to react for 15 half-lives at 60.0°. A time-averaged nmr spectrum of the reacted mixture indicated complete scrambling of the deuterium in the products as evidenced by identical integrals of the proton signals at δ 3.59 (t, $-CH_2Cl$) and 4.50 (t, $-CH_2OCOCF_3$). A time-averaged spectrum taken at 0.5 half-life indicated no scrambling of the deuterium in the nosylate as evidenced by the absence of any signal at δ 4.37 (t, $-CH_2ONs$).

Acknowledgment. This work was supported in part by a grant (GP-10919) from the National Science Foundation. We also acknowledge partial support of the purchase of a Varian HA-100D nmr spectrometer through National Science Foundation Grant No. GP-8510. Contributions to this work by J. M. Indelicato and F. J. Slama (*cf.* Experimental Section) are gratefully acknowledged.

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(28) P. E. Peterson and E. V. P. Tao, *J. Org. Chem.*, **29**, 2322 (1964).

(29) Carried out by J. M. Indelicato.

N,N'-Dimethylcarbodiimide, Pure Monomer. II. Spectroscopic Properties[1,2]

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Contribution from Istituto di Chimica Organica dell'Università
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Florence, Italy. Received July 24, 1970

Abstract: The main spectroscopic properties of *N,N'*-dimethylcarbodiimide have been investigated. Infrared spectra from 4000 to 200 cm^{-1} of gaseous, liquid, and solid samples as well as the Raman spectrum of the liquid were measured and a detailed vibrational assignment was reported. Uv and nmr spectra were examined and discussed. The combined analysis of the spectroscopic data supports a low molecular symmetry structure (C_2 point group) and shows the existence of close analogies with the allene-type compounds.

The problem of the molecular structure of symmetrically substituted carbodiimides has been previously discussed by several authors. Only recently a structure like that of allenes has been proved on the basis of the following results: (i) isolation of the optically active *N,N'*-diferrocenylcarbodiimide; this implies a low symmetry structure of the molecule;[3] (ii) dipole mo-

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(2) Preliminary reports have been published: G. Rapi and G. Sbrana, *Chem. Commun.*, 128 (1968); G. Rapi and G. Sbrana, *Chim. Ind.* (*Milan*), **52**, 1130 (1970).

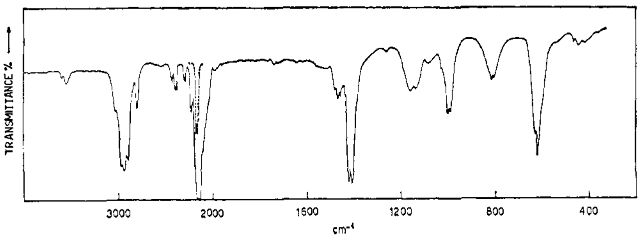

Figure 1. Gas-phase infrared spectrum of *N*,*N*′-dimethylcarbodiimide.

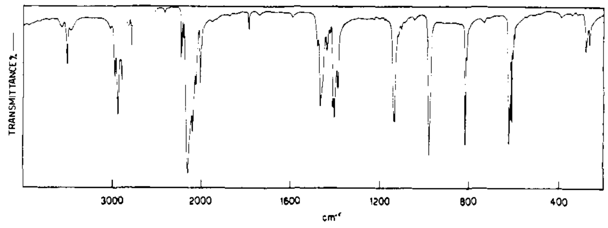

Figure 3. Infrared spectrum of solid *N*,*N*′-dimethylcarbodiimide at liquid nitrogen temperature.

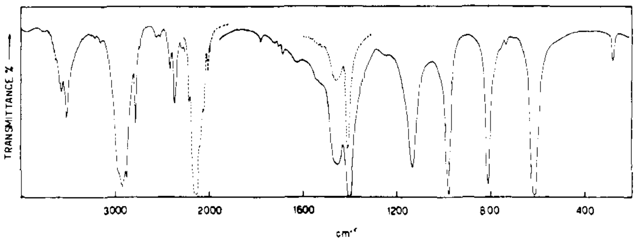

Figure 2. Infrared spectrum of liquid *N*,*N*′-dimethylcarbodiimide: full-line spectrum, thickness 18 μ; dotted line spectrum, liquid film.

ment measurements obtained on the para- and meta-substituted diphenylcarbodiimides which are in agreement with an "allene" structure.[4] Moreover, a structure of this kind is also predicted by assuming, according to the valence bond theory, an sp-type bonding for the central carbon atom and an sp^2 hybridization for the two nitrogen atoms. The chain N═C═N is completely linear but the CH_3N– single bonds lie in planes perpendicular to each other and pass through the N═C═N axis.

Infrared and Raman Spectra

Since the vibrational spectrum usually furnishes important information on the molecular structure, we have undertaken a detailed vibrational analysis on the simplest term of the series, the *N*,*N*′-dimethylcarbodiimide (DMCD). No spectroscopic work has been previously published except an infrared investigation on the antisymmetric stretching N═C═N vibration of several aliphatic and aromatic carbodiimides.[5]

The comparative analysis of the infrared and Raman spectra allows some inferences on the molecular structure of DMCD. On the basis of the number of fundamentals detected in the infrared spectrum as well as of the complete coincidence with the Raman lines, a centrosymmetric structure can be ruled out. On the other hand, the occurrence of almost all the expected 27 fundamentals in the infrared spectrum suggests that the molecular symmetry is very low. While the presence of C_s symmetry can be ruled out by simple arguments based on the structure of the skeletal frame, no definite evidence is obtained from the polarization data of the Raman bands concerned with the presence of a C_2 symmetry axis. However, on the basis of the previous results, C_2 symmetry can be predicted for the skeleton whereas the alternative choice of C_1 symmetry depends on the relative orientation of the CH_3 groups. Since this choice is irrelevant to the vibrational assignment, we shall assume that the methyl groups are oriented in such a manner that a C_2 axis exists. The infrared and Raman spectra are still consistent with this assumption.

Results and Discussion

For C_2 symmetry, 27 fundamentals, both infrared and Raman active, are expected which are classified as 14A and 13B. Eighteen of these modes belong to the methyl groups and the remaining nine to the skeletal motions. The analysis of the rotational structure of the vapor bands (Figure 1) is of little use in elucidating the molecular structure. In fact, the rotational envelope shown by most of the bands is difficult to interpret because it is affected by the free rotation of the methyl groups as well as by the overlap of the other neighboring bands. Only the three bands which occur at 2165, 1413, and 618 cm^{-1} show a well-resolved rotational structure with the characteristic peaks of the "parallel" and "perpendicular" bands of a symmetric top molecule. They correspond to fundamentals which involve motions of the linear chain. Since their rotational behavior is also consistent with the polarization of the corresponding Raman bands, the two "parallel" bands at 2365 and 1418 cm^{-1} have been assigned to stretching and the "perpendicular" band at 618 cm^{-1} to the bending modes of the N═C═N chain.

Because the polarized Raman spectral data are not sufficient for complete identification of the fundamentals, many of the arguments establishing the assignment are based on the "group frequency" behavior and analogies with molecules such as dimethylcyanamide[6] and methyl azide.[7] In addition, several bands which are too weak or too strongly overlapped by close-lying fundamentals to be observed in the vapor and liquid (Figure 2) spectrum are clearly observed in the crystal spectrum at liquid nitrogen temperature (Figure 3). The frequencies of the infrared vapor, liquid, and crystal bands as well as those of the Raman lines are given in Table I. The vibrational assignment together with an approximate description of the molecular motions in terms of group vibrations are listed in Table II.

A Species. The polarized bands at 2932 and 2888 cm^{-1} in the Raman spectrum are assigned to the two CH stretching modes corresponding to the antisymmetric and symmetric vibrations of the CH_3 groups, respectively. The designation "symmetric" or "antisymmetric" concerning the CH stretches and the CH_3 deformations refers only to the symmetry with respect to the methyl groups. The third CH stretching expected in this species has been assigned to the band at 2978 cm^{-1} in the crystal spectrum.

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(3) K. Schlögl and H. Mechtler, *Angew. Chem.*, 78, 606 (1966).
(4) F. Ferchtmeyer and F. Wuoerstlin, *Chem. Ber.*, 67, 434 (1963).
(5) M. Davies and W. J. Jones, *Trans. Faraday Soc.*, 54, 1454 (1958).
(6) F. B. Brown and W. H. Fletcher, *Spectrochim. Acta*, 19, 915 (1963).
(7) E. Mantica and G. Zerbi, *Gazz. Chim. Ital.*, 90, 53 (1960).

Table I. Vibrational Spectrum of *N,N′*-Dimethylcarbodiimide

Infrared			Raman			
Vapor	Liquid	Crystal	Liquid	P	Assignment	Species
3590 vw	3575 w					
3545 w	3520 w	3510 w			$\nu_{18} + \nu_6 = 3545$	B
		2988 vw			ν_{15}	B
		2978 m			ν_1	A
2963 s	2965 m	2970 m	2968 m	dp	ν_{16}	B
2936 s	2930 m	2936 s	2932 s	p	ν_2	A
2900 s	2880 m	2895 m	2888 m	p	ν_3	A
	2860 sh	2878 sh	2872 w	dp	ν_{17}	B
2800 w	2784 w	2781 w			$2\nu_6 = 2810$	A
2430 vw	2420 vw	2416 vw			$\nu_{20} + \nu_{24} = 2435$	A
2380 vw	2370 w				$\nu_6 + \nu_{24} = 2385$	B
2220 w	2212 w	2222 w			$\nu_6 + \nu_9 = 2215$	A
		2200 vw			$2\nu_8 = 2204$	A
2168 vs	2140 vs	2152 vs	2160 vw		ν_{18}	B
2158 vs		2140 sh				
2100 sh	2088 w	2094 m			$\nu_{22} + \nu_{24} = 2110$	A
2065 sh	2053 w	2060 m			$\nu_8 + \nu_{24} = 2082$	B
	2010 w	2011 w			$\nu_6 + \nu_{11} = 2015$	A
	1783 vw	1787 vw			$\nu_{24} \times \nu_9 = 1790$	B
1480 vw		1470 w	1465 w	dp	ν_{19}	B
1468 w		1465 m			ν_4	A
1458 w	1455 m	1456 w	1448 w	dp	ν_{20}	B
		1438 w			ν_5	A
1418 s	1405 vs	1410 m	1398 m	p	ν_6	A
1403 s		1403 m				
1390 sh		1389 m			ν_{21}	B
		1380 sh			ν_7	A
1160 w	1130 s	1133 m			ν_{22}	B
1140 w						
		1120 w			ν_{23}	B
1085 w		1102 w			ν_8	A
997 m	980 vs	976 s			ν_{24}	B
988 m		970 m				
830 sh		818 sh				
815 w	810 vs	816 s	811 s	p	ν_9	A
805 w		811 w				
	735 vw	732 vw			ν_{10}	A
		626 sh				
		621 s			ν_{25}	B
625 s	612 vs	616 s	615 w	dp		
618 s		610 s				
		604 w			ν_{11}	A
		598 vw				
		277 w			ν_{12}	A
	268 w	263 w	262 w	dp	ν_{26}	B

Five skeletal modes are expected in this species. Only two are unequivocally identified by their polarized Raman bands at 1398 and 811 cm^{-1} and are assigned to the ν_6 and ν_9 fundamentals. A value of 1398 cm^{-1} could be considered too high for the N=C=N symmetric stretching vibration by comparison with the values of 1273 and 1335 cm^{-1} found in methyl azide and carbon dioxide, respectively. However, the Raman evidence is so strong as to rule out any other alternative choice.

The assignment of ν_{11} and ν_{25} fundamentals requires a more detailed discussion. These fundamentals involve the N=C=N bending modes which are degenerate in the linear triatomic molecules or ions but which should be well separated in the spectra of DMCD owing to the low molecular symmetry. Although they belong to different species, we shall discuss them together for the sake of convenience.

These modes are expected in the 700–500-cm^{-1} range and occur at 667.3 in CO_2 and at 666 and 555 cm^{-1} in methyl azide. Values of 620 and 530 cm^{-1} have been also found for the in-plane and out-of-plane N—C≡N bending motions of dimethylcyanamide. In the infrared spectrum of liquid DMCD only a single band (612 cm^{-1}) is observed. Since it corresponds to a depolarized Raman band, the assignment to the ν_{25} fundamental seems unquestionable. No other band is available below 700 cm^{-1} to be assigned to the ν_{11} fundamental of A species. One possibility is the occurrence of both fundamentals at such close frequencies to be indistinguishable in the liquid spectrum. The unusual pattern shown, in the crystal spectrum, by the 615-cm^{-1} band which is split into six components seems to support the above interpretation. In fact, the number of components is not justified on the basis of the Davydov splitting theory and therefore, even if the presence of overtones and combination bands cannot be excluded, we have located both ν_{11} and ν_{25} fundamentals at 612 cm^{-1} in the liquid spectrum.

No evidence has been found in the infrared and Raman spectra of the ν_{12} symmetric C—N=C deformation and the ν_{13} torsional modes. In the range 400–200 cm^{-1} where they are expected, only a depolarized band is observed at 263 cm^{-1} which must be undoubtedly assigned to the ν_{26} fundamental of the B species. However, in the crystal spectrum, two bands appear at 263

Table II. Fundamental Vibrations of *N*,*N'*-Dimethylcarbodiimide

Species	Designation	ν	Approximate description
A	ν_1	2978	CH stretch (antisymmetric)
	ν_2	2936	CH stretch (antisymmetric)
	ν_3	2888	CH stretch (symmetric)
	ν_4	1465	CH_3 deform (antisymmetric)
	ν_5	1438	CH_3 deform (antisymmetric)
	ν_6	1405	N=C=N symmetric stretch
	ν_7	1380	CH_3 deform (symmetric)
	ν_8	1102	CH_3 rocking
	ν_9	810	C—N symmetric stretch
	ν_{10}	732	CH_3 rocking
	ν_{11}	610	N=C=N deform
	ν_{12}	277	C—N=C symmetric deform
	ν_{13}		Torsion
	ν_{14}		CH_3 torsion
B	ν_{15}	2988	CH stretch (antisymmetric)
	ν_{16}	2970	CH stretch (antisymmetric)
	ν_{17}	2872	CH stretch (symmetric)
	ν_{18}	2140	N=C=N antisymmetric stretch
	ν_{19}	1470	CH_3 deform (antisymmetric)
	ν_{20}	1455	CH_3 deform (antisymmetric)
	ν_{21}	1389	CH_3 deform (symmetric)
	ν_{22}	1130	CH_3 rocking
	ν_{23}	1120	CH_3 rocking
	ν_{24}	980	C—N antisymmetric stretch
	ν_{25}	621	N=C=N deform
	ν_{26}	263	C—N=C antisymmetric deform
	ν_{27}		CH_3 torsion

and 277 cm^{-1} which, as in the case previously discussed, could be due to the close-lying ν_{26} and ν_{12} fundamentals both involving the N—C=N deformation modes. Even if no other choice seems possible, the assignment of the ν_{12} fundamental is quite arbitrary and must be considered only as tentative.

Finally, we have assigned to the CH_3 antisymmetric deformation modes the bands which occur, in the crystal spectrum, at 1465 and 1438 cm^{-1}. They do not appear in the Raman spectrum, probably being obscured by the depolarized bands at 1465 and 1448 cm^{-1}. The symmetric deformation mode is difficult to identify and it is tentatively assigned to the shoulder at 1380 cm^{-1} in the crystal spectrum.

The two rocking modes, by analogy with dimethylcyanamide, have been located at 1102 and 732 cm^{-1}, whereas no experimental evidence has been found for the CH_3 torsion which is expected at about 200 cm^{-1}.

B Species. The three remaining CH stretching modes are assigned to the depolarized bands at 2968 and 2872 cm^{-1} in the Raman and to the band at 2988 cm^{-1} observed only in the infrared crystal spectrum. The Raman spectrum also gives clear evidence for the identification of the two CH_3 antisymmetric deformation modes at 1465 and 1448 cm^{-1}. The corresponding symmetric vibration is located at 1389 cm^{-1} where a band, overlapped in the liquid spectrum by the strong ν_6 fundamental, is clearly observed in the crystal spectrum.

Finally, the two CH_3 rocking modes, expected to occur at similar frequencies in this species, are associated with the remaining unassigned bands at 1130 and 1120 cm^{-1}. As for the corresponding mode of the A species, an assignment cannot be given for the CH_3 torsional mode.

Two of the four fundamentals associated with the skeletal motions have already been discussed and assigned in the previous section. The remaining two fundamentals, ν_{18}, and ν_{24}, involving N=C=N and CH_3—N= asymmetric stretching motions, occur at 2140 and 993 cm^{-1}, respectively. The assignment of these bands is straightforward and does not require any detailed discussion. However, it is worthwhile to point out that the frequency of the ν_{18} fundamental is characteristic of the carbodiimidic form whereas the corresponding band of the isomeric cyanamidic structure occurs above 2200 cm^{-1}. This can be used as a means of determining which structure prevails in a given molecule.

As previously discussed, the spectroscopic data are in agreement with a low-symmetry molecular structure. However, no information can be obtained from ir and Raman spectra about the value of the CH_3—N=C angle which is expected to be 120° when an sp^2 hybridization for the nitrogen atoms is assumed. Recently, Williams and Damraner[8] on the basis of an INDO molecular calculation suggest an unusual ground-state geometry with unhybridized nitrogen atoms and angles of 90°.

Ultraviolet Spectra

The uv spectra of carbodiimides, which are expected to present a band system very similar to that of allene,[9] have been studied very little.[10,11] Behringer and Meier[12] reported a correlation between these two systems and calculated the length of the C=N bond in agreement with the C=C bond of allene. The absorption spectrum of DMCD in the vapor phase shows a maximum at 1910 Å, a shoulder at 2070–2100 Å, and three weak peaks at 2464, 2525, and 2584 Å. In *n*-heptane solution, a strong band with λ_{max} 2066 Å (log ϵ 4.69) and three peaks at 2475 (log ϵ 2.54), 2540 (log ϵ 2.36), and 2600 Å (log ϵ 2.14) are observed.

The first absorption band found in the vapor phase with its maximum at 1910 Å may be due to an N → R transition while the high intensity band at 2066 Å in *n*-heptane solution (corresponding to the shoulder in the vapor at the same wavelength) has to be ascribed to the N → V transition rising from an in-phase excitation of the two C=N bonds.

This transition is allowed and polarized parallel to the N=C=N system, and is expected to give rise to a very intense band. The very high molar extinction coefficient of the band at 2066 Å (ϵ 49,000), in good agreement with the expected one, favors our assignment. No conjugation bands are shown by cumulated systems above 2000 Å although the π-electron centers are even closer than in the conjugated position. This may be related to the fact that the π-electron orbitals of the two multiple bonds are at right angles instead of parallel and that dipolar structure cannot be significant. The transitions that give rise to the absorption in the 2400–2600-Å region can be associated with the lone pairs of the nitrogen atoms. An n → π^* transition is generally very weak because the two wave functions under the transition moment integral overlap very little, one being to a large extent localized around the heteroatom and the other being an extended molecular orbital. Therefore, if the lone pair is a pure p$_x$ or p$_y$ orbital, the transi-

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(8) D. R. Williams and R. Damraner, *Chem. Commun.*, 1380 (1969).

(9) L. H. Sutcliffe and A. D. Walsh, *J. Chem. Soc.*, 899 (1952).

(10) G. C. Lardy, *J. Chim. Phys.*, 21, 281 (1924).

(11) A. Franssen, *Bull. Soc. Chim. Fr.*, 43, 177 (1928).

(12) H. Behringer and H. Meier, *Justus Liebigs Ann. Chem.*, 607, 73 (1957).

tion would be forbidden and the corresponding band system will have a low extinction coefficient ($10 \leq \epsilon \leq 100$). If, however, the lone-pair orbital is an sp hybrid, the transition will be allowed owing to the s component and the extinction coefficient will be higher, of the order 100–1000.

In the carbodiimides, just like in the azides and ketenimines, the N–R bond makes an angle of about 120° with the linear cumulated system.[12,13] This means that the nitrogen atoms linked to the R groups are sp^2 hybridized (although one of the hybrid orbitals is nonbonding and contains a pair of electrons). Then the three last bands whose intensities, measured in *n*-heptane solution, are ϵ 348 (2475 Å), 229 (2540 Å), and 138 (2600 Å) arise probably from the allowed $n \rightarrow \pi^*$ ($N \rightarrow Q$) transitions polarized perpendicular to the plane of the ring.

We have not measured the extinction coefficient of the corresponding three bands in the vapor phase owing to the uncertainty in the measurement of gaseous concentration. The spectra of dimethylcarbodiimide in the vapor phase and in *n*-heptane solution are reported in Figure 4.

Nmr Spectra

We have measured the H^1 nmr spectra of DMCD as well as those of the corresponding isomer, the dimethylcyanamide. The occurrence of a singlet in both spectra at τ 7.04 and 7.13 ppm, respectively, shows that the methyl groups are, as expected, chemically equivalent. The lower value of τ for DMCD can be explained on the basis of a smaller shielding of the *N*-methyl groups.

It must be pointed out that no inferences concerning the existence of a carbodiimidic or cyanamidic structure can be drawn from the proton magnetic resonance results. In the case of diethylcyanamide and *N*,*N*′-dicyclohexylcarbodiimide,[14] definite evidence concerning these structures has been obtained from the ^{14}N resonance spectra.

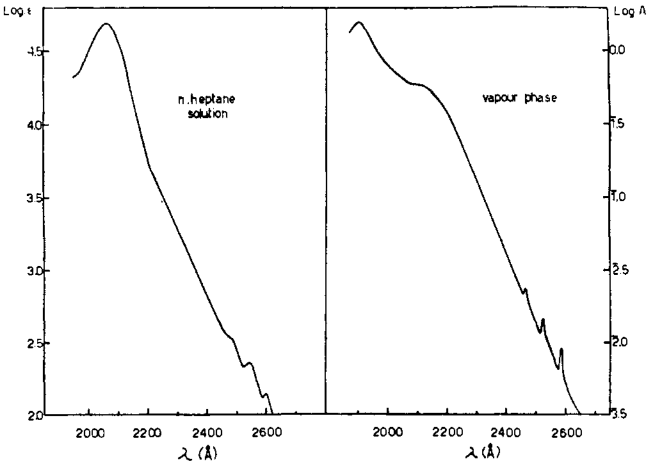

Figure 4. Ultraviolet spectra of *N*,*N*′-dimethylcarbodiimide.

Experimental Section

The infrared spectra between 4000 and 200 cm^{-1} were measured with the aid of a Perkin-Elmer Model 225 double grating spectrograph in the vapor (10-cm cell), liquid (capillary film and 15-μ sealed cell), and solid phases. Crystal spectra were registered, using a low-temperature conventional cell, on polycrystalline films obtained by deposition from the gas phase on a CsI plate cooled at liquid nitrogen temperature. The Raman spectra of the liquid were run on a Cary-81 instrument using a 0.5-ml cell. Polarization data were obtained with standard polaroids. The ultraviolet spectra of the vapor and of the *n*-heptane solution were measured with a Cary Model 14 spectrophotometer. The nmr spectra were registered with a Varian A-56/60 spectrometer in $CDCl_3$ at 20° using TMS as internal reference.

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(13) W. C. Schneider, *J. Amer. Chem. Soc.*, **72**, 761 (1950).

(14) J. D. Ray, L. M. Piette, and D. P. Olls, *J. Chem. Phys.*, **29**, 1022 (1958).