This pronounced disagreement between theory and experiments for isotactic polymers has yet to be resolved.

Theoretical treatment of the configurations of stereoregular chains will be the subject of a later paper.

Structure and Fundamental Vibrations of Cage Molecules. I. 1,4-Diazabicyclo[2.2.2]octane[1]

M. P. Marzocchi, G. Sbrana, and G. Zerbi

Contribution from the Departments of Physical Chemistry and Organic Chemistry, Firenze, Italy, and of the Industrial Chemistry Department of the Politecnico, Milan, Italy. Received September 25, 1964

Infrared spectra of diazabicyclooctane in the gas solution and solid phases as well as Raman spectra of the solution were obtained. By thermal treatment, solid samples with most of the crystallites oriented with the principal axis perpendicular to the cell window were obtained and their spectra studied. The infrared spectrum is compatible with a D_{3h} structure. All the A_2'' and E' infrared active fundamentals and 4 out of the 15 expected frequencies only active in the Raman spectrum have been assigned and discussed. The information obtained from the spectrum of the oriented crystal is more reliable than that obtained from band contours of the gas-phase spectra.

Introduction

Molecules with a "cage structure" exhibit unusual physical properties which can be attributed to their high molecular symmetry. If one or more heteroatoms like nitrogen are present in the ring, the molecule acquires outstanding chemical properties such as complexing ability and catalytic activity.[2]

The purpose of this paper is to discuss the vibrational spectrum of 1,4-diazabicyclo[2.2.2]octane or triethylenediamine (TED), which, to our knowledge, has not been previously studied.

$$
\begin{array}{c}
CH_2-CH_2 \\
N-CH_2-CH_2-N \\
CH_2-CH_2
\end{array}
$$
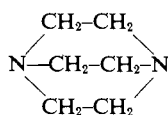
Whereas a large amount of work on the chemistry of TED can be found in the literature, comparatively little is known on its physical chemistry.[3,4] A vibrational assignment and approximated normal coordinate calculation have been carried out by MacFarlane and Ross[5] on the parent molecule bicyclo[2.2.2]octane.

(1) This work was supported by the Consiglio Nazionale delle Ricerche of Italy.
(2) Technical Report of Houdry Process and Chemical Co., Philadelphia, Pa.
(3) A. Farkas, G. A. Mills, W. E. Erner, and H. B. Maerker, *J. Chem. Eng. Data*, **4**, 334 (1959).
(4) S.-S. Chang and E. F. Westrum, Jr., *J. Phys. Chem.*, **64**, 1551 (1960).
(5) J. J. MacFarlane and I. G. Ross, *J. Chem. Soc.*, 4169 (1960).

Only very recently Mirone has studied the Raman spectrum of TED.[6]

Experimental

Samples of TED, purchased from Chemical Procurement Laboratories and from Houdry Chemical Co., were carefully purified by repeated sublimation under vacuum. Spectra were recorded with Perkin-Elmer spectrometers, Models 421, 337, and 301, in the frequency ranges 4000–550, 550–400, and 400–70 cm.$^{-1}$, respectively.

Gas-phase samples were contained in a heated 5-cm. cell at a temperature of 90°. Spectra were also taken in a solution of CCl_4 and CS_2. Solid samples were examined as Nujol mulls, KBr disks, and crystalline films. TED is very hygroscopic and readily absorbs atmospheric water. Even if all the manipulations were performed in dryboxes and great care was taken so as to avoid any humidity, spectra of samples suspended in KBr disks always showed bands due to absorbed water. Crystalline films with no trace of humidity were obtained by melting the substance between two NaCl or KBr windows and by subsequent cooling in a drybox. With the same thermal treatment we were able to obtain oriented crystalline samples as we shall discuss later in this paper. Gas-phase, CCl_4–CS_2 solution, and crystalline spectra are shown in Figures 1, 2, and 3, respectively. Figure 3 also shows the infrared spectra of unoriented, partially oriented, and completely oriented crystalline samples.

In addition to the Raman data from Mirone,[6] we have also obtained the Raman spectra of saturated solutions in chloroform and benzene with a Cary 81 Raman spectrometer.

Structure and Selection Rules. For this kind of cage molecule two molecular structures must be considered. The first is a D_{3h} model in which each pair of CH_2 groups is in the eclipsed configuration. By a suitable rotation of the two NC_3 pyramids in opposite directions about the threefold axis, a new model is obtained in which the hydrogens are in a staggered configuration. The latter model belongs to the D_3 point group.
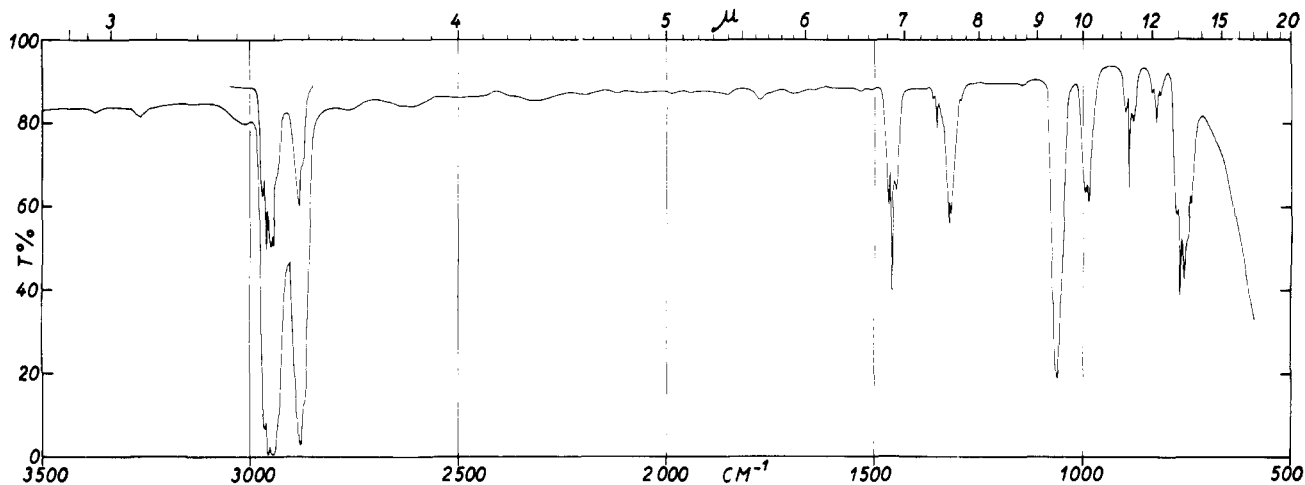
(6) G. Mirone, to be published.

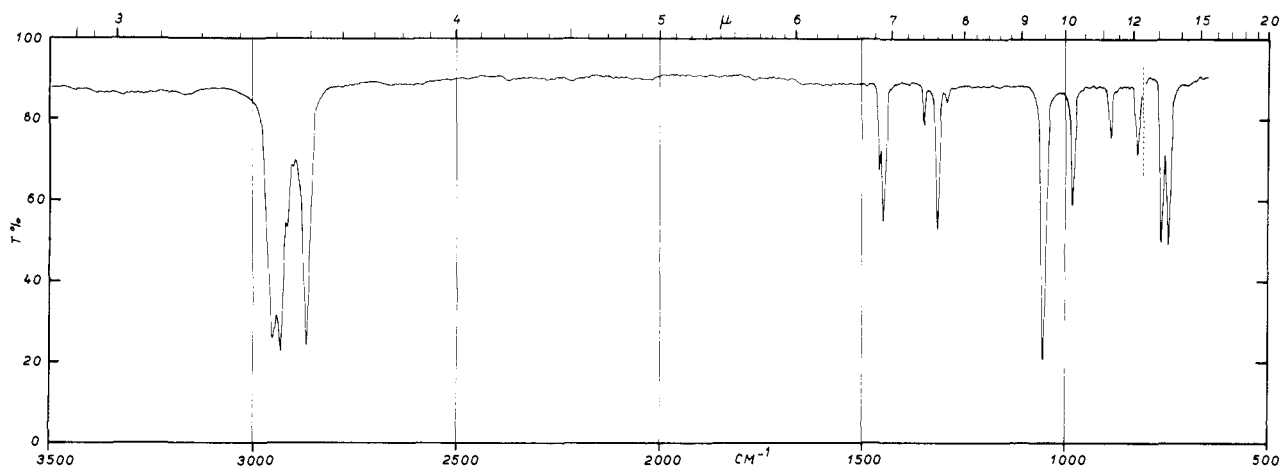Figure 1. Gas-phase infrared spectrum of triethylenediamine.

Figure 2. Infrared spectrum of a CCl_4–CS_2 solution of triethylenediamine.

In Table I the distribution of the various fundamental vibrations and their spectral activity for both models are collected.

Table I. Vibrational Selection Rules for Two Possible Structures of the Triethylenediamine Molecule

D_{3h}	Infrared	$5 A_2''\|$	$9 E' \perp$ f	f
	Raman	f	$9 E'$ dp $9 E''$ dp $6 A'$, p
	Inactive	$3 A_2'$	$4 A_1''$
D_3	Infrared	$8 A_2$	$18 E \perp$
	Raman		$18 E$ dp $10 A_1$ p

Whereas for a D_{3h} structure 14 bands are expected in the infrared with 9 Raman coincidences, for a D_3 structure 26 bands should occur in the infrared with 18 Raman coincidences. The interpretation of the spectrum we are going to discuss is only feasible in terms of a D_{3h} model. The structure compatible with the observed vibrational spectrum is in agreement with a recent X-ray study by Wada, et al.[7] According to these authors, the TED molecule has a D_{3h} structure, and its crystal structure is hexagonal, space group C_{6h}^2-$P6_{3/m}$ ($z = 2$).

(7) T. Wada, E. Kishida, Y. Tomia, H. Suga, S. Seki, and I. Nitta, Bull. Chem. Soc. Japan, 33, 1317 (1960).

Because of its symmetry the molecule is a symmetric top, but calculations of the principal moments of inertia ($I_x = I_y = 348 \times 10^{-40}$ g. cm.^{2}; $I_z = 324 \times 10^4$ g. cm.^{2})[8] show that the molecule may be considered an accidental spherical top. An important feature of the crystal structure, which has been very useful in the interpretation of its infrared spectrum, is that in the crystal the molecular threefold axis is parallel to the crystallographic sixfold axis. Before discussing the detailed interpretation of the vibrational spectrum we shall describe in more detail the experimental findings on the crystalline samples.

The infrared spectra of samples as KBr disks or as Nujol mulls are practically identical with the spectra obtained from CCl_4 or CS_2 solutions. However, striking differences were found when the spectra of the solutions were compared with those obtained from a molten sample upon cooling between two NaCl plates.

The examination of the samples under a polarizing microscope has revealed that, whereas some of the crystals were birefringent, others were only mono-refringent. By repeated melting and cooling we were able to obtain a specimen with practically all the crystals showing monorefringence at the polarizing micro-

(8) The principal moments of inertia have been calculated using the geometry given by Wada, et al.[8] We have taken the C–H distance as 1.09 Å., which seemed to us more reasonable than the value of 0.96 Å., suggested by these authors.

scope. We have then concluded that in that specimen most of the crystallites were oriented with the crystallographic axis perpendicular to the NaCl plate, hence parallel to the direction of propagation of the infrared light in the spectrometer.

For such an oriented sample, the A_2'' fundamental vibrations which give rise to a transition moment parallel to the threefold axis should be strongly weakened in the infrared spectrum if compared with the spectrum of an unoriented solid sample. Moreover, the perpendicular E' fundamentals should give rise to infrared bands which show no dichroism when the spectrum is recorded with polarized light. All of these expectations have been verified in our experiments. In Figure 3 the infrared spectra of unoriented, partly oriented, and completely oriented samples are shown.

With the information obtained from the spectrum of the oriented crystals, the interpretation of the infrared spectrum should have been a straightforward matter. On the contrary, the vibrational analysis carried out only on the basis of the band shapes of the gas-phase spectra disagreed somewhat with that obtained from the crystal. Symmetric-top molecules should show band contours with a strong Q branch for a transition moment parallel to the threefold axis (A_2'' species). Perpendicular bands should occur for E' fundamentals. If we consider the molecule as a quasi-spherical top, all the bands should possess a PQR structure with a prominent Q branch. Coriolis coupling is also likely to occur,[5] and the shape of the bands may be strongly modified. Moreover, some of the observed bands are strongly overlapped, and the decision of the true band contour becomes ambiguous. Because of all these uncertainties, we have decided to give more weight to the information obtained from the spectrum of the oriented crystals. In the text, however, the various discrepancies will be discussed.

Infrared Active Fundamentals. A_2'' Species. For this molecule five A_2'' fundamentals are expected in the infrared spectrum. The five vibrations can be approximately described as one C–H stretch, one CH_2 scissoring, one CH_2 wagging, and two skeletal motions. No coincidence with Raman bands is to be found. Parallel bands of a symmetric-top molecule should be found in the gas-phase spectrum. In the oriented crystals, the corresponding absorptions must be strongly weakened.

In the C–H stretching region the spectrum of the vapors shows three bands with PQR structure. The strong peak at 2960 cm.$^{-1}$ with a prominent Q branch is assigned to the A_2'' C–H stretch. No sure information is obtained from the spectrum of the oriented crystal. In the lower frequency region, bands which become weakened in the spectrum of the oriented crystal, along with the orientation of the crystallites, are observed at 1452, 1350, 990, 770, and 751 cm.$^{-1}$. No coincidence is found in the Raman spectrum. The bands are easily assigned to transitions to an A_2'' excited level.

Whereas the band contour for the 1452- and 1350-cm.$^{-1}$ absorptions is consistent with the expectations, a great uncertainty is encountered in the decision of the type of contour for the other bands of lower frequencies. Without the data from the oriented crystal, on the basis of band shapes only, one could be led to a wrong assignment.
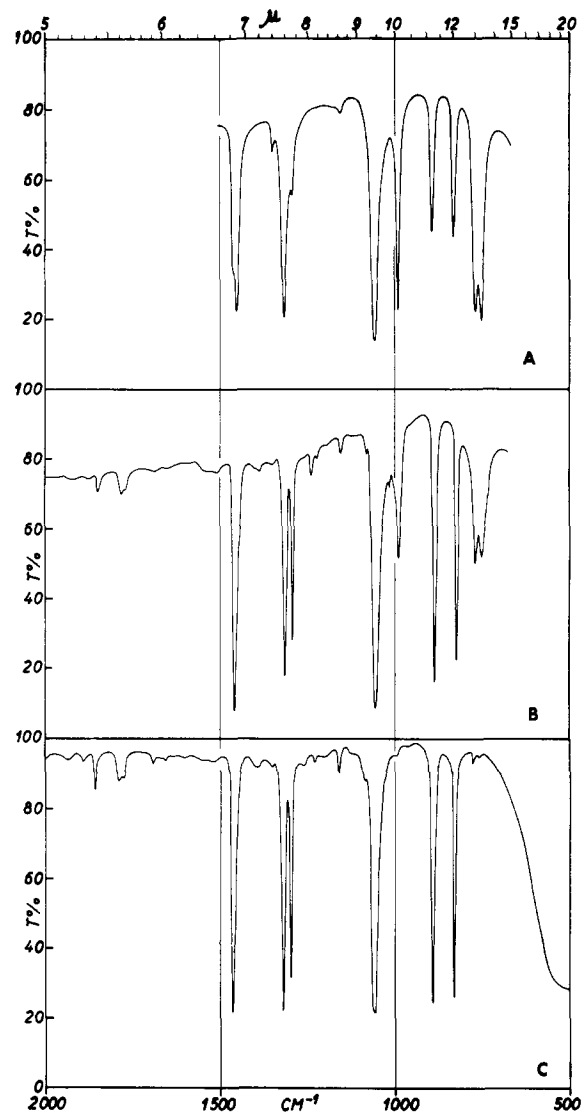

Figure 3. Infrared spectrum of solid triethylenediamine: A, unoriented; B, partially oriented; C, completely oriented.

The number of A_2'' bands found in the spectrum exceeds the number of expected fundamental transitions by 1. We were particularly puzzled in the interpretation of the very strong doublet at 770 and 751 cm.$^{-1}$. The only reasonable explanation we can suggest is that the second peak at 751 cm.$^{-1}$ is a combination tone 335 (E'') + 423 (E') = 758 cm.$^{-1}$ (A_2'') in Fermi resonance with the strong fundamental which occurs very close to it. Such a resonance may well account for its unusual intensity. (Site symmetry selection rules may give rise to other absorptions in the spectrum which are generally rather weak. Site symmetry then cannot account for one of the two strong absorptions at 751 and 770 cm.$^{-1}$.)

E' Fundamentals. Nine infrared bands are expected which should be coincident with nine depolarized Raman bands. Parallel bands should occur in the spectrum of the vapors, and strong bands in the spectrum of the oriented sample should show no dichroism. Two E' C–H stretches occur with perpendicular bands at 2942 and 2880 cm.$^{-1}$ in the gas-phase spectrum. In this frequency region the Raman spectrum does not give any useful information because only two bands

Table II. Fundamental Vibrations of 1,4-Diazabicyclo[2.2.2]-octane (or Triethylenediamine) from Infrared and Raman Spectra

Vapor[a]	Solution[b]	Crystal[c]	Raman	Species	Approx. assignment
2960	2955	..	f	A_2''	CH stretch
1458	1452	1452	f		CH_2 scissor
1350	1349	1350	f		CH_2 wag
987	987	990	f		Skeletal
766 [d]	765 [d]	770 [d]	f		Skeletal
749	749	751	f		335 + 423
2942	2935	2932	(2932)[e]	E'	CH stretch
2880	2871	2870	2870		CH stretch
1470	1460	1464			CH_2 scissor
1320	1318	1320			CH_2 wag or twist
1300	1292	1290	1300		CH_2 twist or wag
1061	1058	1058	1060		Skeletal
892	890	892			Skeletal
825	825	830			CH_2 rock
..	..	423[f]			Skeletal
			(2932)[e]	A_1'	CH stretch
			1335		CH_2 scissor
		(See text)[g]	965		Skeletal
			800		Skeletal
			600		Skeletal
			580	E''	Skeletal
		(See text)[h]			
			335		Skeletal

[a] The frequencies listed refer to the position of the Q branches. [b] CCl_4-CS_2 solution in the appropriate absorption ranges. [c] From the oriented and unoriented samples. [d] The fundamental is in the Fermi resonance with a combination tone at lower frequency; see text. [e] Frequency used twice. [f] From unoriented crystals. [g] One fundamental is missing. [h] Only two of the Raman active E'' fundamentals have been observed.

with uncertain polarization are observed instead of the expected five. At lower frequencies, infrared bands with the predicted behavior are found for the crystal at 1464, 1320, 1290, 1058, 892, and 830 cm.$^{-1}$. A weak band is observed in the spectrum of a thick sample of unoriented crystallites at 423 cm.$^{-1}$.

The Raman spectrum is too weak for showing all the expected features. Nevertheless, depolarized bands are found at 1300, 1060, and 423 cm.$^{-1}$, which nicely coincide with the infrared absorptions.

Raman Active A_1' and E'' Fundamentals. Six A_1' polarized and nine E'' depolarized bands are predicted for TED with D_{3h} structure. Unfortunately, the whole Raman spectrum is very weak, and only a few bands are observed. Besides the two peaks at about 2900 cm.$^{-1}$, which have been previously discussed, polarized bands occur at 1335, 965, 800, and 600 cm.$^{-1}$. Only one A_1' fundamental (CH_2 scissoring) is missing. Out of the nine E'' bands, only two with no infrared coincidence are found at 580 and 335 cm.$^{-1}$. Further study on the Raman spectrum of this substance is needed for the assignment of the remaining fundamentals.

Conclusion

The proposed vibrational assignment is shown in Table II. The observed vibrational spectrum of triethylenediamine is compatible with a molecular structure which belongs to the D_{3h} point group. For such a cage structure the hydrogen atoms are locked into an eclipsed configuration and may give rise to peculiar features in the infrared spectrum. We are carrying out a normal coordinate analysis of such a system, and the results will be reported elsewhere.

From the present work[9] it is evident that great caution must be taken in the interpretation of the infrared spectrum of large molecules only on the basis of band contours of the vapor phase spectra.

(9) NOTE ADDED IN PROOF. After our manuscript was submitted to the editor, a paper by Weiss and co-workers on the vibrational spectrum of triethylenediamine appeared in the literature: G. S. Weiss, A. S. Parkes, E. R. Nixon, and R. E. Hughes, *J. Chem. Phys.*, 41, 3759 (1964). After a careful comparison of the results, we respectfully feel that the results obtained in our work from the spectra of oriented samples give stronger support to the vibrational assignment we propose in the present paper.