Vibrational Analyses and Barrier to Internal Rotation of 1,1-Dichloroethane and 1,1-Dichloroethane-d_4

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The infrared spectra of gaseous and solid 1,1-dichloroethane and 1,1-dichloroethane-d_4 have been recorded from 140 to 4000 cm^{-1}. The corresponding Raman spectra of the gases and liquids have also been recorded and depolarization values have been measured. All spectra have been interpreted in detail and the 18 normal vibrations have been characterized on the basis of the band contours, isotopic shifts, depolarization values, and normal coordinate calculations. The internal torsional mode was observed at 196 cm^{-1} in the infrared spectrum of solid CD_3CDCl_2. The threefold barrier to rotation was calculated to be 4.77 kcal/mol. This value is compared to those reported for other chloroethanes.

Introduction

Since bromine and chlorine substitution appears to affect the barriers to internal rotation in ethane derivatives more than any of the other halogens, it would appear that a comparison of the theoretical and experimental barriers of several bromo- or chloro-substituted ethanes would provide a rather critical test of both empirical and theoretical barrier predictions. Most of the accurately determined barriers have been obtained by the microwave technique but this method does not readily lend itself to the study of multiple bromine or chlorine substitution because of the quadrupole splittings. Recently we reported the methyl torsional frequencies of 290 and 304 cm^{-1} for methylchloroform[1] and methylbromoform,[2] respectively, which gave barriers of 5.5 and 6.08 kcal/mol. It has been postulated in the past that after the initial substitution of fluorine, chlorine, or bromine for a hydrogen atom on "one end" of an ethane molecule, that the barrier height to methyl rotation would not be drastically affected by substitution of the second and third halogen on the "same" end. Thus, the recent data for CH_3CCl_3, CH_3CBr_3, as well as that for CH_3CF_2Cl[3] indicate that this view may not be correct.

There is considerable conflict as to the effect of the addition of a second chlorine atom to the "same" end of ethane. A band assigned as the torsional frequency was reported at 239 cm^{-1} in the Raman spectrum of the liquid by Daasch, *et al.*,[4] but in a more recent Raman study by Allen, *et al.*,[5] the 239-cm^{-1} band could not be confirmed. Instead the latter authors report a weak band at 222 cm^{-1}. The absence of other bands in this region of the Raman spectrum and the complete absence of bands below 274 cm^{-1} in the infrared spectrum of 2-mm thick liquid films led Allen, *et al.*, to tentatively assign the torsional mode to the 222-cm^{-1} Raman line. The heat capacity of 1,1-dichloroethane has been measured[6] and a comparison of the statistical and experimental entropy resulted in a barrier height of 3550 ± 450 cal/mol. It is interesting to note that in the heat capacity report the authors state that an unpublished infrared spectrum of liquid 1,1-dichloroethane showed a weak band at 240 cm^{-1} which was compatible with the thermodynamic barrier. Wulff[7] has calculated a barrier height of 3490 ± 200 cal/mol from thermal data on the solid phase.

We recently investigated[1] the far-infrared spectrum of 1,1-dichloroethane and reported the torsional mode at 231 and 232 cm^{-1} for the vapor and solid, respectively. However, we could find no indication of the reported Raman bands. About the same time as our paper appeared, a neutron inelastic scattering study of 1,1-dichloroethane was reported by Brier, *et al.*[8] These authors reported bands at 290 and ~230 cm^{-1} with the higher frequency one being more intense and tentatively assigned to the torsional mode for the gas. This value did not differ significantly from the 293 ± 10 cm^{-1} torsional frequency which Brier[9] reported earlier for the liquid. Brier, *et al.*, suggested that the ~230 cm^{-1} might be a hot band transition, $\nu = 2 \leftarrow 1$, of the anharmonic torsion but pointed out that it should only be about 12 cm^{-1} lower than the fundamental. They concluded that further work on this molecule is required. Thus, we have investigated the infrared and Raman spectrum of the corresponding deuterium com-

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(1) J. R. Durig, S. M. Craven, K. K. Lau, and J. Bragin, *J. Chem. Phys.* **54**, 479 (1971).

(2) J. R. Durig, S. M. Craven, C. W. Hawley, and J. Bragin, *ibid.*, **57**, 131 (1972).

(3) C. Graner and C. Thomas, *ibid.*, **49**, 4160 (1968).

(4) L. W. Daasch, C. Y. Liang, and J. R. Nielson, *ibid.*, **22**, 1293 (1954).

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(6) J. M. Li and K. S. Pitzer, *J. Amer. Chem. Soc.*, **78**, 1077 (1956).

(7) C. A. Wulff, *J. Chem. Phys.*, **39**, 1227 (1963).

(8) P. N. Brier, J. S. Higgins, and R. H. Bradley, *Mol. Phys.*, **21**, 721 (1971).

(9) P. N. Brier, *J. Mol. Struct.*, **6**, 23 (1970).

pound in order to try and remove the discrepancies which currently exist for the torsional mode. The Raman spectrum of the "light" compound in the gaseous state has not been previously reported nor has there been any data reported on the mid-infrared spectrum of the solid.

Experimental Section

CH_3CHCl_2 was obtained from Columbia Organic Chemicals and purified by vapor-phase chromatography. CD_3CDCl_2 was prepared by the addition of PCl_5 to acetaldehyde-d_4 which was obtained from Merck & Co., Inc., of Canada. The resulting product was distilled and further purified by vapor-phase chromatography using a Carbowax column at 60°.

The far-infrared spectra were recorded from 33 to 350 cm^{-1} with a Beckman Model IR-11 spectrophotometer. The atmospheric water vapor was removed from the instrument housing by flushing with dry air. The instrument was calibrated by using atmospheric water vapor.[10] Single beam energy checks were made periodically to ensure the energy transmission was at least 10–15% at all times. A low-temperature cell similar to one described earlier[11] was employed to record the spectra of solid samples. Modifications have been made to allow the circulation of cold nitrogen liquid through a hollow brass cold finger. A wedged silicon window was used for the solid film support plate. Conventional vacuum deposition techniques were used to obtain the solid film on the silicon substrate with the additional precaution that the samples were allowed to sublime slowly onto the silicon plate from the solid phase. The silicon substrate was held at $-190°$ during deposition. The solid films were then annealed until there was no change in the spectrum.

The Raman spectra were recorded on a Cary Model 82 Raman spectrophotometer[12] equipped with an argon ion laser source with a frequency of 5145 Å for excitation. The spectra of gas samples were recorded using a multipass gas cell, and the spectra of the liquids were obtained with the samples contained in sealed capillary tubes.

The mid-infrared spectra were recorded from 4000 to 350 cm^{-1} with a Perkin-Elmer Model 620 spectrophotometer. A low-temperature cell equipped with a CsI window was employed to record the spectra of solid samples. Again, conventional vacuum techniques were used to obtain the solid film on the CsI substrate. A 20-cm gas cell with CsI windows was employed to record the spectra of the gaseous samples.

Vibrational Assignment

Assuming C_s molecular symmetry, the 18 fundamental modes of 1,1-dichloroethane may be divided into 11a′ and 7a″ vibrations. The a′ vibrations have polarized Raman bands, and may have B, C, or B/C hybrid contours in the infrared spectrum. The a″ vibrations have depolarized Raman lines and type A band contours in the infrared spectrum.

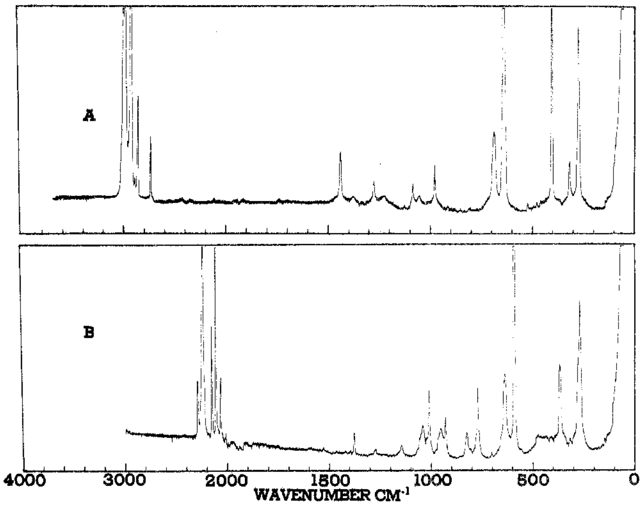

Figure 1. (A) Raman spectrum of CH_3CHCl_2 in the gas phase. (B) Raman spectrum of CD_3CDCl_2 in the gas phase.

For the calculation of the infrared band contours, the moments of inertia for the "light" molecule were assumed to be 219.26, 154.17, and 79.31 amu Å^2; the moments for the "heavy" molecule were 234.88, 159.80, and 97.34 amu Å^2. The resulting P–R separations for type A, B, and C contours were 15.8, 10.8, and 18.0 cm^{-1}, respectively, in the "light" molecule, and 15.2, 8.7, and 22.8 cm^{-1}, respectively, in the "heavy" compound.

The Raman spectra of the gases are shown in Figure 1. The polarized lines were characterized by strong Q branches whereas the depolarized lines were usually quite broad with considerably weaker Q branches. By using the Raman depolarization measurements along with the characteristic infrared band contours, a complete vibrational assignment is proposed. The frequencies for the observed bands along with the vibrational assignment are summarized in Tables I and II, for the light and heavy molecules, respectively.

The infrared spectrum of gaseous CH_3CHCl_2 shows (see Figure 2) a type C band at 3015 cm^{-1} which is partially overlapped, with a type A band centered at 2995 cm^{-1}. The 3015-cm^{-1} band has a polarized Raman counterpart, and it is assigned as the C–H stretch, ν_1. With deuteration this band shifts to 2168 cm^{-1}. A polarized Raman band appearing at 2997 cm^{-1} in the gas phase might be considered to be the counterpart of the 2995-cm^{-1} infrared band. However, the 2995-cm^{-1} band has a type A contour, and, therefore, is unequivocally assigned as an a″ vibration. Since the polarized band at 2997 cm^{-1} is due to an a′ motion, we assign the

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(10) R. T. Hall and J. M. Dowling, *J. Chem. Phys.*, **47**, 2454 (1967); **52**, 1161 (1970).

(11) F. G. Baglin, S. F. Bush, and J. R. Durig, *ibid.*, **47**, 2104 (1967).

(12) This instrument was purchased with funds from the National Science Foundation through Grant No. GP-28068.

Table I: Observed Vibrational Frequencies for 1,1-Dichloroethane[a]

Raman $\Delta\nu$, cm^{-1}		Infrared ν, cm^{-1}		Calculated values	Assignment and approximate descriptions
Gas	Liquid	Gas	Solid		
3017	3009 m, p	3015 m, C	2999	3025	$\nu_1(a')$ C–H stretch (97%)
2997	2991 m, p	3001 w	2990	3003	$\nu_2(a')$ CH_3 antisymmetric stretch (97%)
	2990 m, dp	2995 m, A	2980	3004	$\nu_{12}(a'')$ CH_3 antisymmetric stretch (99%)
2947	2936 s, p	2946 m, B	2931	2949	$\nu_3(a')$ CH_3 symmetric stretch (100%)
2879	2864 w, p	2876 w, B	2864		$2\nu_4 = 2896$
2749	2740 w		2738		$2\nu_5 = 2762$
1448	1442 m, dp	1446 m, C	1441	1450	$\nu_4(a')$ CH_3 antisymmetric deformation (92%)
			1435	1450	$\nu_{13}(a'')$ CH_3 antisymmetric deformation (92%)
1387	1380 vw, p	1381 m, B/C	1376	1367	$\nu_5(a')$ CH_3 deformation (100%)
1284	1278 w, p	1280 m, B	1283 1278	1297	$\nu_6(a')$ CH symmetric bend (78%), C–C stretch (18%)
1232	1227 vw, dp	1229 s, A	1208	1219	$\nu_{14}(a'')$ CH antisymmetric bend (87%)
1089	1087 w, p	1091 w, ?	1088	1056	$\nu_7(a')$ CH_3 in-plane rock (60%), C–C stretch (21%)
1067	1055 vw, dp	1058 s, A	1044	1051	$\nu_{15}(a'')$ CH_3 out-of-plane rock (66%), CH bend (13%)
984	979 m, p	982 B	978	970	$\nu_8(a')$ C–C stretch (50%), CH_3 in-plane rock (22%), CH symmetric bend (20%)
967					$\nu_{16} + \nu_{11}$
707	689 m, dp	704 s, A	680		$\nu_{16}(a'')$ CCl_2 antisymmetric stretch (55%), CCl_2 twist (27%), CH_3 rock (16%)
652	643 vs, p	650 m, B	641	654	$\nu_9(a')$ CCl_2 symmetric stretch (71%), CCl_2 scissor (14%)
636					?
405	406 s, p	405 w, B		399	$\nu_{10}(a')$ CCl_2 wag (60%), CCl_2 stretch (16%)
	319 m, dp		324	317	$\nu_{17}(a'')$ CCl_2 twist (60%), CCl_2 antisymmetric stretch (40%)
275	276 s, p		280	269	$\nu_{11}(a')$ CCl_2 scissor (70%), CCl_2 stretch (10%)
			274	277	$\nu_{18}(a'')$ CH_3 torsion (98%)

[a] Abbreviations used are as follows: vw = very weak, w = weak, m = medium, s = strong, vs = very strong, bd = broad, p = polarized, dp = depolarized; A, B, C refer to characteristic band contour types observed in the infrared spectrum of the gas phase.

2997, 2995 cm^{-1} pair as the approximately degenerate antisymmetric CH_3 stretches, ν_2 and ν_{12}. In the heavy compound, these vibrations shift to 2253 and 2248 cm^{-1} with the higher frequency one being depolarized. The symmetric CH_3 stretch, ν_3, is assigned to the strong, polarized Raman bands at 2947 and 2128 cm^{-1} in the light and heavy molecules, respectively.

The a′ component of the antisymmetric CH_3 deformation, ν_4, is assigned to a sharp Q branch in the infrared spectrum at 1446 cm^{-1} which shifts to 1047 cm^{-1} for the heavy molecule. The a″ component, ν_{13}, is not obvious in the spectrum of the gas, although two bands at 1441 and 1435 cm^{-1} are clearly visible in the spectrum of the low-temperature solid. The symmetric CH_3 deformation, ν_5, is assigned to a weak Q branch at 1381 cm^{-1} (apparently, the center of a B/C hybrid contour) which shifts to 1013 cm^{-1} in 1,1-dichloroethane-d_4.

Between 1200 and 1300 cm^{-1}, there are two infrared bands which are due to the CCH bending vibrations. A type B contour centered at 1280 cm^{-1} on the infrared is assigned as ν_6, the in-plane C–H bending motion. The out-of-plane bend, ν_{14}, is assigned to a strong infrared band of type A contour centered at 1229 cm^{-1}. Deuteration results in a shift to 964 cm^{-1} for ν_{14}. The assignment for the in-plane bend is less certain because of the strong mixing with the symmetric CD_3 deformation. However, ν_6 is tentatively assigned to a polarized Raman band near 772 cm^{-1} in the deuterated molecule.

The in-plane and out-of-plane CH_3 rocks, ν_7 and ν_{15}, are assigned to bands at 1091 and 1058 cm^{-1}, respectively. The 1091-cm^{-1} band is featureless in the infrared, but has a weak polarized Raman counterpart. The 1058-cm^{-1} band has a well-defined type A contour which is indicative of an a″ mode. The type B band centered at 982 cm^{-1} with a polarized Raman counterpart is assigned as ν_8, the C–C stretch. Normal coordinate calculations reveal a strong mixing of CH_3 rock/C–C stretch in both ν_7 and ν_8.

In the heavy compound, a type A band in the infrared spectrum at 829 cm^{-1} is assigned as the out-of-plane CH_3 rock, ν_{15}. Location of the in-plane CH_3 rock is more difficult because of greater mixing of the normal modes in the deuterated molecule. However, for completeness, the band at 933 cm^{-1} is assigned as ν_7. A weak, polarized Raman band with a strong infrared counterpart of type B contour at 1150 cm^{-1} is assigned as predominantly the C–C stretching motion for the deuterated molecule on the basis of the normal coordinate calculations.

The symmetric and antisymmetric CCl_2 stretches, ν_9 and ν_{16}, are assigned to bands at 650 and 704 cm^{-1},

Table II: Observed Vibrational Frequencies for 1,1-Dichloroethane-d_4[a]

Raman $\Delta\nu$, cm^{-1}		Infrared ν, cm^{-1}		Calculated values	Assignment and approximate descriptions
Gas	Liquid	Gas	Solid		
2325	vw				?
2311	2298 w, p		2298		$2\nu_8$
2307					
2253	2248 s, dp	2256 m, C	2243	2248	ν_{12}(a'') CD_3 antisymmetric stretch (98%)
2248	2242 s, p	2248 m, A	2238	2245	ν_2(a') CD_3 antisymmetric stretch (67%), CD stretch (30%)
			2193		$1045 + 1149 = 2194$
2168	2158 s, p	2165 w, B	2156	2230	ν_1(a') CD stretch (68%), CD_3 antisymmetric stretch (31%)
2128	2118 vs, p	2125 w, B	2116	2124	ν_3(a') CD_3 symmetric stretch (98%)
2105	(shoulder)				?
2081	2072 m, p	2084 w, B	2078		$2\nu_{4,13} = 2094$
2073					
2025	2022 w, p		2020		$2\nu_5 = 2028$
	1380 w, p				$\nu_{10} + \nu_5 = 1387$
	1276 w, p				$2\nu_{16} = 1284$
1150	1150 w, p	1151 s, B	1149	1172	ν_8(a') C–C stretch (70%), CD_3 symmetric deformation (23%), CD bend (20%)
	1045 w, dp	1047 m, C	1045	1045, 1045	$\nu_{4,13}$(a', a'') CD_3 antisymmetric deformation (92%), CD_3 antisymmetric deformations (95%)
1013	1015 m, p	1014 m, B	1016	1025	ν_5(a') CD_3 symmetric deformation (67%), CD bend (21%)
957 bd	957 w, dp	964 vs, A	943	1010	ν_{14}(a'') CD antisymmetric bend (43%), CD_3 rock (26%), CCl_2 stretch (21%)
			937		?
933	933 m, p		932	872	ν_7(a') CD_3 in-plane rock (45%), CD bend (21%)
818 bd	829 w, dp	829 m, A	819	797	ν_{15}(a'') CD_3 out-of-plane rock (32%), CD bend (56%)
772	774 m, p	775 m, B	776	749	ν_6(a') CD in-plane bend (45%), CD_3 rock (21%), C–C stretch (18%)
649 bd	649 m, dp	650 s?	637	602	ν_{16}(a'') CCl_2 antisymmetric stretch (47%), CD_3 rock (36%), CCl_2 twist (10%)
594	601 vs, p	600 m, B	597	595	ν_9(a') CCl_2 symmetric stretch (64%), CD_3 rock (22%), CCl_2 scissor (10%)
484 bd	483 vw, p				?
369	372 s, p	368	366	365	ν_{10}(a') CCl_2 wag (59%), CCl_2 stretch (12%)
358					"Hot band"
342					"Hot band"
272	275 m, dp (shoulder)		283	292	ν_{17}(a'') CCl_2 twist (62%), CCl_2 stretch (32%)
264	271 s, p		276	267	ν_{11}(a') CCl_2 scissor (71%)
			196	198	ν_{18}(a'') CD_3 torsion (98%)

[a] Abbreviations used in this table are identical with those in Table I.

respectively. The 704-cm^{-1} band has a distorted type A contour, whereas the 650-cm^{-1} band gives rise to a very strong polarized Raman line. These bands are shifted to 594 and 650 cm^{-1} in the spectrum of the heavy molecule. There are three other low lying vibrational modes expected for the CCl_2 group; these are the CCl_2 wag (a'), the CCl_2 twist (a''), and the CCl_2 scissor (a'). The two a' modes, ν_{10} and ν_{11}, are readily identified from the Raman spectrum as strong bands at 405 and 275 cm^{-1}, respectively. The twisting motion, ν_{17}, is assigned to a depolarized line of medium intensity at 319 cm^{-1}. On deuteration, ν_{10} shifts to 369 cm^{-1}, while ν_{11} shifts to 264 cm^{-1}. The CCl_2 twist, ν_{17}, is assigned to a band at 272 cm^{-1} which appears as a high-frequency shoulder on ν_{11} for the heavy compound.

With this vibrational assignment along with that given for the torsional mode in the next section, the Teller–Redlich product rule was found to be satisfied within 3.5% for the a'' symmetry species and 6% for the a' symmetry species. The difference between the experimental and calculated values for the a'' modes is consistent with that expected due to anharmonicity. However, the difference for the a' modes is larger than expected from this effect and may be due to Fermi resonance for which no corrections have been made.

Torsional Mode and Barrier

An inspection of Figure 3B shows a broad, well-defined peak at 196 cm^{-1} in the spectrum of solid CD_3-$CDCl_2$. Since the spectrum was taken at such a low temperature, it is clear that it is not a difference band. Similarly it cannot be ascribed to a lattice mode or a two-phonon process because the band did not show the expected broadening or frequency shift with temperature that is observed for such modes. Thus, it is concluded that this band is the torsional mode since the

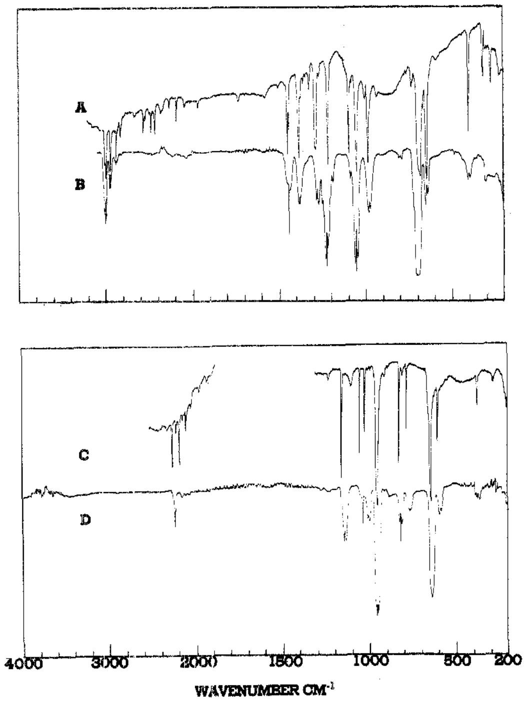

Figure 2. (A) Infrared spectrum of solid CH_3CHCl_2. (B) Infrared spectrum of gaseous CH_3CHCl_2. (C) Infrared spectrum of solid CD_3CDCl_2. (D) Infrared spectrum of gaseous CD_3CDCl_2.

three low-frequency bending modes are confidently assigned to other bands and no other intramolecular fundamental is expected in this frequency range.

From the expected shift factor of 1.414 with deuteration, one predicts the torsional frequency to fall at 277 cm^{-1} in the light compound. Unfortunately, this is very nearly the frequency for the CCl_2 scissor which gives rise to a relatively strong infrared band (see Figure 3A). However, there is evidence for a shoulder on the low-frequency side of this CCl_2 scissoring mode which was measured to be approximately 274 cm^{-1}. The obscurity of this shoulder would certainly account for the fact that the torsional mode has appeared very elusive in previous studies.[4,5] This assignment is then consistent with the recent inelastic neutron work[8] on both the liquid and solid in which the torsional mode was assigned to a band at 293 ± 15 cm^{-1}. Since the neutron study is dependent on the density of states, the agreement is quite satisfactory.

This assignment of the torsion leaves unexplained the band at 232 cm^{-1} previously reported in both the infrared[3] and neutron studies.[8] Since this band was reported in both the infrared spectrum of the gas and low-temperature solid, it cannot be ascribed to a difference tone. Also, it is doubtful that it could have arisen from water vapor leaking into the cell and condensing on the cold silicon plate. The most reasonable explanation seems to be that it arose from an impurity in the sample used in the previous investigations.

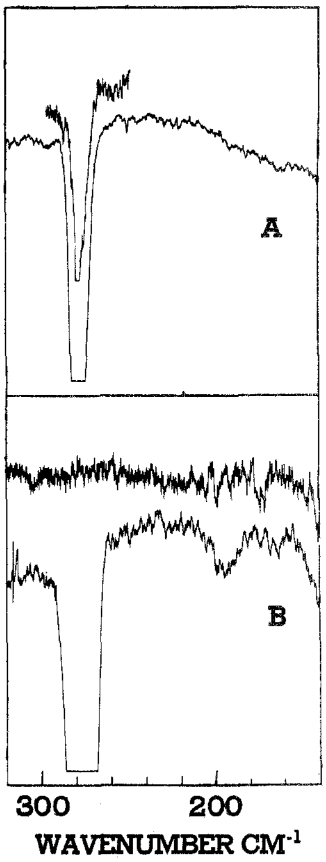

Figure 3. (A) Far-infrared spectrum of solid CH_3CHCl_2. (B) Far-infrared spectrum of solid CD_3CDCl_2.

To calculate the torsional barrier, we have assumed a cosine type potential of the form

$$V(\alpha) = {}^1/_2V_3(1 - \cos 3\alpha)$$

with all terms higher than threefold being considered negligible. The barrier was calculated according to the procedure outlined by Fateley and Miller.[13] The periodic barrier calculated for CD_3CDCl_2 was 4.77 kcal/mol for the solid state.

With this new value of 4.77 kcal/mol for the barrier it is interesting to reconsider the effect of adding chlorine atoms to one "end" of ethane. The addition of one chlorine atom raises the barrier in the solid by 1.24 kcal/mol. The addition of a second chlorine atom *further* raises the barrier in the solid by 0.37 kcal/mol. The addition of a third chlorine atom again raises the barrier by about 0.64 kcal/mol. Although not following a linear relationship the barriers do seem to follow a trend of increasing restriction of the methyl rotation as the chlorine atoms are added. If one assumes nearly equal intermolecular effects for the three chlorine-containing compounds, then it appears that the second chlorine has the smallest effect. This trend is different from that found for the corresponding fluorides where

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[13] W. G. Fateley and F. A. Miller, *Spectrochim. Acta*, **17**, 857 (1961).

the addition of the second and third fluorines to one end of ethane actually lowers the barrier. However, the trend is very similar to the one found for the substitution of a methyl group (see Table III) to one end of ethane. It is not possible to compare the bromide series since the barrier for the 1,1-dibromoethane molecule has not been reported.

Table III: Torsional Barriers (kcal/mol) for Some Chloro-, Fluoro-, and Methyl-Substituted Ethanes

Molecule	Gas	Solid	Reference
CH_3CH_3	2.928	3.24	*a*, *b*
CH_3CH_2Cl	3.71	4.48	*c*, *d*
CH_3CHCl_2		4.77	*e*
CD_3CDCl_2		4.84	*e*
CH_3CCl_3	5.10	5.49	*f*
CD_3CCl_3	5.05	5.41	*f*
CH_3CH_2F	3.33		*g*
CH_3CHF_2	3.18		*h*
CH_3CF_3	3.1	3.29	*f*
$CH_3CH_2(CH_3)$	3.33	3.96	*i*, *j*, *k*
$CH_3CH(CH_3)_2$		3.94	*l*
$CH_3C(CH_3)_3$		4.3	*m*

[a] R. R. Getty and G. E. Leroi, 24th Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, Sept 1969, Paper Q-7. [b] S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 968 (1968). [c] C. M. Player, private communication. [d] R. H. Schwendeman and G. D. Jacobs, *J. Chem. Phys.*, **36**, 1245 (1962). [e] This work. [f] Reference 1; J. R. Durig, M. M. Chen, and Y. S. Li, *J. Mol. Struct.*, in press. [g] G. Sage and W. Klemperer, *J. Chem. Phys.*, **39**, 371 (1963). [h] O. R. Herschbach, *J. Chem. Phys.*, **25**, 358 (1966); W. G. Fateley and F. A. Miller, *Spectrochim. Acta*, **17**, 857 (1961). [i] L. H. Scharpen and V. W. Laurie, Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, June 1965. [j] E. Hirota, C. Matsumura, and Y. Morino, *Bull. Chem. Soc. Jap.*, **40**, 1124 (1967). [k] P. M. Grant, R. J. Pugmire, R. C. Livingston, K. A. Strong, H. L. McMurry, and R. M. Brugger, *J. Chem. Phys.*, **52**, 4424 (1970). [l] J. R. Durig, S. M. Craver, and J. Bragin, *ibid.*, **53**, 3850 (1970). [m] J. R. Durig, S. M. Craven, and J. Bragin, *ibid.*, **52**, 2046 (1970).

Recently Abraham and Parry[14] calculated the internal rotational barriers for a series of halogenated ethane molecules by the summation of all steric and electrostatic interactions between nonbonded atoms plus a torsional term which was directly related to the intrinsic barrier to rotation in ethane. For example, they calculated barriers of 3.78, 4.56, and 5.89 kcal/mol for 1-chloro-, 1,1-dichloro-, and 1,1,1-trichloroethane, respectively. These results agree well with the latest experimental values of 3.71, 4.5, and 5.1 kcal/mol for these respective molecules (See Table III) for the vapor state. It would seem that a similar treatment for the bromo and methyl series would also provide barrier heights in agreement with the experimentally determined values.

Normal Coordinate Analysis

As an aid in making the vibrational assignment, a normal coordinate analysis of CH_3CHCl_2 and CD_3CDCl_2 was undertaken. The calculations were carried out by using the Wilson GF matrix method[15] with computer programs written by Schachtschneider.[16] The G matrix was calculated using assumed structural parameters.[17] Frequencies were given the weight $(1/\lambda)$ in the least-squares procedure. Initial force constants for the CH_3–C group were taken from the published values of Duncan[18] and force constants for the $-CHCl_2$ group were estimated from the work of Dempster and Zerbi.[19] Twelve force constants were adjusted to fit 34 observed frequencies, and the final force field of 18 constants is shown in Table IV. The calculated and observed frequencies for CH_3CHCl_2 and CD_3CDCl_2 are listed in Tables I and II, with an average error of 0.82 and 2.37%, respectively.

Table IV: Internal Force Constants for CH_3CHCl_2[a]

Force constant	Group	This work	CH_3–C group
K_r	C–H_3 stretch	4.86 ± 0.04	4.86
K_R	C–C stretch	4.28 ± 0.20	4.45
F_r	CH_3 str./CH_3 str.	0.07 ± 0.03	0.04
K_d	CH stretch	4.99 ± 0.04	
H_α	∠HCH bend	0.53 ± 0.01	0.55
H_β	∠HCC bend	0.64 ± 0.03	0.64
$F_{R\beta}$	C–C str./∠HCC bend	0.25^b	0.30
F_β	∠HCC bend/∠HCC bend	-0.02^b	−0.02
H_γ	∠CCH bend	0.64 ± 0.04	
H_θ	∠HCCl bend	0.61 ± 0.01	
H	∠CCCl bend	1.46 ± 0.13	
H_δ	∠ClCCl bend	1.05 ± 0.17	
H_τ	CH_3 torsion[c]	0.016^b	
K_X	C–Cl stretch	2.50 ± 0.13	
F_X	CCl/CCl stretch	0.67 ± 0.13	
$F_{X\delta}$	CCl str./∠CCl_2 bend	0.25^b	
F_{RX}	CC str./CCl str.	0.40^b	
$F_{X\theta}$	CCl str./∠HCCl bend	0.20^b	

[a] Stretching force constants in millidynes per ångström; bending constants in millidyne ångström per square radian; stretch–bend interaction constants in millidynes per radian. [b] Fixed during perturbation cycle. [c] Torsional coordinate is defined as the sum of three trans torsions about the C–C bond.

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The PED (potential energy distribution) in Tables I and II reveals several cases of strong mixing between symmetry coordinates, although the exact nature of this mixing is somewhat dependent upon the assumed force field. In particular, the $-CCl_2$ motions are strongly mixed. The resulting force constants show good agreement with the results of Duncan[18] for the CH_3–C group. The C–Cl stretching constant of 2.5 mdyn/Å is somewhat smaller than the value of 3.2 mdyn/Å calculated by Dempster and Zerbi[19] for CH_3CH_2Cl.

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The Crystal Structure of 2,4,6-Trinitroaniline

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The crystal structure of 2,4,6-trinitroaniline, $C_6H_4N_4O_6$, has been determined by X-ray diffraction. The unit cell is monoclinic ($a = 6.137$, $b = 9.217$, $c = 15.323$ Å, $\beta = 99.67°$), space group $P2_1/c$ with four molecules per cell. The 2-, 4-, and 6-nitro groups are rotated 22.5, 4.0, and 8.5°, respectively, out of the plane of the benzene ring. This noncoplanarity and the type of intermolecular hydrogen bonding found in the structure of trinitroaniline are different than in the previously reported structures of diaminotrinitrobenzene and triaminotrinitrobenzene.

Introduction

The crystal structure of 2,4,6-trinitroaniline (TNA) has been determined by single-crystal X-ray diffraction techniques as part of a study of the molecular conformations and hydrogen bond networks present in nitroaromatic amines. The structure completes the set of primary amines of *sym*-trinitrobenzene, because the structures of 1,3-diamino-2,4,6-trinitrobenzene (DATB)[1] and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)[2] have been reported. These two compounds crystallize as planar molecules joined by intermolecular hydrogen bonds in which an amine group bonds to both oxygen atoms of the same nitro group of an adjacent molecule.

In contrast, 4-nitroaniline[3] and 2,3,4,6-tetranitroaniline (TENA)[4] form intermolecular hydrogen bonds in which the amine group is bound to oxygen atoms from two different molecules.

The cell dimensions and space group of 2,4,6-trinitroaniline have been reported as $a = 6.02$, $b = 9.30$, $c = 15.3$ Å, $\beta = 99.2°$ (converted from kX units), $P2_1/c$[5] and the density as 1.762 g/cm^3.[6] The values obtained in this study agree adequately with these early reports.

Experimental Section

Suitable crystals of 2,4,6-trinitroaniline were grown from a commercial sample[7] by evaporation of an ethyl acetate solution. Cell dimensions and reflection intensities were determined from the same 0.30 × 0.40 × 0.49 mm crystal. After preliminary examination by Weissenberg and precession methods, this crystal was aligned on a Picker FACS-1 computer-controlled automatic diffractometer equipped with a lithium fluoride monochromator. The following monoclinic cell dimensions were obtained from a least-squares fit of the diffraction angles of 12 strong reflections using 0.70926 Å as the wavelength of Mo Kα radiation: $a = 6.137 \pm 0.003$, $b = 9.217 \pm 0.007$, $c = 15.323 \pm 0.007$ Å, $\beta = 99.67 \pm 0.02°$. These values give a calculated density

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