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Vibrational studies and *ab initio* calculations of the conformers of 1,2-dichloro-1,1,2-trifluoro-2-iodoethane

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Abstract

Infrared and Raman spectra of 1,2-dichloro-1,1,2-trifluoro-2-iodoethane have been recorded at ambient and sub-ambient temperatures. Tentative assignments of bands have been made. The energy difference between the conformers has been determined from the temperature dependence of the infrared spectral bands using the van't Hoff equation. The molecule has also been studied by *ab initio* molecular orbital calculations using an all-electron basis set as well as two basis sets employing effective core potentials. The calculated energy differences between the two conformers were found using MP2 single-point calculations with the geometry from the all-electron calculation. These computational results are in agreement with the experimental results.

Introduction

The rotational mobility of a polymer chain is an important determinant of viscosity [1]. The torsional barriers around the several bonds in a polymer chain influence the rotational mobility. Thus, a better understanding of the structural features influencing torsional barriers will lead to a better understanding of the determinants of viscosity. 1,2-Dichloro-1,1,2-trifluoro-2-iodoethane is a molecule which has a torsional barrier influenced by bulky moieties, but without the complicating factors which are introduced by additional fluorocarbon groups. Presented here is a spectroscopic and computational study of this molecule, which has three equilibrium conformers and three transition states, all having different energies.

Experimental

1,2-Dichloro-1,1,2-trifluoro-2-iodoethane ($CF_2ClCFClI$) was purchased from PCR, Inc. As reported [2], it was contaminated with *c.* 15% $CFCl_2CF_2I$.

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Using a GC/FTIR instrument equipped with a 20 m Carbowax capillary column, the former elutes at 1.28 min and the contaminant at 1.07 min. The desired material was obtained by three successive separations using preparative GC methods. The purity of the final sample was found by GC/FTIR to be in excess of 99.9%.

Infrared spectra were recorded using a Perkin-Elmer 1750 FTIR spectrometer in the 4000–400 cm^{-1} range at 1 cm^{-1} resolution. A KBr beam splitter and a DTGS detector were used and each spectrum was an average of 20 accumulated scans. Low-temperature spectra were obtained as a thin film on CsI plates held by a liquid-nitrogen-cooled Spectra Tech sample holder. The lowest temperature attained was -120 °C.

Far-IR spectra from 500–50 cm^{-1} were obtained by using a Nicolet 70 SX FTIR system equipped with a 6.25 mm Mylar beam splitter and a polyethylene–DTGS detector. The resolution was set at 2 cm^{-1} and a typical run involved the accumulation of 32 scans.

GC/FTIR chromatograms and spectra were from a Hewlett-Packard 5965A infrared detector coupled to a 5890 gas chromatograph. A KBr beam splitter and a wideband MCT detector were used.

The Raman system used was a Spex 1401 double monochromator instrument. Laser excitation at 514.5 nm was provided by a Spectra Physics 165 argon ion laser. The laser power used was about 15 mW. The low temperature was obtained by passing the vapor from liquid nitrogen boiloff past a capillary tube in which the sample was sealed.

Ab initio molecular orbital calculations were performed using Gaussian 90 [3] on a Cray X-MP/216 computer. The geometry of the molecule was defined in terms of the position of the atoms on the asymmetric carbon atom relative to the lone chlorine atom of the chlorodifluoromethyl group, shown in Fig. 1. Thus, the equilibrium structures are named *trans*(I–Cl),

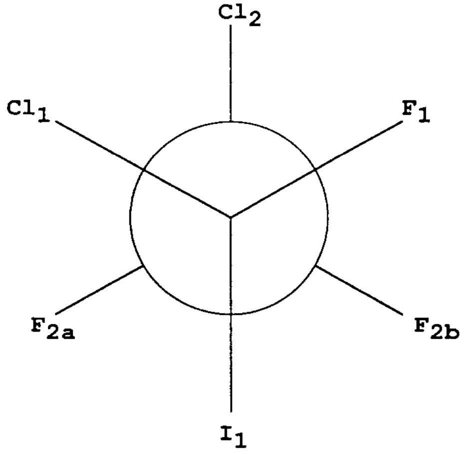

Fig. 1. Defining projection of 1,2-dichloro-1,1,2-trifluoro-2-iodoethane.

trans(Cl–Cl) and *trans*(F–Cl). Likewise, for simplicity, the three transition states are named *cis*(I–Cl), *cis*(Cl–Cl) and *cis*(F–Cl).

All of the equilibrium and transition state geometries were first optimized employing a minimal basis set having an effective core potential (LANL1MB) [3]. This geometry was then used as the input for an optimization with a basis set having an effective core potential plus double zeta valence orbitals (LANL1DZ) [3]. In turn, calculations were completed with the LANL1DZ basis set augmented by d-orbitals [4], and with an all-electron basis set having polarization functions on carbon and fluorine atoms [5]. The basis set was contracted as follows: C and F, (10s5p1d)/[3s2p1d]; Cl, (13s9p1d)/[6s4p1d]; and I, (16s13p8d)/[6s5p3d]. Single-point second-order Moeller–Plesset correlation energy calculations were performed with the LANL1DZ and the all-electron basis sets. Harmonic frequencies and IR and Raman intensities were analytically calculated with the all-electron basis set.

Results and discussion

Vibrational studies

Only the lowest symmetry element, C_1, is present in $CF_2ClCFClI$. All 18 fundamentals belong to the A species and should be infrared and Raman active. The liquid-phase infrared spectrum at room temperature is shown in Fig. 2. The far-infrared spectrum is shown in Fig. 3. The Raman spectrum of the liquid phase at room temperature is shown in Fig. 4. Table 1 lists the observed vibrational bands and their tentative assignments.

Based on the *ab initio* calculations, the *trans* (I–Cl) structure has the lowest energy of the three conformers. Therefore, the population of the *trans*(I–Cl) species is expected to be greater than the other two conformers.

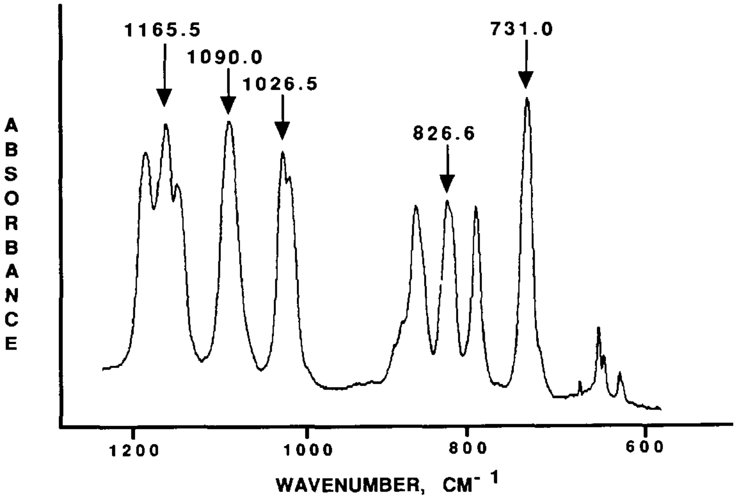

Fig. 2. Infrared spectrum of $CF_2ClCFClI$.

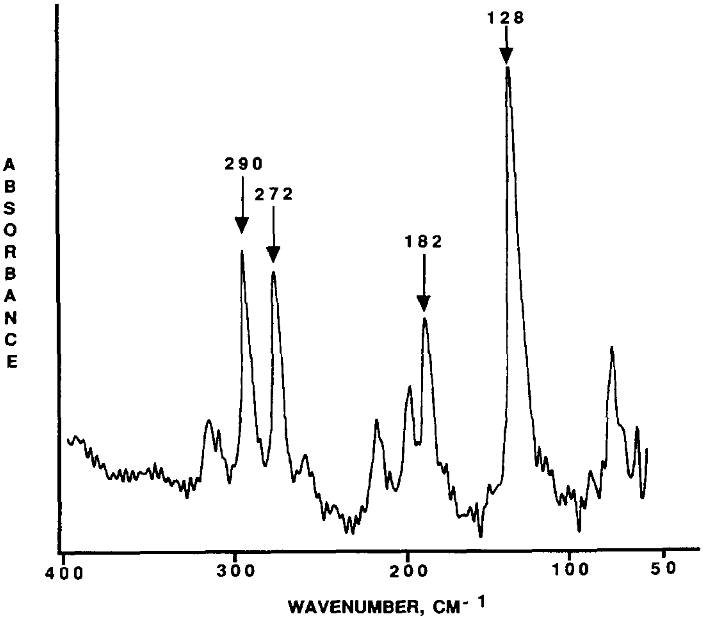

Fig. 3. Far-infrared spectrum of $CF_2ClCFClI$.

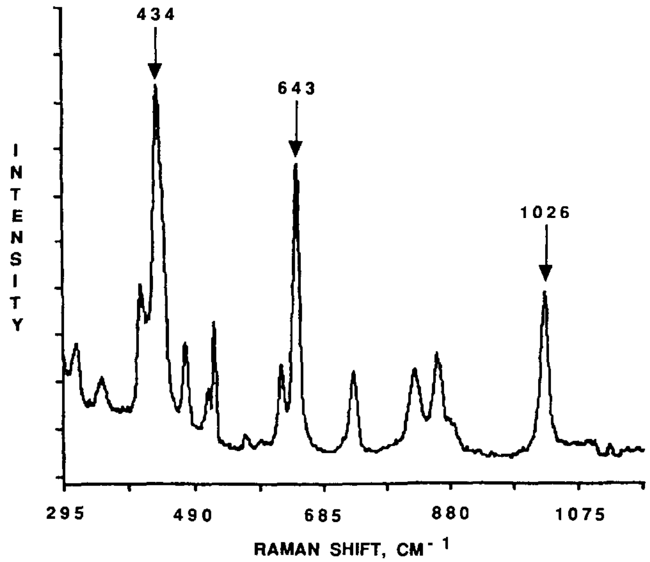

Fig. 4. Raman spectrum of $CF_2ClCFClI$.

The energy difference between the *trans*(Cl–Cl) and *trans*(F–Cl) species is small and so the temperature variation technique used cannot differentiate between the conformers. Consequently, the energy difference determined

TABLE 1

Raman and infrared frequencies and tentative assignments

Raman (liquid) (cm^{-1})		IR (liquid) (thin film) (cm^{-1})		Computational (cm^{-1})	Assignments	
		1189.6	vs	1241.0	1	$\nu_s(CF_2)$
				1238.8		
				1234.8		
		1165.5	vs	1229.1	2	$\nu_{as}(CF_2)$
		1151+	vs	1226.4		$\nu_{as}(CF_2)$
				1214.3		
		1090	vs	1141.0	3	$\nu(CF)$
				1138.0		
				1122.9		
1026	w	1026.5	vs	1065.2	4	$\nu(C - C)$
		1017.5−	vs	1063.9		$\nu(C - C)$
				1052.3		
860	vw	864.6	s			731+127
825	vw	826.6	s	879.5	5	$\delta(CF_2)$
		822−	s	848.6		$\delta(CF_2)$
				875.9		
		792	s	741.4	6	$\nu(C - Cl)$
				794.2		
				838.7		
731	vw	731	vs	639.9	7	$\nu(C - Cl)$
				632.7		
				611.4		
643	m	646+	m	503.0	8	$\nu(C - I)$
		639−	w	503.7		$\nu(C - I)$
				466.5		
618	w	620−	w			
518	w					
		510.5	vw			
505	vw					
475	vw	477+	vw	436.3	9	$\delta(CF_2)$
		473	vw	435.2		
				437.8		
		445	vw	429.8	10	$\delta(C - F)$
		412.1				
		418	vw	343.0	11	$\delta(FCC)$
409	w	411+	vw	353.5		
				346.3		
		314	vvw	309.7	12	$\delta(FCC)$
				288.5		
				307.1		
352	vw					
313	vw					
		290	vw	273.3	13	$\delta(ClCF)$
				266.9		
				289.7		

(*continued*)

TABLE 1 (*continued*)

Raman (liquid) (cm^{-1})		IR (liquid) (thin film) (cm^{-1})		Computational (cm^{-1})	Assignments	
269	m	272	vw	207.4	14	δ(ICF)
				255.9		
				252.9		
256	m					
204	s	213	vvw	201.2	15	δ(ClCC)
				190.0		
				189.5		
		182	vvw	182.2	16	δ(ICC)
				180.8		
				167.4		
185	w					
		127	vw	124.9	17	δ(ICCl)
				119.2		
				121.2		
		70	vvw	64.8	18	τ(C − C)
				66.1		
				69.9		

experimentally was equated to the difference between the *trans*(I–Cl) conformer and the *trans*(Cl–Cl) conformer which, according to computational results, has a lower energy than the *trans*(F–Cl) conformer. The experimental confirmation of the energy difference between the *trans*(Cl–Cl) and *trans*(F–Cl) conformers is not presently accessible.

The assignment of most of the fundamentals follows closely the work of Klaeboe *et al.* [6] with $CF_2ClCFCl_2$ and CF_2ICF_2I and the work of Kalasinsky *et al.* [7] with CF_2HCFH_2 and CF_2HCF_2H.

As in most of the halogen-substituted ethanes, there are no important bands located in the region 4000–1400 cm^{-1}, except some overtone bands shown at *c.* 2100 cm^{-1}. Between 1300 and 1000 cm^{-1}, four fundamentals are expected. The 1189 cm^{-1} band was assigned to the symmetric stretching mode for the CF_2 group in the *trans*(I–Cl) and *trans*(Cl–Cl) conformers. Because the 1151 cm^{-1} band gained intensity at −120 °C, it was attributed to the antisymmetric modes for the *trans*(I–Cl) conformer, with the 1165 cm^{-1} band assigned to the corresponding vibration of the *trans*(Cl–Cl) conformer. The band at 1090 cm^{-1}, showing no intensity variation at low temperature, was assigned to CF stretching of both conformers. The doublet at 1026 and 1017 cm^{-1} was attributed to the C−C stretching mode for *trans*(I–Cl) and *trans*(Cl–Cl), respectively, because the intensity of the 1017 cm^{-1} band decreased at a temperature of −120 °C. In CF_2ICF_2I [6], this stretching mode was assigned to a band at *c.* 974 cm^{-1}. A strong band at 1026 cm^{-1} in the Raman spectrum supports the proposed assignment because the C−C stretching vibration is usually a strong scatterer. In preliminary normal-coordinate calculations, the CF_2 and CF stretches were found to be highly mixed with the C—C stretch, as described in the literature. Because of the weak scattering of CF_2 and CF stretching modes, they were not observed in the Raman spectra.

For most of the CF_2XCF_2X molecules, where X=Cl, Br, I, there are three bands or fewer in the region between 1000 and 700 cm^{-1}. However, in $CF_2ClCFClI$, four bands at 864, 826, 792 and 731 cm^{-1} were present. The 'extra' band was a problem in the band assignment. The 864 cm^{-1} band was tentatively assigned as a combination band of two fundamentals at 731 and 127 cm^{-1}. Fermi resonance [8] is proposed to occur between 864 and 826 cm^{-1} bands. The intensity 'borrowing' for the 864 cm^{-1} from the 826 cm^{-1} fundamental is apparent. The proposed scheme is depicted in Fig. 5.

The 826 cm^{-1} band was assigned to the bending mode of the CF_2 group. In the case of CF_2ICF_2I, this mode was assigned to a band at 835 cm^{-1} for the gauche conformer [7]. Following the assignment of bands in $CF_2ClCFCl_2$, the 792 and 731 cm^{-1} bands were attributed to the C—Cl stretches [9].

Below 650 cm^{-1} the IR bands are generally of low intensity, and so a thicker film was needed to obtain a good quality spectrum. The doublet at 646 and 639 cm^{-1} showed a clear temperature variation, displayed in Fig. 6, and was used to calculate the experimental energy difference between the two conformers (*vide infra*). These bands were assigned to the C—I stretching modes for the *trans*(I–Cl) and *trans*(Cl–Cl) conformers, respectively. At low temperatures, the 620 cm^{-1} band decreased in intensity concomitantly with the 639 cm^{-1} band. It was tempting to assign it to the C—I stretching mode for the third conformer, *trans*(F–Cl). However, the triplet pattern at 646, 639 and 620 cm^{-1} did not appear elsewhere in the spectrum, making this assignment doubtful. Consequently, the 620 cm^{-1} band was left unassigned. The possible assignments for the rest of the lower frequencies are listed in Table 1.

Preliminary normal-coordinate calculations show that the mode mixing is severe in the low-frequency band, similar to the high frequency region. Therefore, the tentative assignments given are largely based on group frequency comparisons with compounds such as CF_2ICF_2I and $CF_2ClCFCl_2$.

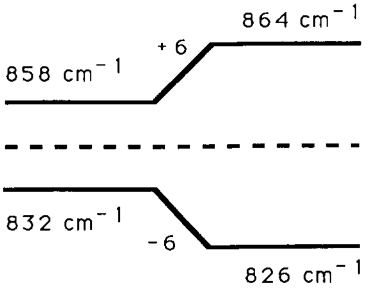

Fig. 5. Fermi resonance diagram for 864 cm^{-1} and 826 cm^{-1} bands.

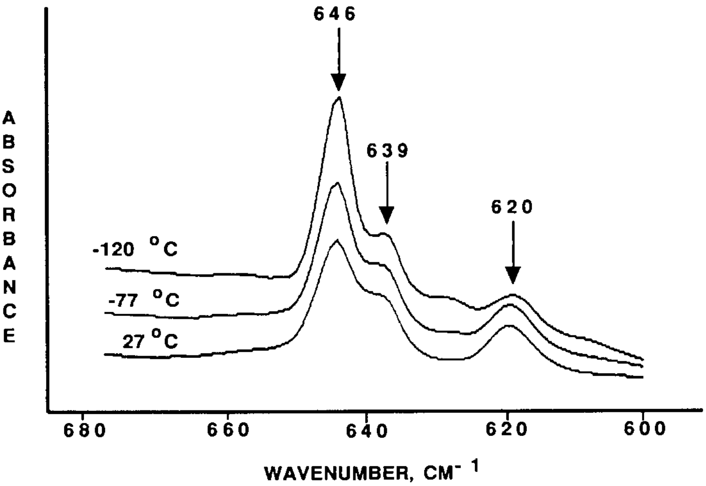

Fig. 6. Variation of the relative intensities of the infrared bands with temperature.

Conformation studies

As previously discussed, the energy differences between the three conformers are small. The band intensity variation at low temperatures is less obvious than is the case with the highly symmetric molecule, CF_2ICF_2I [6]. Nevertheless, five pairs of bands, 1026 and 1019, 827 and 822, 646 and 639, 445 and 436, and 417 and 412 cm^{-1}, did show some intensity variation at low temperatures for the thin film samples. This variation was not observed in the vapor-phase spectra. At lower temperatures, the bands of the more stable conformer, *trans*(I–Cl), should increase in intensity. Those bands that gained intensity at −120 °C are marked with a '+' next to the frequency in Table 1 and are assigned to the *trans*(I–Cl) species. The band contours at low temperature return to their room-temperature patterns as the samples are gradually warmed. The change in the intensity pattern is a totally reversible process. This confirms that the band intensity variations are due to the interconversion between conformers induced by temperature changes. The average separation for *trans*(I–Cl) and *trans*(Cl–Cl) conformers is *c.* 7 cm^{-1}. Also given in Table 1 are the calculated vibrational frequencies for all the *trans*(I–Cl), *trans*(Cl–Cl) and *trans*(F–Cl) conformers, obtained using the all-electron basis set. These frequencies have been multiplied by 0.9 to account for corrections due to anharmonicity and electron correlation. The calculated frequencies for the higher energy vibrations are found to be higher than the experimental values. At lower energies, the calculated frequencies are lower than the experimental values. This same behavior was observed for 1,1,2-trichloro-1,2,2-trifluoroethane [10].

Using the intensity variation of the doublet at 646 and 639 cm^{-1}, and the van't Hoff equation

$$\frac{A_{trans(\text{I–Cl})}}{A_{trans(\text{Cl–Cl})}} = \text{C}\exp(-\Delta H^0/\text{R}T)$$

the experimental energy difference can be calculated. The constant, C, is a function of the entropy difference and the relative molar absorptivities of the two conformers, $A_{trans(\text{I–Cl})}$ and $A_{trans(\text{Cl–Cl})}$ are absorbances for the respective conformer bands and T is the absolute temperature. Figure 7 shows the plot of $\ln\{A_{trans(\text{I–Cl})}/A_{trans(\text{Cl–Cl})}\}$ against $1/T$, where the temperatures are 27 °C, −77 °C and −120 °C. From the slope of the straight line, the energy difference was found to be 0.33 kcal mol^{-1} (1 kcal = 4.184 kJ). In other words, the *trans*(I–Cl) conformer is more stable than the *trans*(Cl–Cl) by 0.33 kcal mol^{-1} in the liquid state. This value is in agreement with the calculated value of 0.6 kcal mol^{-1}. Ordinarily, one would use the integrated intensities rather than peak heights when applying the observed data to the van't Hoff equation. However, Bernstein [11] and Kagarise and Paasch [12] have pointed out that in the case of CH_2ClCH_2Cl and CF_2BrCF_2Br there are no significant differences between the results obtained with integrated intensities or peak heights. Consequently, peak-height measurements were adopted for this investigation.

The solvent-variation technique [13] was also employed to attempt identification of the spectral bands of the conformers. In this technique, polar solvents are found to enhance the fundamental bands of the more polar conformers. Three solvents of varying polarity, hexane, benzene and DMSO, were used. Concentrations were kept as low as possible, and in no case exceeded 0.1 mol l^{-1}. Spectra of the solutions were obtained using 0.015 or 0.025 mm KBr liquid cells. Bands at 1166 and 1091 cm^{-1} in neat samples shifted to 1162 and 1085 cm^{-1} respectively, in benzene solution. As expected, only the C—F stretching modes showed solvent effects because

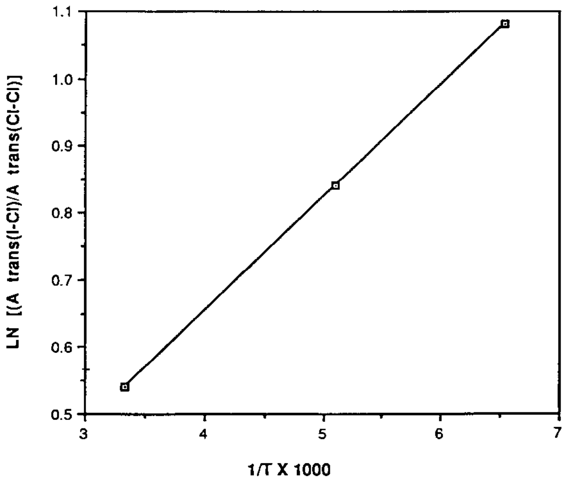

Fig. 7. Plot of $\ln\{A_{trans(\text{I–Cl})}/A_{trans(\text{Cl–Cl})}\}$ versus $1/T$.

TABLE 2

Calculated conformational energies

Basis set	Conformer					
	trans(I–Cl)	*trans*(Cl–Cl)	*trans*(F–Cl)	*cis*(I–Cl)	*cis*(Cl–Cl)	*cis*(F–Cl)
Total energies (Hartrees)						
LANL1MB	−409.44786	−409.44844	−409.44232	−409.43410	−409.43410	−409.43422
LANL1DZ	−414.50334	−414.50180	−414.50058	−414.48467	−414.48720	−414.49107
LANL1DZ(d)	−414.70525	−414.70423	−414.70349	−414.68691	−414.68860	−414.69142
LANL1DZ/MP2	−415.85831	−415.85744	−415.85698	−415.84116	−415.84283	−415.84486
All-electron	−8206.01486	−8206.01372	−8206.01316	−8205.99632	−8205.99791	−8206.00092
All-electron/MP2	−8207.21911	−8207.21814	−8207.21767	−8207.20176	−8207.20304	−8207.20616
Relative energies (kcal mol^{-1})						
LANL1MB	0.36	0	3.84	9.00	9.00	3.27
LANL1DZ	0	0.96	1.73	11.72	10.13	7.70
LANL1DZ(d)	0	0.64	1.10	11.50	10.44	8.68
LANL1DZ/MP2	0	0.54	0.84	10.76	9.72	8.44
All-electron	0	0.72	1.07	11.64	10.64	8.75
All-electron/MP2	0	0.61	0.91	10.89	10.08	8.13

the C—F bond has a stronger dipole than the C—Cl and C—I bonds. The shift observed was not large enough for the identification of the conformers. This supports the conclusion that the energy barrier between these conformers is small.

Computational studies

Calculated total and relative energies of the three equilibrium conformers and the three transition states are given in Table 2. The relative energies are plotted in Fig. 8. It is seen that the results using the minimal basis set were inconsistent with those using the other basis sets. Most importantly, the finding that the lowest energy equilibrium conformer has *trans*-chlorine atoms, leaving the bulky iodine atom in a gauche position relative to the vicinal chlorine, was intuitively unreasonable as well as being inconsistent with the other results. As shown in Fig. 9, the variation in the dipole moments calculated with the several basis sets also shows the minimal basis set results to be inconsistent.

Zero-point vibrational energies [*ZPVE*] and thermal contributions to the enthalpy [$H(T)-H(0)$], calculated from scaled frequencies using standard formulae [14], are given in Table 3. The net corrections to the *trans*(Cl–Cl) and *trans*(F–Cl) equilibrium conformations are small (-0.01 kcal mol^{-1}), but larger for the transition states (-0.78 to -0.88 kcal mol^{-1}).

The geometrical parameters calculated for the three equilibrium structures and transition states using the all-electron basis set are given in Table 4. Bond lengths, angles and the torsion angle calculated with the LANL1DZ

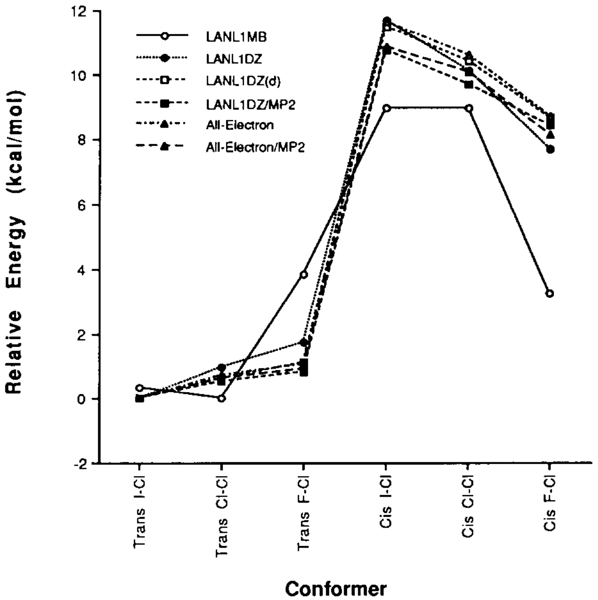

Fig. 8. Variation in calculated relative energies with various basis sets.

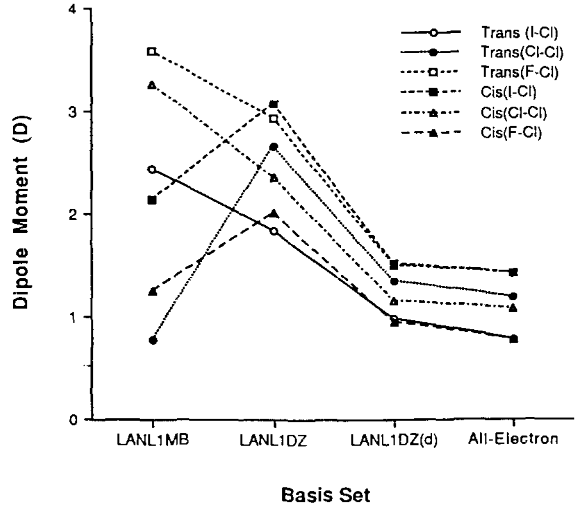

Fig. 9. Variation in computed dipole moments with various basis sets.

TABLE 3

Thermodynamic factors[a]

Quantity	Conformer					
	trans(Cl–Cl)	*trans*(F–Cl)	*trans*(I–Cl)	*cis*(I–Cl)	*cis*(Cl–Cl)	*cis*(F–Cl)
ZPVE	14.30	14.31	14.31	14.17	14.21	14.22
$H(T)-H(0)$	5.87	5.86	5.87	5.29[b]	5.27[b]	5.27[b]
$\Delta[ZPVE]$	−0.01	0.00	0.00	−0.15	−0.10	−0.09
$\Delta[H(T)-H(0)]$	−0.00	−0.01	0.00	−0.73	−0.70	−0.69
Net correction	−0.01	−0.01	0.00	−0.88	−0.80	−0.78

[a] Quantities have been calculated using frequencies scaled by 0.90. They are given at 298.15 K in units of kcal mol^{-1}.

[b] The torsional motion at the barriers was treated as free rotation.

basis set augmented with polarization functions on all elements gave results that are in excellent agreement with the all-electron basis set. Average bond lengths agree to within 0.2% and bond angles are within 0.02% of the all-electron calculation. Without the polarization functions the averages differ by 2.6% for bond lengths and 0.3% for bond angles.

It is seen in Table 4 that the C—F bond lengths are quite insensitive to changes among the equilibrium and transition-state conformations. They do show the expected shortening with an increasing fluorine substitution on carbon with the average $R(\text{CF}_2)$ 1.3 pm shorter than $R(\text{CF}_\text{I})$. The C—Cl bond for the chlorine of the chlorodifluoro group is also insensitive to the conformation and its average length is also slightly shortened (0.3 pm) relative to that seen in the CFClI group. The C—Cl bond length for the chlorine on the asymmetric carbon is more variable and, along with the C—I bond length,

TABLE 4

Structural parameters calculated using all-electron basis set[a]

Parameter	Conformer					
	trans(I–Cl)	*trans*(Cl–Cl)	*trans*(F–Cl)	*cis*(I–Cl)	*cis*(Cl–Cl)	*cis*(F–Cl)
$R(\mathrm{CC})$	155.2	155.4	155.5	160.1	159.8	159.3
$R(\mathrm{CF_1})$	133.0	133.0	133.3	133.2	133.1	133.0
$R(\mathrm{CF_{2a}})$	131.6	131.9	131.9	131.7	131.9	131.7
$R(\mathrm{CF_{2b}})$	131.9	131.7	131.9	131.7	131.7	143.7
$R(\mathrm{CCl_1})$	175.7	176.2	175.7	176.4	175.9	176.1
$R(\mathrm{CCl_2})$	175.7	175.6	175.3	175.6	175.6	175.7
$R(\mathrm{CI})$	217.0	216.4	216.3	217.2	217.6	217.5
$\angle\mathrm{CCF_1}$	107.2	107.2	105.3	106.2	106.4	109.1
$\angle\mathrm{CCF_{2a}}$	109.8	108.5	108.3	107.4	110.3	110.5
$\angle\mathrm{CCF_{2b}}$	108.6	109.7	108.1	110.2	107.5	110.6
$\angle\mathrm{CCCl_1}$	110.9	109.0	110.7	110.4	114.1	110.9
$\angle\mathrm{CCCl_2}$	112.3	112.6	114.2	116.4	116.1	112.3
$\angle\mathrm{CCI}$	110.7	112.7	112.7	117.1	112.7	112.8
$\angle\mathrm{F_1CCl_1}$	109.0	108.4	108.3	107.4	107.0	107.2
$\angle\mathrm{F_1CI}$	108.1	108.8	107.8	105.9	106.8	106.4
$\angle\mathrm{Cl_1CCI}$	110.8	110.6	111.7	109.2	109.4	110.1
$\angle\mathrm{F_{2a}CF_{2b}}$	108.2	108.1	107.4	107.3	107.1	106.5
$\angle\mathrm{F_{2a}CCl_2}$	109.4	108.3	109.4	108.0	107.3	108.5
$\angle\mathrm{F_{2b}CCl_2}$	108.3	109.6	109.2	107.3	108.3	108.3
$\Phi\mathrm{ICCCl_2}$	180.2	−62.8	59.0	−0.8	117.2	−120.6

[a] Bond lengths in pm and angles in degrees.

is generally longer for the transition-state structures than for the equilibrium structures. The greatest impact of conformation is on the C—C bond where the average bond length for the transition state structures is seen to be 4.4 pm longer than that for the equilibrium structures. Bond angles are seen to change in a predictable manner with the atoms eclipsing the more bulky chlorine and iodine atoms in the various transition states bending away from the C—C bond axis.

Conclusions

Results of infrared spectral studies of 1,2-dichloro-1,1,2-trifluoro-2-iodoethane show a separation of 0.33 kcal mol^{-1} between the lowest energy conformer, *trans*(I–Cl) and what is expected to be the *trans*(Cl–Cl) conformer. Fundamentals were tentatively assigned for these conformers. The energy separation between the *trans*(Cl–Cl) and the *trans*(F–Cl) conformers was too small to be observed with the techniques employed in this study.

The energy difference between the *trans*(I–Cl) and *trans*(Cl–Cl) conformers from *ab initio* calculations was found to be 0.6 kcal mol^{-1}. The calculated energy difference between the *trans*(I–Cl) and *trans*(F–Cl) conformers was 0.9 kJ mol^{-1}.

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