

## Conformational Analysis. XVI. The Structure of 1,3-Difluoropropane (CH<sub>2</sub>F)<sub>2</sub>CH<sub>2</sub> as Determined by Electron Diffraction and Vibrational Spectroscopy and Compared with Molecular Mechanics Calculations

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Gaseous 1,3-difluoropropane was studied at a nozzle temperature of 20 °C. Infrared spectra were obtained of the vapour, of a solution, and of the unannealed and annealed solid from 4000 to 30 cm<sup>-1</sup>. Raman spectra of the liquid, including polarization measurements, of the sample in solvents of different polarity, and of the unannealed and annealed solid were recorded.

The compound is shown to exist with the following ratio of conformational abundance in the vapour phase: *GG*(63), *AG*(27), *GG'*(10). These values are compared with those calculated by molecular mechanics. The dominant *GG* conformer is also shown to be the one which persists in the crystalline state.

A complete vibrational assignment for the *GG* conformer and a partial one for the *AG* conformer are proposed, backed by a simple normal coordinate analysis. A comparison is made between the torsional modes observed in the infrared spectra and those predicted from the normal coordinate calculations.

Although 1,3-difluoropropane (DFP) was first prepared more than 30 years ago,<sup>1</sup> only three previous articles dealing in any way with its structure have appeared. Assuming that only staggered conformations are possible, four spectroscopically distinguishable forms are possible: *AA*, *AG*, *GG* and *GG'*; these are shown in Fig. 4 of Ref. 2.

In the only experimental work done previously, Lere-Porte, Petrisans and Gromb, in a study of the

infrared spectra of some polyhalogenopropanes in the region 1400–1500 cm<sup>-1</sup>, assigned two CH<sub>2</sub> scissoring modes, one to the *AG* and the other to the *GG* conformer.<sup>3</sup>

Meyer, using molecular mechanics calculations, predicted populations in CCl<sub>4</sub> solution as follows: *GG* (31%), *AG* (45%), *GG'* (17%) and *AA* (7%).<sup>4</sup>

Lere-Porte and Petrisans also performed CNDO/2 and PCILO calculations from which they concluded that the conformational energies of *GG*, *AG* and *AA* are approximately equal while *GG'* is about 1 kcal/mol higher in energy.<sup>5</sup>\* Essentially the same order of energies was obtained from Meyer's molecular mechanics calculations.<sup>4</sup>

In these laboratories we have long been involved in the study of the conformational behaviour of halogenated propanes. This work follows most closely our earlier studies of other 1,3-dihalogenated propanes. By electron diffraction, conformer *GG* was shown to be favoured in the vapour phase in both 1,3-dichloro-<sup>6</sup> and 1,3-dibromopropane:<sup>7</sup>

$$\begin{aligned} E(AG) - E(GG) &\approx 1.0 \text{ kcal/mol} \\ E(AA) - E(GG) &\approx 1.5 \text{ kcal/mol} \\ E(GG') - E(GG) &\approx 3.0 \text{ kcal/mol} \end{aligned}$$

Following earlier studies by Sheppard and co-workers,<sup>8</sup> 1,3-dichloro-, 1,3-bromochloro-, 1,3-dibromo-, and 1,3-diiodopropane were shown to crystallize at low temperature exclusively in the *GG*

\* 1 kcal = 4.184 kJ.

conformation by the use of infrared and Raman spectroscopy.<sup>2</sup> In this work it was also shown that the dibromo compound crystallized at high pressure as a *GG* conformer, but that the diiodo compound crystallized in the *AA* conformation.

Another compound in which the same conformational possibilities exist is 1,1,3,3-tetrachloropropane. This compound not only crystallizes in the *GG* conformation, but no detectable amounts of any other conformer were found in the vapour or liquid states.<sup>9</sup>

Relevant also to this study is our earlier work on 1,2,3-trichloro- and 1,2,3-tribromopropane. In both of these compounds the dominant form in the vapour phase was a conformer analogous to that dominant in the 1,3-dihalopropanes;<sup>10,11</sup> this form persisted in the crystalline solid in both cases.<sup>12</sup>

## EXPERIMENTAL

The sample used for electron diffraction (ED) was provided by W. Lüttke and J. Zeitzling of the University of Göttingen and had a purity of *ca.* 99%. That used for the spectroscopic measurements was prepared in the laboratories in Oslo, purified by gas chromatography, and had a purity in excess of 99%.

ED-diagrams were recorded with the Balzers apparatus<sup>13,14</sup> at a nozzle temperature of 20 °C. Two sets of plates were obtained: *Set 1* (5 plates, electron wavelength 0.05858 Å, nozzle-to-plate distance 500.12 mm) and *set 2* (6 plates, 0.05858 Å, 250.12 mm). The electron wavelength was determined by calibration against TlCl and

benzene.<sup>15</sup> The data were treated in the usual way<sup>16</sup> to yield an intensity curve for each plate. Average curves for each set of distances were formed. A composite curve was then made by connecting the two average curves after scaling. The final experimental intensity curve is shown in Fig. 1. The intensities have been modified by  $s\{|f'_F|/|f'_C|}\}^{-1}$ . Scattering amplitudes ( $f'$ ) were calculated by the partial-wave method<sup>17</sup> using Hartree-Fock atomic potentials.<sup>18</sup> The radial distribution (RD) curves<sup>16</sup> are shown in Fig. 2.

The infrared spectra were recorded with a Perkin-Elmer model 225 spectrometer (4000–200  $\text{cm}^{-1}$ ) and with a Bruker fast scan Fourier transform spectrometer model 114 C (4000–30  $\text{cm}^{-1}$ ). Beamsplitters of germanium on KBr and of Mylar (3.5, 6, 12 and 24  $\mu$  thickness) were employed in the mid- and far infrared regions, respectively.

Vapour cells of 10 cm (CsI windows) and 20 cm path lengths (polyethylene windows) were used with pressures ranging from 6 to 130 Torr. Conventional sealed cells with KBr windows were used for the carbon tetrachloride solution of the sample, while vacuum tight cells with polyethylene windows were employed below 600  $\text{cm}^{-1}$ . Spectra of the unannealed and annealed solid were recorded with cryostats cooled with liquid nitrogen which had windows of CsI and polyethylene. Attempts to form a crystal in a diamond anvil cell at a pressure of *ca.* 25 kbar were not successful.

Raman spectra were recorded with a modified<sup>19</sup> Cary 81 spectrometer excited by a CRL model 52 G argon ion laser, using the 5145 and the 4880 Å lines. Spectra were taken of the pure liquid contained in a sealed ampoule (including semi-quantitative polarization measurements), of  $\text{CCl}_4$  and  $\text{CH}_3\text{OH}$

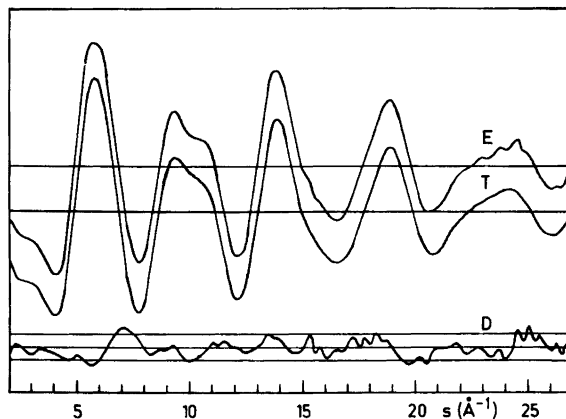


Fig. 1. Experimental (*E*) and theoretical (*T*) intensity curves for 1,3-difluoropropane and  $D = 2(E - T)$  corresponding to the final least-squares parameters. The straight lines show the experimental uncertainties ( $\pm 3$  times the experimental standard deviations).

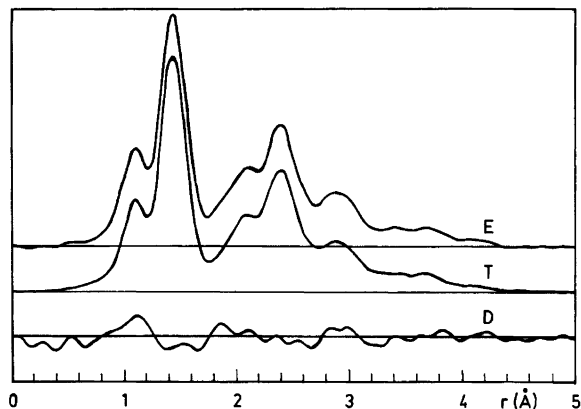


Fig. 2. Experimental (*E*) and theoretical (*T*) radial distribution curves for 1,3-difluoropropane and  $D = 3(E - T)$ . The artificial damping constant was  $0.002 \text{ \AA}^2$ .

solutions, and of the unannealed and annealed solid deposited on a copper block cooled by liquid  $\text{N}_2$ .

## CALCULATIONS

*Calculations of conformational energies and torsional barriers.* Molecular-mechanics calculations of conformational energies and barriers were performed using non-bonded potential functions in the Morse formulation.<sup>20</sup> The potential parameters<sup>20,21</sup> are found in Table 1, and the diagonal force constants of Crowder and Mao were used.<sup>22</sup> Potential parameters of the  $\text{F}\cdots\text{C}$  interaction type were adjusted to fit the energy difference  $\Delta E = E(\text{anti}) - E(\text{gauche}) = 0.47 \text{ kcal/mol}$  observed in 1-fluoropropane.<sup>23</sup> The charges on the atoms were calculated as suggested by Sanderson,<sup>24</sup> but were reduced by a factor of two.<sup>25</sup>

Calculated results are given in Table 2. Each energy value has been obtained by adjusting bond

lengths ( $r$ ) and bond angles ( $\theta$ ), and at the energy minima the values of the torsional angles ( $\phi$ ) were also adjusted. All energies, expressed in kcal/mol, are relative to the energy of the *GG* form. Energy minima are represented by the values 0 (*GG*), 0.3 (*GG'*), 1.2 (*AG*) and 2.4 (*AA*). Each energy minimum, represented by the central number in each block of Table 2, is surrounded by torsional barriers, represented by the remaining eight numbers in each block, corresponding to forms with one or both terminal groups eclipsing the central  $\text{CH}_2$  group. The horizontal variation in energy values corresponds to a change of ca.  $60^\circ$  in the torsional angle  $\phi_{1-2}$ , while the vertical variation corresponds to a change of ca.  $60^\circ$  in  $\phi_{2-3}$ . Clearly, *AG*, *GG'* and *GG* have nearly staggered conformations, while *AA* is exactly staggered. The geometry of each conformer corresponds to well-defined minima.

The lowest barrier (2.9) is found for the transition  $\text{GG}'(0.3) \rightarrow (3.2) \rightarrow \text{GG}(0)$ . In 1-fluoropropane<sup>23</sup> the barrier  $G \rightarrow A$  is  $4.2 \pm 1.5 \text{ kcal/mol}$  in good

Table 1. Potential parameter values.<sup>a</sup>

Type	$r_0$ (Å)	$r_{\text{min}}$ (Å)	$\epsilon$ (kcal/mol)	Ref.
$\text{F}\cdots\text{F}$	1.97	2.64	3.60	21
$\text{F}\cdots\text{H}$	2.37	2.90	0.29	21
$\text{F}\cdots\text{C}$	2.74	3.26	0.61	This work
$\text{C}\cdots\text{H}$	2.90	3.30	0.043	20
$\text{H}\cdots\text{H}$	2.76	3.15	0.023	20

<sup>a</sup>The electrostatic terms of the potential have been calculated with the following charges ( $q$ ) on the atoms:  $q(\text{F}) = -0.175e$ ,  $q(\text{C}_1) = q(\text{C}_3) = +0.027e$ ,  $q(\text{C}_2) = 0.001e$ ,  $q(\text{H}_1) = q(\text{H}_3) = 0.059e$ ,  $q(\text{H}_2) = 0.030e$ .

Table 2. Conformational energies for 1,3-difluoropropane obtained by molecular-mechanics calculations.

Type of conformer and (symmetry) $C_1C_2C_3$		Energies in kcal/mol			Deviations from staggered form ( $C_1C_2C_3$ )	
		Horizontal $\phi(1-2)$	Vertical $\phi(2-3)$		$\Delta\phi(1-2)^\circ$	$\Delta\phi(2-3)^\circ$
AA ( $C_{2v}$ )	HHH	10.0	6.5	9.9	0 <sup>b</sup>	0 <sup>b</sup>
	FCCCF	6.5	2.4	6.5		
	HHH	9.9	6.5	10.0		
AG ( $C_1$ )	HHH	9.9	4.6	9.0	0.5	1.0
	HCCCF	6.5	1.2	4.9		
	FHH	10.0	4.9	9.0		
GG' ( $C_3$ )	HHH	9.0	3.2	9.8	-2.1	+2.1
	HCCCH	4.6	0.3	3.2		
	FHF	9.9	4.6	9.0		
GG ( $C_2$ )	HHF	10.0	4.9	9.0	+1.5	+1.5
	HCCCH	4.9	0 <sup>a</sup>	3.2		
	FHH	9.0	3.2	9.8		

<sup>a</sup>Energies relative to this value. <sup>b</sup>Exactly staggered form.

agreement with 4.1 for the transition  $AG \rightarrow AA$  as calculated here. The calculated energies suggest that  $GG$  will be the predominant conformer in the gas phase at 20 °C. The high-energy form is  $AA$ , not  $GG'$  as suggested by earlier calculations.<sup>4,5</sup> We consider the present energy values superior to our earlier calculations<sup>21</sup> mainly because of the new and better  $F \cdots C$  potential parameters. The conformational differences between parameter values of bond angles were small. The largest value was found for  $\theta = \angle CCC$  with  $\theta(GG') - \theta(AA) = 0.5^\circ$  and  $\theta(GG) - \theta(AG) = 0.1^\circ$ .

#### CALCULATION OF VIBRATIONAL QUANTITIES

One of the most fruitful areas of interplay between electron diffraction and vibrational spectroscopy is that concerned with the torsional vibrations. For example, we have recently exploited this connection in our comparison of the low frequency vibrations of 1,3-dichloro-, 1,3-dibromo-, 1,2,3-trichloro-, and 1,2,3-tribromopropane found experimentally<sup>26</sup> with those calculated earlier,<sup>6,7</sup> in this case the agreement between calculation and experiment was very satisfying.

Leading up to this comparison, a normal-coordinate analysis was carried out for each conformer,<sup>27</sup> and mean amplitudes of vibration ( $u$ -

values) were computed.<sup>28</sup> The force constants, except for the torsional ones, were transferred from 1-fluoropropane.<sup>22</sup> The torsional force constants were estimated by adjusting two values to fit the experimental torsional frequencies observed for 1-fluoropropane.<sup>23</sup> The final values are  $F_\phi(\text{gauche}) = 0.142$  and  $F_\phi(\text{anti}) = 0.039$  in units of  $\text{mdyn } \text{Å}(\text{rad})^{-2}$ . From the formula in Ref. 29 and partial force constants  $F_g^*(\text{HH})$ ,  $F_g^*(\text{CH})$ ,  $F_g^*(\text{FC})$  and  $F_g^*(\text{FH})$  equal to 0.013, 0.017, 0.065 and 0.021  $\text{mdyn } \text{Å}(\text{rad})^{-2}$ , the estimates became  $F_\phi(\text{anti}) = 0.102$  and  $F_\phi(\text{gauche})$  equal to the value 0.142 above. Molecular-mechanics estimates are  $F(\text{anti}) = 0.10 - 0.11$  and  $F(\text{gauche}) = 0.12 - 0.13$  depending on which conformer is considered.

All estimates agree in predicting  $F_\phi(\text{gauche}) > F_\phi(\text{anti})$  as intuitively expected. The values used in calculating the  $u$ -values were  $F_\phi(\text{anti}) = 0.039$  and  $F_\phi(\text{gauche}) = 0.142 \text{ mdyn } \text{Å}(\text{rad})^{-2}$ . The calculated mean amplitudes of vibration are found in Table 3 and the torsional frequencies in Table 4, while the calculated fundamental frequencies are compared with the experimental values in Table 8.

In these tables, the assumption, which will be discussed later, is made that the  $GG$  conformer persists in the crystalline phase. As in our earlier work, it can be seen that here also the agreement between the experimental torsional frequencies and those calculated is very good.

Table 3. Calculated mean amplitudes of vibration ( $u$ ). The range of  $u$ -values and corresponding internuclear distances ( $r$ ) are given including values for the conformers  $AA$ ,  $AG$ ,  $GG$ ,  $GG''$ .  $T=293$  K.

Type of dist.	$r$ (Å)	$u$ (Å)
C—F	1.391	0.047
C—C	1.513	0.050
C—H	1.094	0.078
C···F	2.39	0.069
C···H	2.15	0.107—0.108
C···C	2.51	0.068
F···H	2.04	0.105
H···H	1.78	0.127—0.129
F···H(a)	3.32	0.103
F···H(g)	2.61—2.66	0.156—0.198
H···H(g)	2.44—2.52	0.204—0.172
H···H(a)	3.06	0.130
C···F(g)	2.91—2.96	0.139—0.140
C···F(a)	3.69	0.069
C···H(g)	2.72—2.74	0.158—0.204
C···H(a)	3.46	0.105
F···F(gg)	3.54	0.235
F···F(aa)	4.70	0.085
F···F(ag)	4.15	0.166
F···F(gg'')	2.71	0.225
F···H(gg)	2.59	0.227—0.268
F···H(ga)	3.89	0.152—0.162
F···H(ag)	4.02	0.181—0.196
F···H(gg)	3.25—3.30	0.320—0.241
F···H(aa)	4.53	0.118
H···H(gg)	2.99—3.11	0.247—0.368
H···H(ga)	3.69—3.75	0.195—0.170
H···H(aa)	4.29	0.144
H···H(gg'')	2.43—2.52	0.230—0.305

Table 4. Calculated values of the torsional frequencies in  $\text{cm}^{-1}$ .  $F_\phi$  values in  $\text{mdyn \AA}(\text{rad})^{-2}$ .

$F_\phi(\text{gauche})$	0.114	0.142	0.170
$GG$	81	90	97
	158	173	186
$GG''$	104	112	119
	104	115	126
$AG^a$	69	69	69
	126	138	148
$AG^b$	108	108	108
	126	138	148

<sup>a</sup>  $F_\phi(\text{anti})=0.039$ . <sup>b</sup>  $F_\phi(\text{anti})=0.102$ .

The torsional frequency variation with the various values employed for  $F_\phi(\text{gauche})$  and  $F_\phi(\text{anti})$  is shown in Table 4.

## RESULTS AND DISCUSSION

*Structure and composition in the gas phase.* RD-curves for the four possible conformers and the final experimental curve are shown in Fig. 3. Clearly the conformers  $GG$  and  $AG$  are present and  $GG$  is the most abundant conformer. The percentage of  $AA$  has to be very small. The fact that  $GG''$  is present in detectable concentration is not so easily seen directly from the curves in Fig. 3. According to the energy values in Table 2  $AG$  and  $AA$  are less stable than  $GG''$ , corresponding approximately to the percentages 55 ( $GG$ ), 30 ( $GG''$ ), and 15 ( $AG$ ) with less than one percent of  $AA$  at 20 °C. The composition parameters  $\alpha(AG)$  and  $\alpha(GG)$  were refined with the restrictions  $\alpha(AA)=0$  and  $\alpha(GG'')=100-\alpha(AG)-\alpha(GG)$ .

It was assumed that the  $\text{C}-\text{CH}_2\text{F}$  groups are equivalent and possess  $C_s$  symmetry, the  $\text{C}-\text{CH}_2-\text{C}$  group possesses  $C_{2v}$  symmetry, and thus the conformers have identical structures except for the values of the torsional angles  $\phi_{1-2}$  and  $\phi_{2-3}$  which define the rotations around the  $\text{C}_1-\text{C}_2$  and  $\text{C}_2-\text{C}_3$  bonds.

The torsion angles were not all refined independently. A relationship between a deviation

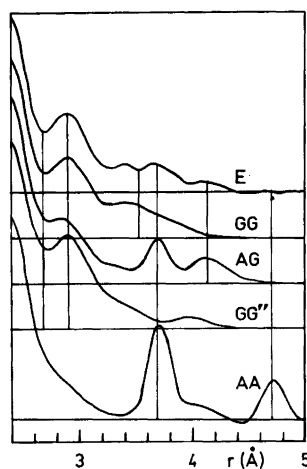


Fig. 3. Radial distribution curves for conformers of 1,3-difluoropropane. Calculated curves for the conformers  $AA$ ,  $AG$ ,  $GG$  and  $GG''$  are shown together with the final experimental curve.

Table 5. Structural parameters and conformational composition for 1,3-difluoropropane. Standard deviations ( $\sigma$ ) apply to the last digit given.

Bond lengths ( $r_s$ ) in Å and bond angles ( $\angle \alpha$ ) in deg.			
C-H	1.094(5)	$\angle$ CCC	112.9(0.8)
C-C	1.513(3)	$\angle$ CCF	110.1(0.3)
C-F	1.391(2)	$\angle$ CC <sub>1</sub> H	112.1(1.4)
$\angle$ FCH	107.8(0.8) <sup>b</sup>	$\angle$ HC <sub>2</sub> H	108.5 <sup>a</sup>
$\angle$ HC <sub>1</sub> H	105.9(1.5) <sup>b</sup>	$\angle$ (HC <sub>1</sub> H)*	119.5 <sup>a</sup>
$\angle$ CC <sub>2</sub> H	108.5(1.2) <sup>b</sup>		
Torsional angle deviations from staggered forms			
Conformer <sup>c</sup> (C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> )	GG	AG	GG''
$\Delta\phi_{1-2}$ (deg.)	-4.0(2.0)	-2.0(2.0)	+4.0(2.0)
$\Delta\phi_{2-3}$ (deg.)	-4.0(2.0)	-2.0(2.0)	-4.0(2.0)
Composition (%)	63(4)	27(2)	10(5)

<sup>a</sup> Assumed values. <sup>b</sup> Dependent angles. <sup>c</sup> See also Table 2.

parameter ( $\phi_0$ ) and the torsion angles was introduced as suggested by the molecular-mechanics results of Table 2. For the GG conformer

it was assumed that  $\phi_{1-2} = 120^\circ + \phi_0 = \phi_{2-3}$ , and for GG''  $\phi_{1-2} = 120^\circ - \phi_0 = -\phi_{2-3}$ . For AG  $\phi_{1-2} = 120^\circ + 0.5\phi_0$  and  $\phi_{2-3} = 0.5\phi_0$ , while AA has  $\phi_{1-2} = \phi_{2-3} = 0^\circ$ . The value  $\phi_0 = 0^\circ$  corresponds to exact staggered conformations, and the results in Table 2 suggest a value of  $\phi_0$  close to  $+2^\circ$ , while  $-4^\circ$  was found by least-squares refinement with  $\sigma = 2^\circ$ .

The parameters  $\phi_0$ ,  $r(\text{C-H})$ ,  $r(\text{C-C})$ ,  $r(\text{C-F})$ ,  $\angle$  CCC,  $\angle$  CCF and  $\angle$  CC<sub>1</sub>H were refined simultaneously while  $\angle$  HC<sub>2</sub>H and  $\angle$  (HC<sub>1</sub>H)\*, which is the projection of the HC<sub>1</sub>H angle on a plane perpendicular to the C<sub>1</sub>-C<sub>2</sub> axis, were kept at fixed values as shown in Table 5. Parameters from the final least-squares refinements and standard deviations ( $\sigma$ ) corrected for correlation<sup>30</sup> are also given in Table 5. The uncertainty in the *s*-scale (0.14%) has been included in the standard deviations for the bond lengths. Non-bonded distances were computed as dependent parameters, restricted under the constraints of  $r_x$  parameters.<sup>31,32</sup>

Calculated mean amplitudes of vibration (*u*) were included in the least-squares analysis as fixed parameters (Table 3), except for the following values:  $u(\text{C-H}) = 0.066(4)$ ,  $u(\text{C-F}) = 0.052(5)$  and  $u(\text{C}\cdots\text{F}/\text{gauche}) = 0.121(6)$  Å found by refinement.

Table 6. Experimental ED-results for three 1,3-dihalopropanes. Standard deviations are shown in parentheses ( $\sigma$ ).

XCH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> X	X=F This work	X=Cl Ref. 6	X=Br Ref. 7
Bond length			
$r_g(\text{C-C})$ in Å	1.515(3)	1.531(4)	1.529(5)
Bond angles ( $\angle_x$ ) in deg.			
$\angle$ CCC	112.9(0.8)	112.9(0.5)	111.4(1.6)
$\angle$ CCX	110.1(0.3)	111.6(0.1)	112.0(0.3)
Torsional angle deviations from staggered form in the conformer GG			
$\Delta\phi(\text{GG})$	-4.0(2.0)	-5.8(1.0)	-6.6(2.0)
Percentages of conformers			
GG	63(4)	73(2)	67(2)
AG	27(2)	24(2)	30(2)
AA	0(-) <sup>a</sup>	3(3)	3(2)
GG''	10(5)	0(-) <sup>a</sup>	0(-) <sup>a</sup>
Temp. (°C)	20	38	65

<sup>a</sup> Experimentally not detected.

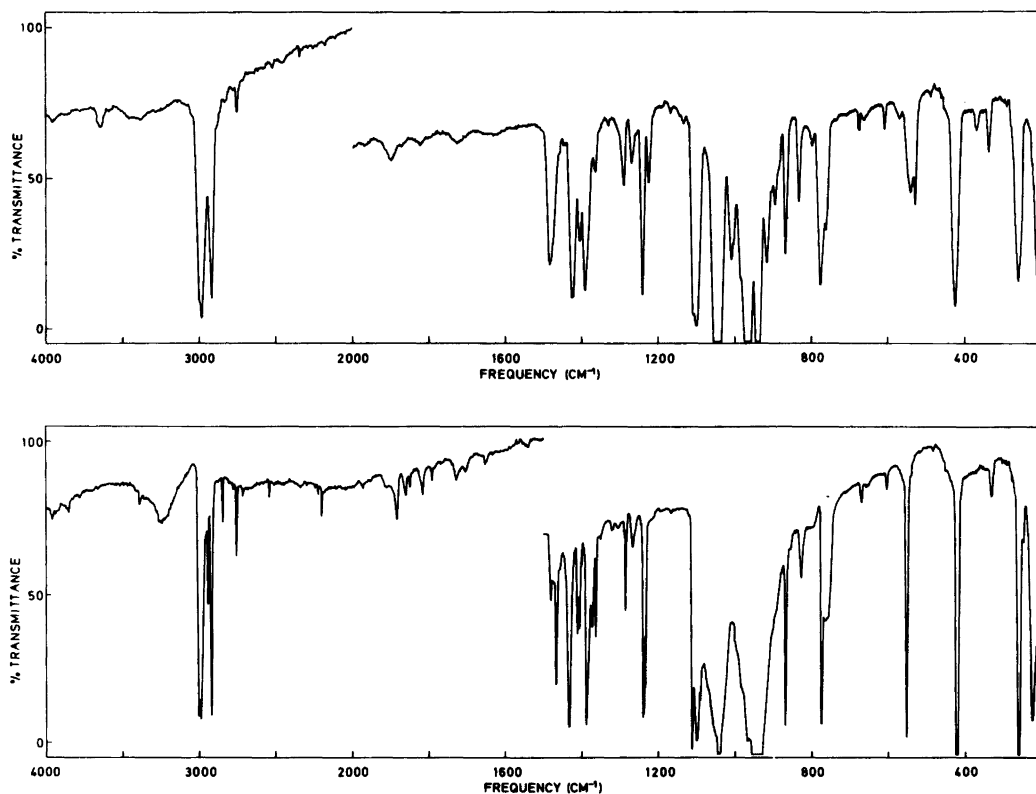


Fig. 4. Infrared spectra of 1,3-difluoropropane as an unannealed solid (upper curve) and as an annealed crystalline solid (lower curve) at *ca.*  $-180^{\circ}\text{C}$ .

The following correlation coefficients ( $\rho$ ) had absolute values greater than 0.4:  $\rho(1,2) = -0.42$ ,  $\rho(3,4) = -0.69$ ,  $\rho(3,5) = +0.43$  and  $\rho(5,6) = -0.43$ . The numbering of the parameters was 1, 2, 3, 4, 5 and 6 for  $r(\text{C}-\text{C})$ ,  $\angle \text{CCF}$ ,  $\angle \text{CCC}$ ,  $\phi_{\text{o}}$ ,  $\alpha(\text{AG})$  and  $\alpha(\text{GG}')$ , respectively.

Assuming equal vibrational and rotational partition functions for the conformers, the values of the conformational energies calculated from the percentages in Table 5 are  $\Delta E(\text{AG}) = E(\text{AG}) - E(\text{GG}) = 0.9$  and  $\Delta E(\text{GG}') = F(\text{GG}') - E(\text{GG}) = 1.1$  in kcal/mol. However, using values for the vibrational partition functions corresponding to the calculated frequencies, the  $\Delta E$  values become  $\Delta E(\text{AG}) = 1.5$  and  $\Delta E(\text{GG}') = 1.2$ . With  $F_{\phi}(\text{anti}) = 0.102$  mdyne  $\text{\AA}(\text{rad})^{-2}$  one gets  $\Delta E(\text{AG}) = 1.1$ . Including error limits the value  $1.1 \pm 0.4$  is suggested for  $\Delta E(\text{AG})$  in agreement with the value 1.2 in Table 2. For  $\Delta E(\text{GG}')$  the lower limit of about 0.5 was estimated. However, the calculated value of 0.3 for  $\Delta E(\text{GG}')$  is

too small compared to the best value of about 1.2 estimated above. The calculated value 2.4 for  $\Delta E(\text{AA})$  is consistent with the fact that  $\text{AA}$  was not present in detectable concentration.

Electron diffraction results for three 1,3-dihalopropanes have been compared in Table 6.

*Spectral interpretations.* We present in Table 7 the IR and Raman frequencies in the regions where fundamentals may appear. In Figs. 4 and 5 are given the IR spectra of the unannealed and annealed crystals in the mid and far IR. In Fig. 6 the Raman spectra of the liquid and of the annealed crystal are shown.

The most important problem we faced in our interpretation of the spectra was that of which conformer persists in the low temperature crystal. In our earlier work on the other 1,3-dihalopropanes,<sup>2</sup> not only could the evidence from the vapour phase compositions as determined from electron diffraction be employed, but also use could be made

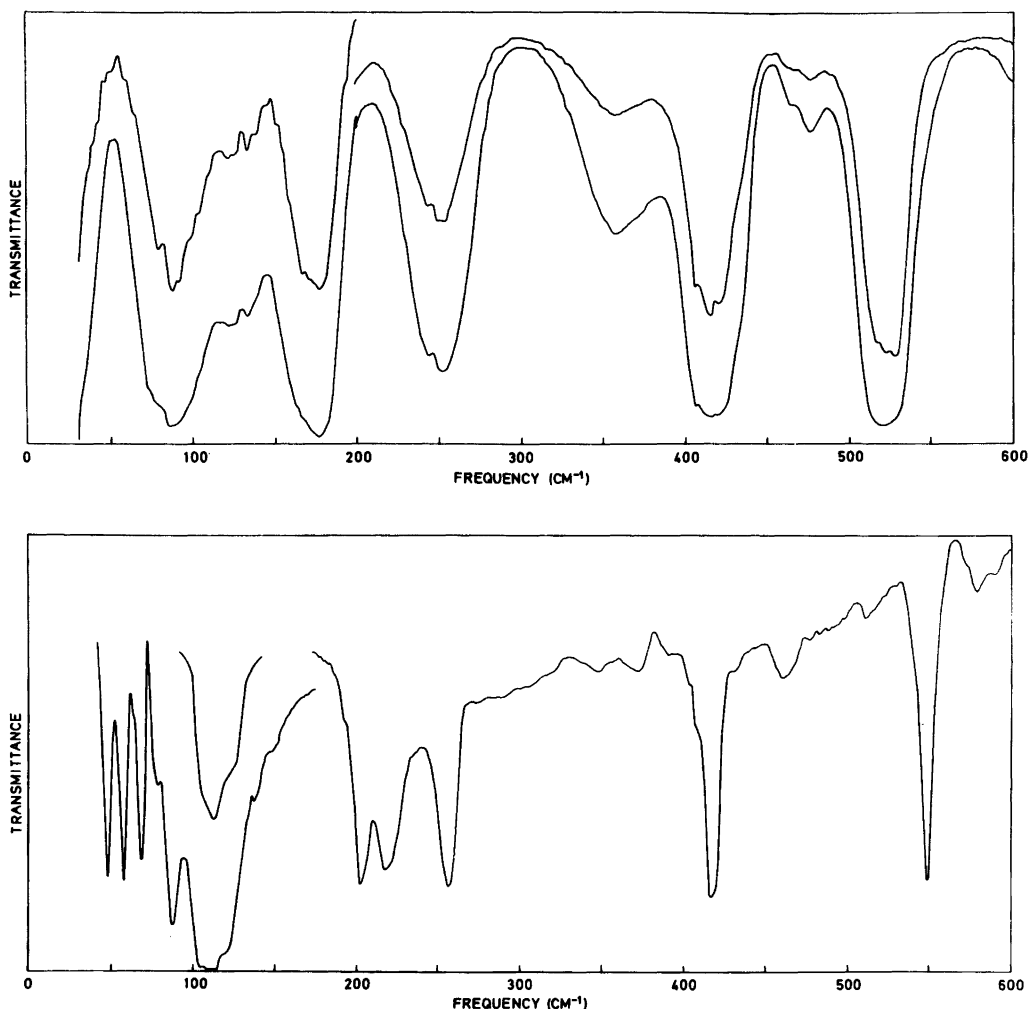


Fig. 5. Far infrared spectra of 1,3-difluoropropane as a vapour (upper curve) and as an annealed crystalline solid at *ca.*  $-180^{\circ}\text{C}$  (lower curve).

of the various empirical rules for the dependence of the C–X stretching modes on conformation.<sup>33</sup> Unfortunately, in the case of the fluoroalkanes, such rules do not exist because of the highly mixed character of the modes involving C–F stretching (*cf. e.g.* Ref. 34).

We now are certain that the conformer which persists in the crystal is the *GG*, but since this assignment is not completely straightforward we feel obligated to explain our reasoning.

On the basis of our experience with the other 1,3-dihalopropanes we would expect the *GG* form to

persist in the crystal. Further, since it is the *GG* which is the dominant form in the gas phase at room temperature, it would be most likely that form would be the one which “takes over” in the crystal.

Our normal coordinate calculations are admittedly crude, and it can be easily seen that plausible assignments can be made assuming either that *GG* or that *AG* is the stable form in the crystal once one ascends past the first 4 fundamentals. However, for those lowest 4 fundamentals the more convincing assignment occurs with *GG* taken as the form in the crystal.



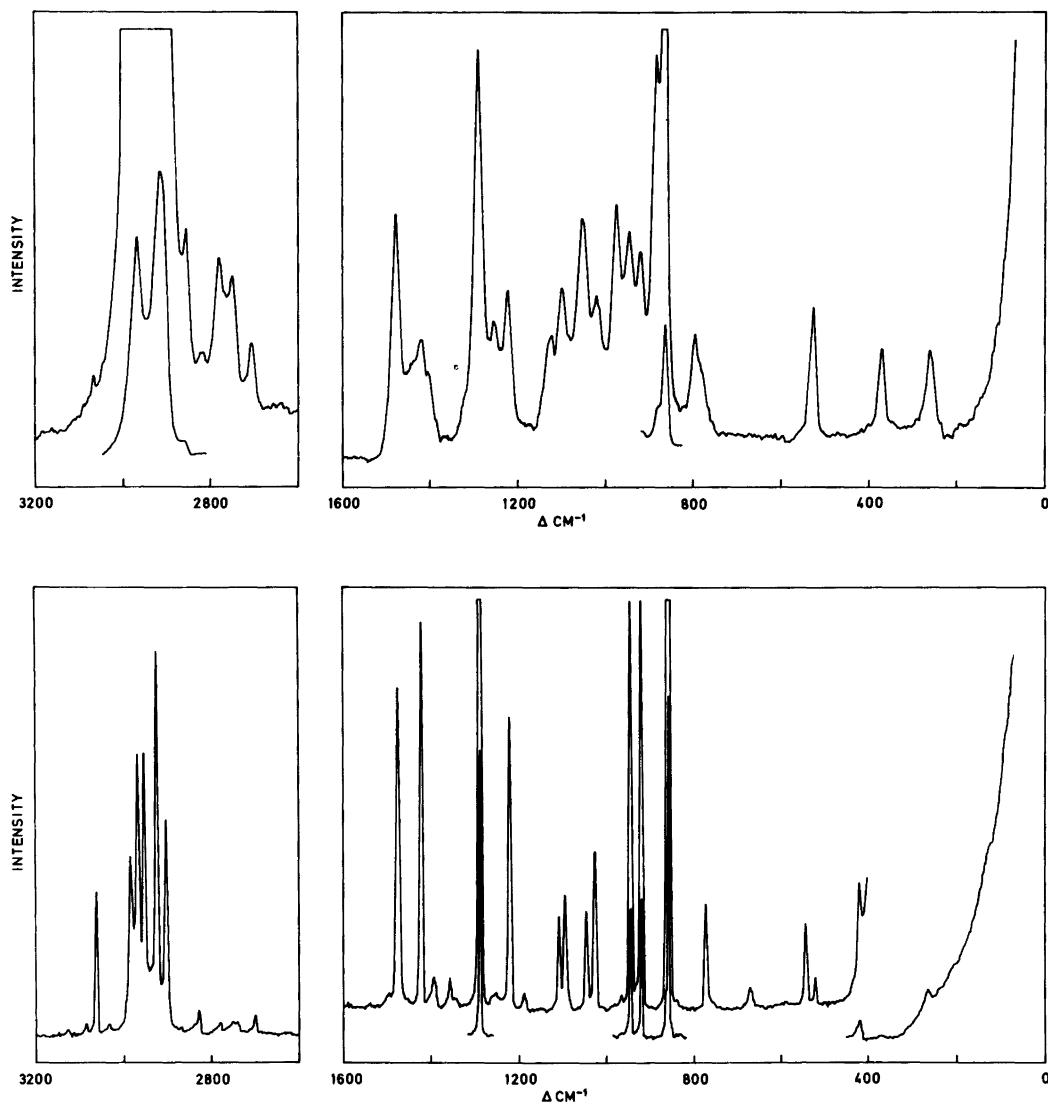


Fig. 6. Raman spectra of 1,3-difluoropropane as a liquid at room temperature (upper curve) and as an annealed crystalline solid at *ca.*  $-180^{\circ}\text{C}$  (lower curve).

A portion of this can be made even more convincing. Our calculations of the torsional frequencies (*cf.* Table 4) which can be made almost independently of the force field employed for the rest of the molecule agree much better with the experimental results when one assumes that the *GG* form is the one which crystallizes.

The infrared data, which provide the only complete link between the known composition of

the gas phase and the crystal, strongly support this argument. There are no unexpected intensity variations as we proceed from vapour to solution to unannealed and annealed crystals; that is, it is in general the weaker bands in the spectra which disappear upon crystallization.

The Raman data, however, tell an inconsistent story. Lending support to the hypothesis given are the polarization data. Almost all the bands which

disappear upon crystallization are clearly polarized. This is the behaviour which would be expected if an unsymmetrical species was being destroyed. The *AG* conformer has no symmetry; hence all its bands should be polarized. On the other hand, 13 of the 27 fundamental bands for the *GG* conformer should be depolarized. The obvious conclusion to be drawn is that it is an unsymmetrical conformer which is being removed. It must be pointed out, though, that in the Raman spectra several of the more prominent bands disappear upon crystallization, notably those at 366, 520, 792, 884 and 977  $\text{cm}^{-1}$  (cf. Fig. 6).

Dealing only with the evidence from the Raman data, we are inclined to give more credence to the polarization data. Arguments based on it rely only on symmetry with no intervening assumptions. By contrast, arguments based on intensities seem much shakier to us. Lacking both heavy atoms and multiple bonds, DFP lacks also the very intense Raman bands connected with the C–F stretches which could serve as the sort of undeniable landmarks which characterize the spectra of the chloro-, bromo-, and iodoalkanes (as shown, *e.g.*, in Refs. 2 and 12).

Finally, when we consider the weight of all the evidence at once, we return firmly to our initial statement, the assertion that the crystal is made up of conformers in the *GG* form. With this decision made, we can proceed to our consideration of the spectra.

Somewhat as we expected, the dipole moments of the two major individual conformers must be nearly the same inasmuch as we could observe almost no change in relative intensities of the bands in going from the Raman spectrum of the  $\text{CCl}_4$  solution through that of the pure liquid to that of the  $\text{CH}_3\text{OH}$  solution, a series in which the dielectric constant of the medium increases greatly. The lone exception to this, a weak band at 363  $\text{cm}^{-1}$  which does increase through these three spectra and which disappears upon crystallization, is the only band which we assign to the *GG'* conformer. The *GG''* conformer, since in it the 2 C–F bonds are nearly parallel, should have a much higher dipole moment than the *GG* and *AG* conformers and should be highly favoured in media of higher dielectric constant. Thus, even though from our electron diffraction work we obtain the result that the third most abundant conformer, the *GG''*, is present in 10% abundance at 20 °C in the vapour, the failure of this conformer to make its presence known to a greater extent in the more polar media suggests that this

10% value must be regarded as an extreme upper limit and that the abundance is probably considerably lower.

Of aid to us in our assignments were the infrared band contours, the Raman polarization data, and the normal coordinate calculations. For the *GG* conformer, the 14 fundamentals of species *a* should have type *B* band contours and should be polarized; the 13 fundamentals of species *b* should have *A/C* hybrid band contours and should be depolarized. With the aid of these pieces of information, we present the assignments shown in Tables 7 and 8. The agreement between calculated and observed frequencies seems to us quite good in view of the fact that the frequencies were in no way refined.

On the whole, in our assignments we have been able to find agreement both with the calculated frequencies and also with the spectral evidence. We note below only those cases where all the pieces of evidence do not agree.

In the C–H stretching region 4 of the 6 C–H stretches are ascribed to polarized Raman bands rather than the 3 which we expect. In this region, where there should be nearly complete correspondence between the fundamentals of the various conformers, each band should have components from the different conformers. Since all bands of the *AG* conformer will be polarized, nearly all bands in this region should appear polarized. Except for this, assignment in this region is reasonably straightforward and agrees well, for example, with the values reported by Harris *et al.* for 1,2-difluoroethane.<sup>35</sup>

Assignment of the 3  $\text{CH}_2$  scissoring modes between 1400 and 1500  $\text{cm}^{-1}$  posed no difficulty.

Thirteen fundamentals are expected to lie between 600 and 1400  $\text{cm}^{-1}$ . It is easy to pick out some of these, with their great intensity in the infrared, in which C–F stretching is playing a large role. However, with the highly mixed character of these modes, we prefer not to identify individual bands as being the C–F stretches. Our assignment for  $\nu_7$  is to a type *A* band whose Raman counterpart, though, is polarized. We reversed the numerical order of the normal coordinate results for  $\nu_{10}$  and  $\nu_{24}$  so as to satisfy the spectral evidence.

Below 600  $\text{cm}^{-1}$  lie 5 fundamentals. The band at 416  $\text{cm}^{-1}$  appears depolarized in the Raman; it does have the expected type *B* contour though. More serious is the problem of the band at 252  $\text{cm}^{-1}$  which, against expectations, appears polarized in the Raman. We have no explanation for this once we

Table 7. Infrared and Raman spectral data<sup>a</sup> for 1,3-difluoropropane.

Infrared			Raman		Assignments
Vapour	Solution	Solid(90K)	Liquid	Solid(90K)	
3087w <sup>b</sup>					
3062w					
		3027vw			
		3004s		3005ms	$\nu_{1,}$ GG
		2999s			$\nu_{15,}$ GG
2985vs	} 2975vs	2989s		2986s	
2979vs		2972m,sh	2979vs,p	2973s	$\nu_{2,}$ GG
2973vs					
		2945m	2963m,dp	2956w	
			2927vs,p	2945vs	$\nu_{16,}$ GG
2925s	} 2915s				
2919s		2924s	2922vs,p	2924s	$\nu_{17,}$ GG
2912s					
2850w		2877vw			
		2866vw	2867w,p		$\nu_{3,}$ GG
		2847w		2844w	
2828w	2821w,sh		2828w,p		
1486m	} 1476m	1480w	1479m,dp	1484s	$\nu_{4,}$ GG
1475m		*	1470w,sh	1481w,sh	
1465w				*	$\nu_{7,}$ AG
	1456w	1465m			
	1440w		1444w,dp	*	$\nu_{8,}$ AG
1435m		1430s		1430s	$\nu_{18,}$ GG
1424m,sh	1419m	1409m	1421w,dp		$\nu_{5,}$ GG
1415m,sh	} 1400m	1403m			
1407m,sh		*	1404vw	*	$\nu_{9,}$ AG
1394s					
				1401w	} GG comb?
				1397w	
1385s C	1382m	1386s			$\nu_{19,}$ GG
1371w	1363w	1371vw			
		1362w	1365vw	1363w	$\nu_{6,}$ GG
		1348vw			
	1325w	*	1325w	*	$\nu_{12,}$ AG
1307vw					
1280w	1289w	1287vw			
		1284w	1291s,dp(?)	1295vs	$\nu_{20,}$ GG
1272m					
	1250w	1265w	1255w,p	*	$\nu_{13,}$ AG
1258w	} A 1235m				
1245m		1238w			
		1235s	1225m,p	1227s	$\nu_{7,}$ GG
1238m		1231s			
1229m	1218w	*			
			1191vw	1193w	$\nu_{21,}$ GG
		1164vw			
1135w	1126w		1129w,p	1113m	$\nu_{8,}$ GG

Table 7. Continued.

1113s } 1107s } C 1099s }	1100vs	1110s } 1097s }	1100m,dp 1085vw,sh	1099s	$v_{22}$ , GG
1074vs } 1067vs } A 1057vs }	1052vs	1049vs 1034vs	1051s,dp 1019m,dp	1050s 1030m	$v_{23}$ , GG $v_9$ , GG
1045s } 1038s } 994s } B 987s } 980s,sh 958s } C 952s } 942s }	1021vs 977s 943s	* 977w } * 966w }	973s,dp 944m,dp	969w *	$v_{18}$ , AG $v_{19}$ , AG
928s } 923s } 916s } 910s,sh	917m	935s 932s	917mw,p	948s 935vw 921s	$v_{10}$ , GG $v_{24}$ , GG
891m	881w	892m,sh 878w,sh(?)	884m,p	*	$v_{20}$ , AG
872w } 860w }	863w	868s	864vs,p	867w,sh } 861vs } 856w,sh }	$v_{11}$ , GG
821w	824w <sup>c</sup> 791w <sup>c</sup>	854vw 826w *	827vw 792m,p	* *	$v_{21}$ , AG $v_{22}$ , AG
784w,sh } B 773m }	778m <sup>c</sup> 660w <sup>c</sup>	773s 763w } 746w } 668w 654vw	777w,dp 755vw(?)	774m 758vw	$v_{25}$ , GG
606vw		570vw 549s		542m	$v_{24} + v_{27}$ , AG $v_{12}$ , GG
548w } 526m } A 522m } 514m }	536vw 520m	*	520m,p	*	$v_{23}$ , AG
472vw 433w,sh 419m } B 415m } 413m } 406m }	471w 416m	* 418s	470vvw? 419w,dp		$v_{24} + v_{27}$ , AG $v_{13}$ , GG
375w 357w	397vvw(?) 363m	* *	396w,p 366m,p	* *	$v_{24}$ , AG $v_{14}$ , GG''
302w } 289vw }	333w 301vw	330w	325vw(?)		$v_{14} + v_{26}$ , GG $v_{25}$ , AG

Table 7. Continued.

253w } 248w } 243w }	252m	258s } 255s }	254m,p	263w	$\nu_{26}$ , GG
178m } B 166m }	205w <sup>d</sup> 182m <sup>d</sup>	216m 202s	184vw	205w	$\nu_{27}$ , GG
133w } 126w }	135vw <sup>d</sup>	172vw 154vw *			$\nu_{26}$ , AG
93w } 87w } 82w }	94w <sup>d</sup>	112s 87s 68m 58m 48m	100vw	120w	$\nu_{14}$ , GG
35vw	41w <sup>d</sup>				lattice modes

<sup>a</sup>The spectra are reported only for the regions 3100 to 2800  $\text{cm}^{-1}$  and below 1500  $\text{cm}^{-1}$ . <sup>b</sup>s, strong; m, medium; w, weak; v, very; sh, shoulder; A,B,C, vapour contours; p, polarized; dp, depolarized; asterisks (\*) indicate bands which vanish in the crystalline solid. <sup>c</sup>Determined in  $\text{CS}_2$  solution. <sup>d</sup>Determined in cyclohexane solution.

Table 8. Observed<sup>a</sup> and calculated normal frequencies for 1,3-difluoropropane.

GG Obs.	Calc.	AG Obs.	Calc.	GG'' Obs.	Calc.	AA Calc.
3004	3002(a) <sup>b</sup>		3001		3002(a') <sup>b</sup>	3001(b <sub>1</sub> ) <sup>b</sup>
2999	2999(b)		3000		2999(a'')	3000(a <sub>2</sub> )
2975	2943(a)		2942		2943(a')	2942(a <sub>1</sub> )
2945	2942(b)		2942		2942(a'')	2941(b <sub>2</sub> )
2915	2918(b)		2917		2917(a')	2917(b <sub>1</sub> )
2867	2857(a)		2857		2858(a')	2857(a <sub>1</sub> )
1479	1526(a)	1476	1520		1525(a')	1513(a <sub>1</sub> )
1435	1510(b)	1440	1500		1512(a'')	1487(b <sub>2</sub> )
1419	1457(a)	1400	1442		1454(a')	1426(a <sub>1</sub> )
1382	1397(b)		1389		1397(a'')	1383(a <sub>1</sub> )
1363	1390(a)		1366		1391(a')	1354(b <sub>2</sub> )
1289	1346(b)	1325	1350		1347(a'')	1342(b <sub>2</sub> )
1235	1262(a)	1250	1256		1262(a'')	1249(a <sub>2</sub> )
1191	1150(b)		1136		1145(a'')	1146(b <sub>1</sub> )
1126	1121(a)		1128		1135(a')	1094(a <sub>2</sub> )
1100	1104(b)		1085		1091(a'')	1056(b <sub>1</sub> )
1052	1050(b)		1043		1058(a')	1038(a <sub>1</sub> )
1019	1036(a)	1021	1028		1034(a')	1027(a <sub>1</sub> )
917	981(a)	977	1017		953(a'')	1024(b <sub>1</sub> )
943	966(b)	881	934		928(a'')	981(b <sub>2</sub> )
863	835(a)	824	890		919(a')	915(a <sub>2</sub> )
778	823(b)	791	808		809(a')	779(b <sub>1</sub> )
536	553(a)	520	528		552(a')	485(b <sub>2</sub> )
416	435(a)	397	358		367(a'')	383(a <sub>1</sub> )
252	275(b)	301	301	363	360(a')	232(a <sub>1</sub> )
182	173(b)	135	138		115(a'')	87(a <sub>2</sub> )
94	90(a)		69		112(a')	71(b <sub>1</sub> )

<sup>a</sup>When possible, frequency values taken from the liquid spectra are given. <sup>b</sup>a and b represent symmetry species for  $C_{2v}$ , a' and a'' for  $C_s$ , and a<sub>1</sub>, a<sub>2</sub>, b<sub>1</sub>, b<sub>2</sub> for point group  $C_{2v}$ .

rule out the tempting supposition that it possesses a contribution from another conformer. The *AG* fundamentals in this region seem well accounted for otherwise. Finally, the band at  $182\text{ cm}^{-1}$  seems to be type *B*; however, we still confidently assign it as  $\nu_{27}$ .

Numerically, the fundamentals which we assign to the *AG* conformer show even closer agreement between calculated and observed values than they do for the *GG*. It must be kept in mind, though, that polarization data and band contours were of no use here and that the assignments were done only by the numbers.

In all the spectra perhaps the most interesting feature were the two (for each conformer) torsional modes to be found in the far IR. For the dominant conformer we identify these as the two bands found at  $87$  and  $172\text{ cm}^{-1}$  in the vapour and shifting to  $112$  and  $202\text{ cm}^{-1}$  in the infrared spectrum of the crystal. Both have Raman counterparts. It will be seen in Table 4 that the agreement with the calculated values is quite satisfying no matter which value is taken for  $F_\phi$ . One of the torsions for the disappearing conformer must be identified with the band at  $135\text{ cm}^{-1}$ ; for the other we have no direct evidence. We do, however, note the band at  $417\text{ cm}^{-1}$  which disappears upon crystallization. If we restrict ourselves to first overtones and binary combinations of conformer *AG*, this can only be the combination  $\nu_{24} + \nu_{27}$  which leads to a value of about  $75\text{ cm}^{-1}$  for the lower torsion. If true, this value is also in excellent agreement with that calculated. The series of medium to strong bands which appear between  $45$  and  $90\text{ cm}^{-1}$  upon crystallization are obviously lattice modes.

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