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GAS-PHASE ELECTRON DIFFRACTION DETERMINATION OF THE MOLECULAR STRUCTURE OF PERFLUORO(METHYLOXIRANE)

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SUMMARY

The molecular geometry of perfluoro(methyloxirane) has been studied using gas-phase electron diffraction data, effective least-squares refinement of the structure being achieved with the aid of constraints to limit the number of variable parameters. With the C—CF_3 bond constrained to be 0.078 Å longer than the ring C—C, the refined bond-length values C—F (av.) = 1.323(2), C—O (av.) = 1.410(8), and C—C (ring) = 1.467(7) Å ($\underline{r}_g$ values, with e.s.d. in parentheses) were obtained; the angles between ring bonds and substituent C—F bonds were C—C—F (av.) 121(1) and O—C—F (av.) 114(1)°, the corresponding parameters involving the bulkier C—CF_3 fragment being larger by 3° in each case [∠C—C—CF_3 124(1)°; ∠O—C—CF_3 117(2)°]. The remaining refined parameters were ∠C—C—F(of CF_3) = 110.6(4)° and τ , a torsion angle defining the orientation of the C—F bonds of the CF_3 group with respect to ring bonds, = 29(2)°. Dependent bond angles possessed the values 62.7 (C—O—C), 58.7 [O—C—C (ring)], 108.3 [F—C—F (CF_3 group)], 114 [F—C—F (ring CF_2)], and 111° (F—C—CF_3).

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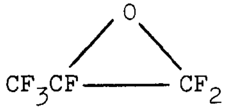
INTRODUCTION

Very few oxiranes have been examined by gas-phase electron diffraction methods, and the molecular parameters available are restricted to compounds of the hydrocarbon class [1]. The first data for a fluorocarbon oxirane, namely hexafluoropropene oxide {perfluoro(methyloxirane) (**1**) [2], b.p. -27.4 °C}, are now reported, the study involved having been carried out as an adjunct to a theoretical investigation of ring-opening reactions of perfluorinated 1,2-epoxides and their oxaziridine counterparts [5].



(**1**; HFPO)

EXPERIMENTAL

Gas-phase e.d. photographs of perfluoro(methyloxirane) (**1**) were obtained using the Balzers KDG2 instrument at UMIST [8], with camera distances of 25, 50 and 100 cm (nominal). The sample [9] was allowed to enter the gas-nozzle (temp. 310 K) from a Pyrex reservoir cooled to 180 K (toluene 'slush' bath); the temperature at the diffraction point was estimated to be 260 K. The wavelength of the electron beam, calibrated using diffraction patterns for benzene recorded at 303 K under otherwise identical conditions, was 0.056 75±0.000 04 Å.

Two Kodak electron image plates from the 100 cm experiment, one from the 50 cm, and three from the 25 cm were scanned by an automated Joyce-Loebl microdensitometer in its raster mode [11]. The optical density data were processed routinely [12] to provide the radial distribution curve shown in Fig. 1 [13].

Radial Distribution (r.d.) Curve

The r.d. curve (Fig. 1) shows five significant peaks (A-E) and a minor one (F); these six account for a total of 45 distances. Molecules of perfluoro(methyloxirane) possess no symmetry (each enantiomer belongs to point group C_1), so each peak is likely to contain contributions from a variety of different, though often similar, internuclear distances. For example, peak A embraces all ten bond distances, i.e. six C—F, two C—O and two C—C, and these are both spectroscopically and symmetrically independent except for any assumptions concerning local symmetry which may be made. Peak B is caused mainly by the second-neighbour distances (16 in total), and peaks C and D mostly represent the third-neighbour distances [e.g. F(4)----F(6) and F(6)----F(9) (13 in all)]; clearly, the latter peaks contain information on the torsion angles in the molecule. Finally, peaks E and F contain most of the six fourth-neighbour distances, i.e. those between F(4) or F(5) and the fluorines of the CF_3 group; thus, the 4-5 Å region of the r.d. curve provides important information bearing on the relative orientation of the CF_3 group.

Since a molecule of perfluoro(methyloxirane) possesses no overall symmetry, twenty-four ($3N-6$, where N = number of component atoms) parameters are required to define its geometry uniquely. With only six peaks on the r.d. curve, nowhere near this number can be determined. As described in the following section, local symmetry and other aspects can be applied to reduce the number of geometrical parameters required for structure refinement.

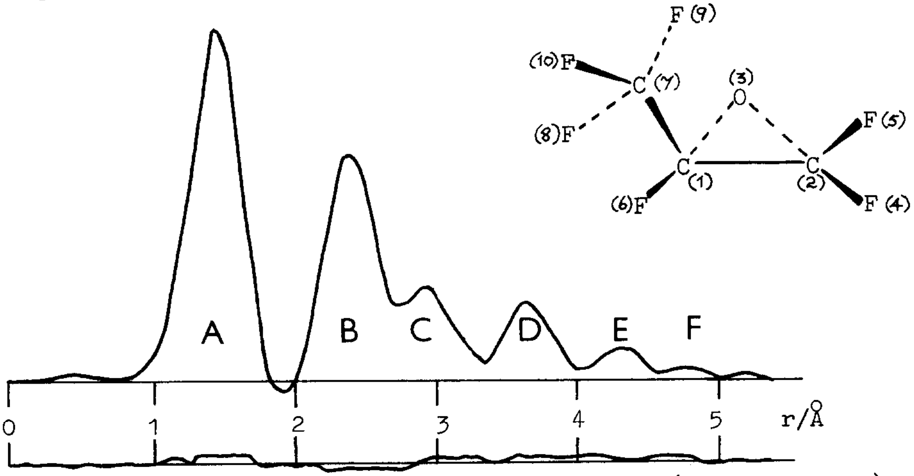


Fig. 1 Radial distribution curve for perfluoro(methyloxirane)

Least-squares Refinement of Structure

To ensure that initial least-squares calculations would converge smoothly, a simplified molecular model with only six geometrical variables was devised. This model, with the same number of variables as peaks on the r.d. curve, was developed by making a number of reasonable assumptions about the geometry, and by applying certain constraints whose validity is supported by previous structure determinations (see later). Subsequently, these assumptions and constraints were relaxed, wherever possible and reasonable, until no further significant improvement in the agreement between observed and calculated molecular intensity data was achieved.

The simplified molecular model comprised an isosceles $\overline{\text{C—O—C}}$ triangle with substituents attached so that all three O—C—F angles were identical and equal to ∠O—C—CF$_3$ (the CF$_3$ group was assigned local threefold symmetry); the four angles C—C—X [X = F(4), F(5), F(6) or CF$_3$] involving the ring C—C bond were also presumed to be equal. All six C—F bond lengths were constrained to be equal to an average value; and the C—C and C—O lengths were related according to the constraints that C—CF$_3$ is a fixed amount, Δ_1, longer than the ring C—C bond which, in turn, exceeds C—O by Δ_2 (the values of these increments are discussed later). Thus, the simplified model is defined by only six independent geometrical parameters:

- an average C—F bond length
- a common C—O bond length
- •• average angles C—C—X and O—C—X (X = F or CF$_3$)
- the angle C—C—F(of CF$_3$)
- a torsion angle (τ) describing the orientation of the CF$_3$ group (see footnote d of Table).

Vibrational amplitudes were constrained in groups to reasonable values.

Least-squares refinement of these six independent parameters (plus scale factors) gave the results listed in column I of the Table. Estimated standard deviations

TABLE

Refined structural parameters[a] for perfluoro(methyloxirane) (**1**)

Parameter	Refinement I	Refinement II	Refinement III
R(%)[b]	7.4	6.8	6.7
C–F (av.)	1.327(2)	1.330(4)	1.323(2)
C–O (av.)	1.392(5)	1.380(8)	1.408(9)
∠C–C–X (av.)[c]	121.4(4)	122.7(6)	122.8(6)
∠O–C–X (av.)[c]	114.6(8)	115.8(9)	114.3(8)
∠C–C–F (CF_3)	110.2(3)	110.7(5)	110.1(4)
τ[d]	32.7(11)	32.4(14)	33.6(14)
C–C (ring)	-	-	1.455(5)
∠C–C–CF_3	-	-	-
∠O–C–CF_3	-	-	-
Amplitudes[e]	f	r	r
Fixed parameters[f]			
Δ_1	0.07	0.07	0.078
Δ_2	0.07	0.07	-

Dependent parameters (calculated from the refined parameters in the final column)

C–CF_3 1.545(7)

Ring angles:	
at O	62.7
at C	58.7
Bond angles:	
F–C–F (CF_3)	108.3
F–C–F (ring)	114
F–C–CF_3	111

Torsion angles[g] around C(7)–C(1)	
8-7-1-6	-51
10-7-1-6	69
9-7-1-3	-38
9-7-1-2	31
8-7-1-3	82
10-7-1-2	-89

(continued on next page)

IV	V	VI	Mean of V & VI
5.7	5.7	5.7	-
1.324(2)	1.322(2)	1.323(2)	1.323(2)
1.401(7)	1.409(8)	1.411(8)	1.410(8)
120.2(14)	120.8(13)	120.9(11)	121(1)
114.1(18)	114.1(15)	113.3(14)	114(1)
110.6(4)	110.4(4)	110.7(4)	110.6(4)
29.2(19)	30.0(21)	28.5(21)	29(2)
-	1.467(8)	1.467(7)	1.467(7)
124.1(10)	124.2(11)	123.1(10)	124(1)
118.4(18)	117.5(18)	116.8(18)	117(2)
r	r	r	r
0.07	0.078	0.078	0.078
0.07	-	-	-

[a] Distances on r_g basis in Å (1 Å = 10^{-10} m); angles in degrees. E.s.d. are given in parentheses in units of the last significant figure quoted.

[b] Residual $R = \sum|\Delta| \,/\, \sum|I_{obs}|$, where $\Delta = I_{obs} - I_{calc}$, and I_{obs} and I_{calc} are observed and calculated molecular intensities. The summations are taken over all available data. Intensities were calculated using the scattering factors of ref. 14.

[c] Refinements I-III, X = F, CF_3; refinements IV-VI, X=F.

[d] τ is the angle between the CCC and CCF(8) planes, i.e. τ = 60° minus torsion angle[g] 9-7-1-2 (see Fig. 3).

[e] f = Fixed. r = Refined.

[f] Δ_1 = C—CF_3 minus C—C (ring). Δ_2 = C—C (ring) minus C—O (av.)

[g] The first column contains the numbers of the four atoms involved; the second gives the torsion angles according to the Klyne- Prelog convention [15]. See Figures 1 and 3 for the key to the numbering.

(e.s.d.) are given in parentheses in units of the last significant figure quoted. The e.s.d. values from refinement I are liable to be underestimated owing to the severity of the assumptions made. Column II of the Table shows the modest reduction in the residual R which occurred when the main grouped amplitudes were allowed to refine. Changes in parameter values of up to about three e.s.d. are also noteworthy.

The remaining refinements noted in the Table were carried out to test or relax the constraints on which the simplified molecular model had been based. Values adopted initially for Δ_1 and Δ_2 were influenced by work on related molecules (particularly the hydrocarbon oxiranes studied by Smith and Kohl [1]), estimates of the likely perturbations caused by the fluorine substituents having to be made. Refinement III shows the result of permitting the C—O bond length to vary independently of the two C—C distances. The initial estimate of 0.07 for Δ_2 refined to 1.455-1.408 = 0.047 Å (e.s.d. 0.010 Å), revealing that whereas the latter value is not significantly different from the original fixed value for Δ_2, the ring C—C bond is significantly longer than the C—O linkage. Attempts to free the Δ_1 constraint produced unstable refinements, although the need for a larger value was apparent; the final figure adopted was 0.078 Å. One other notable feature of refinement III is that its residual is scarcely different from that of II, showing that the diffraction data are not particularly sensitive to small differences in bond lengths. This was further demonstrated in attempts to separate the ring C—F distances from those of the CF_3 group; no evidence supporting a policy other than the retention of an average C—F distance was forthcoming.

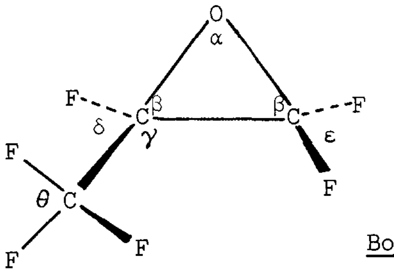
Non-bonded interactions between the ring components and the CF_3 group were considered in refinement IV. Angles C—C—CF_3 and O—C—CF_3 were allowed to refine separately from the other C—C—X and O—C—X angles, for which an average value was retained. Significant changes were observed and, as might be expected, many e.s.d. values increased. The residual also improved significantly, and the changes which occurred may be considered to give a truer picture of the molecular structure; principally, both $\angle C{-}C{-}CF_3$ and $\angle O{-}C{-}CF_3$ increased in value (with the other C—C—X and O—C—X angles adjusting accordingly), leading to a reduction in steric crowding involving the CF_3 group. [The distances principally associated with steric repulsion are those between F(9) of the CF_3 group and F(5) of the ring CF_2 (see Figures 1 and 3), between O(3) and F(9), and between O(3) and F(8); these three values increased from 2.65 to 2.69, 2.72 to 2.79, and 3.04 to 3.12 Å, respectively, in passing from refinement II to IV.]

Refinement V added the treatment of III to that of IV, and led to no further improvement (cf. III with II). Refinement VI was similar to V except that a slightly modified treatment of the vibrational amplitudes was employed. In the final column of the Table, the results of refinements V and VI have been averaged, and rounded, to take proper account of the e.s.d's; these data are the final estimates, and they have been used to calculate the remaining (dependent) structural parameters given in the lower half of the Table.

The observed molecular intensity curves upon which the refinements were based had been optimised with empirical background corrections using strict smoothness criteria. Refinements were carried out using a new least-squares programme [16], designated LSQ3, which employs as its basic data the partly levelled curves [12] for each camera distance. The data covered the following ranges (s_{min} - s_{max}) of the scattering variable $s = (4\pi/\lambda)\sin\theta$: 100 cm data, s = 1.00-7.50 $Å^{-1}$; 50 cm, 2.00-15.75 $Å^{-1}$; 25 cm, 7.0-31.0 $Å^{-1}$. The s-increments were 0.025, 0.05, and 0.1 $Å^{-1}$, respectively. Calculations were performed on the joint ICL 1906A/CDC 7600 computer system of the University of Manchester Regional Computing Centre.

DISCUSSION

The molecular parameters and preferred conformation assigned to perfluoro(methyloxirane) as a result of the e.d. study described above are summarised in Figures 2 and 3.



<u>Angles/°</u>

α 62.7; β 58.7;
γ 124 ; δ 111;
ε 114 ; θ 108.3;
C—C—F (av.) 121;
O—C—F (av.) 114;
O—C—CF_3 117

<u>Bond lengths/Å</u>

C—F (av.) 1.323;
C—O (av.) 1.410;
C—C (ring) 1.467;
C—CF_3 1.545

Fig. 2 Molecular parameters of perfluoro(methyloxirane)

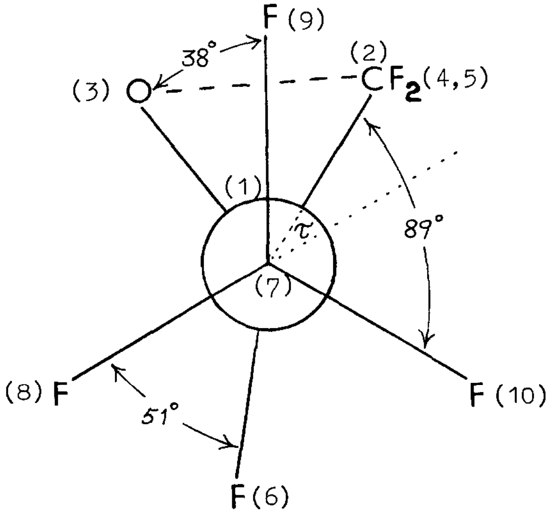


Fig. 3 Stereoformula of perfluoro(methyloxirane) viewed along the CF_3—C bond (numbers in parentheses refer to the component atoms, and correspond to those used in the Table and Fig.1).

Thus, the molecule possesses a semi-staggered conformation when viewed along the CF_3—CF bond; and, as expected from the bulky nature of a trifluoromethyl compared to a fluorine substituent, the angles C—C—CF_3 and O—C—CF_3 are distended by an increment of 3^{o} compared with the average intra-ring angles C—C—F and O—C—F.

The several assumptions which were made to reduce the number of independent parameters to be determined inevitably introduced systematic errors in the final values obtained; validities of the principal assumptions were discussed above in the Experimental Section, and some of the less certain constraints were relaxed in the final refinements. The most uncertain remaining feature is probably the value of 0.078 Å adopted for Δ_1, the difference between the lengths of the external and ring C—C bonds; for the hydrocarbon oxiranes studied by Smith and Kohl [1], the corresponding Δ_1 values are 0.058 and 0.071Å, so an e.s.d. of 0.01 Å for Δ_1 in the case of perfluoro(methyloxirane) seems a reasonable estimate, particularly since replacement of a C—CH_3 bond by C—CF_3 in related oxygen-based systems lengthens the C—C bond {*cf.* 1.546(5) Å in CF_3CO_2H [17] with 1.520(5) Å in CH_3CO_2H [18]}. The e.s.d. quoted in the final column of the Table include a component for the uncertainty in the remaining constraints.

No geometrical data appear to be available for perfluoro-oxirane, $\overline{CF_2CF_2O}$ [19], so it is possible to compare the present results only with those for oxirane and methyloxirane, both of which have been studied by microwave spectroscopy. The ring-bond lengths of C—C = 1.467(7) and C—O = 1.410(8) Å [Δ_2 = 0.057(11) Å] compare with r_0 values of 1.470(3) and 1.434(2) Å in oxirane [20], and 1.464(20) and 1.448(10) Å in methyloxirane [21][Δ_2 = 0.036(4) and 0.016(22) Å, respectively]; thus, the C—C bond lengths in these three molecules agree very well, as might be expected from consideration of the situation in perfluorocyclopropane [22] and cyclopropane [23] [1.505(3) and 1.509(2) Å, respectively], where the C—C lengths are hardly affected by fluorination. The larger Δ_2 value in the case of perfluoro(methyloxirane) stems from its C—O bonds being

0.024(9) Å shorter than the corresponding bonds in its hydrocarbon analogue; this is not unusual, since bonds from carbon to electronegative atoms generally shorten when additional electronegative substituents are introduced [24]. C—O Bond shortening brought about by perfluorination of methyloxirane is accompanied by lengthening of the external C—C bond from $\underline{r}_o$ = 1.499(10) to 1.545 Å.

In oxirane [20], ∠C—C—H and ∠O— C—H are 119.2 and 115.0°, respectively, and ∠H—C—H is 116.3(7)°. The corresponding angles in the present molecule, ∠C—C—F (av.) and O—C—F (av.), are 121(1) and 114(1)°, respectively, and angle F—C—F(ring) is 114°. Hence, the H—C—H and F—C—F(ring) planes both lean more towards the ring oxygen than the ring carbon, despite the fact that the C—O bonds are shorter than the C—C (ring) bonds. In methyloxirane [21], ∠C—C—C is 123(1)°, compared with 124(1)° for the perfluoro-compound, i.e. a little larger in both cases than the respective C—C—H and C—C—F (av.) angles, suggesting that CH_3 and CF_3 are exerting similar non-bonding interactions. In all three systems, oxirane, methyloxirane, and perfluoro(methyloxirane), the ring angles at oxygen are all a little larger than 60°, while all those at carbon are a little less.

Summarising the above discussion, the structural differences between perfluoro(methyloxirane) and its hydrocarbon analogue appear to be quite unremarkable except, perhaps, for the shorter C—O bonds in the former compound and the lengthening of the external C—C bond which accompanies fluorination.

ACKNOWLEDGEMENT

We are deeply indebted to the SRC for an equipment grant and to Norman Ramsey [9] for a pure sample of perfluoro(methyloxirane).

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