Molecular Structure of Bis(trifluoromethyl)hydroxylamine: an Electron Diffraction Study

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The molecular structure of bis(trifluoromethyl)hydroxylamine, $(CF_3)_2NOH$, has been determined in the vapour phase by the sector microphotometer electron diffraction method. Principal structural parameters with estimated standard deviations in parentheses are: r(N–O) 1·40(3), r(C–N) 1·435(fixed), and r(C–F) 1·322(2) Å; F–C–F 109·8(0·4), C–N–C 120·6(1·3), C–N–O 111·3°(0·8°). The longer N–O bond and smaller sum of angles at nitrogen than in $(CF_3)_2NO$ result in rather similar F · · · O distances in the two molecules.

Following our electron diffraction study of the stable free radical $(CF_3)_2NO$,[1] we have studied the related molecule $(CF_3)_2NOH$.

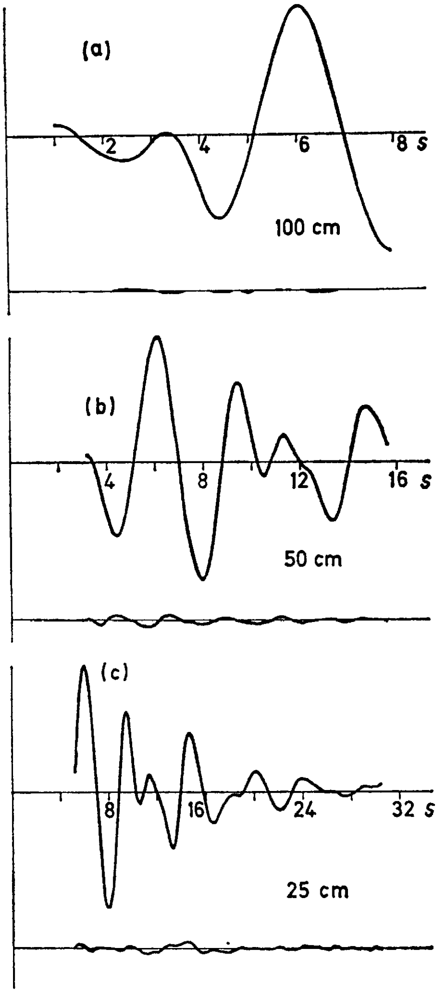

Figure 1 Observed and difference molecular intensity data

EXPERIMENTAL

Samples of $(CF_3)_2NOH$ were prepared from CF_3I by standard methods,[2,3] and purified by fractional condensation in a vacuum system. Electron diffraction data were recorded on Ilford N60 plates by use of the Balzers KDG2 apparatus at U.M.I.S.T., and transferred to punched paper tapes with an automated Joyce–Loebl microdensitometer. The electron wavelength was 0·05667 ± 0·00005 Å, and data were obtained at nozzle-to-plate distances of 100, 50, and 25 cm, giving a range of 1—30·4 cm^{-1} in the scattering variable, s. Our usual computational techniques[4,5] were employed in the data reduction, and in the least-squares refinements based on the molecular intensity curve. The complex scattering factors of Cox and Bonham were used.[6] All distances are r_a, and no correction for shrinkage has been applied.

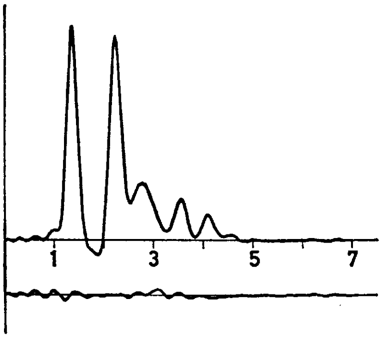

Figure 2 Observed and difference radial distribution curve, $P(r)/r$. Before Fourier inversion the data were multiplied by $s \exp(-0{\cdot}002\, s^2)/(Z_C - f_C)(Z_F - f_F)$

Molecular Model.—(a) *Geometry*. Certain plausible assumptions have been made about the molecular geometry in order to reduce the total number of parameters in the refinement. These were: (i) all C–F bond lengths are identical, and all F–C–F angles are equal; (ii) the two C–N bond lengths are identical, and any twisting of the CF_3 groups away from normal staggering about the C–N bonds is such as to maintain either C_2 or C_s symmetry for the entire $(CF_3)_2N$ group; and (iii) the oxygen atom is equidistant from the two carbon atoms. The principal structural parameters of the $(CF_3)_2N$ group were taken as the C–F and C–N bond lengths, and the F–C–F and C–N–C angles. The oxygen atom position was defined by the N–O bond length and by a co-ordinate Z, the distance of the oxygen atom from the CNC plane. Interatomic distances involving hydrogen were ignored apart from

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[1] C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, and S. M. Williamson, *J. Chem. Soc.* (*A*), **1971**, 2599.

[2] W. D. Blackly and R. R. Reinhard, *J. Amer. Chem. Soc.*, 1965, **87**, 802.

[3] P. M. Spaziante, Ph.D. Thesis, Cambridge University, 1969.

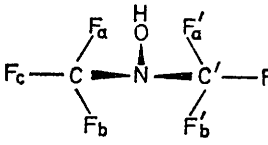
[4] B. Beagley, A. G. Robiette, and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1968, 3002.

[5] D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. J. Aylett, I. A. Ellis, and J. J. Monaghan, *J. Chem. Soc.* (*A*), 1969, 1224.

[6] H. L. Cox and R. A. Bonham, *J. Chem. Phys.*, 1967, **47**, 2599.

O–H, which was given the magnitude and vibrational amplitude found for H_2O.[7] We have also investigated the effect of twisting the CF_3 groups about their three-fold axes, and the effect of a tilt of these three-fold axes in the CNC plane.

(b) *Vibrational amplitudes.* Since in the radial distribution function there is extensive overlapping of peaks due to different atom pairs, it was found necessary to impose some constraints on the refinement of vibrational amplitudes. The amplitudes of the N–O, C–N, and N···F distances were fixed at appropriate values. Groups of remaining non-bonded amplitudes were constrained to have equal values. The amplitudes of distances through one angle (F···F at 2·16 Å, O···C and C···C) formed one group. The other distances were grouped according to the relative motions of atom pairs expected on the basis of torsional motion of the CF_3 groups about their three-fold axes [see (I)]. The distances $F_a\cdots O$, $F_c\cdots O$, $F_a\cdots C'$, $F_a\cdots F_a'$, and $F_b\cdots F_b'$, together with their primed equivalents, formed a second group. The third group contained the distances $C\cdots F_c'$, $F_a\cdots F_b'$, $F_b\cdots O$, $F_c\cdots F_c'$, and their equivalents. It was expected that the amplitude of vibration of this group would be smaller than that for the second group, since the relative motion of the pairs of atoms produced by a twisting about the local three-fold axes is more nearly perpendicular to the line joining them than is the case for the second group. The last group consisted of the remaining non-bonded distances, $F_c\cdots F_a'$ and $F_c\cdots F_b'$, together with their equivalents. In this way a satisfactory set of refined amplitudes was obtained.



(I)

RESULTS

Subject to these constraints, the C–F bond length, the F–C–F and C–N–C angles, and the out-of-plane co-ordinate *Z* of the oxygen atom were well determined. Attempts to refine both the C–N and N–O bond lengths independently led to unreasonably short values for the C–N bond length of about 1·41 Å, whereas in the similar molecules $(CF_3)_2N{\cdot}N(CF\ )_2$ [8] and $(CF_3)_2NO$ [1] the values obtained were 1·433 and 1·441 Å respectively. For most of the refinements reported here, the C–N bond length was fixed at 1·435 Å, close to the mean of these two values. This additional constraint allowed the N–O bond length to be refined successfully, and was found to influence the other geometrical parameters by less than one e.s.d.

The study[1] of $(CF_3)_2NO$ investigated the effects of varying the values of the C–N, N–O, and N···F amplitudes over a wide range. It was not felt necessary to repeat that work here, the values being taken from those found to be appropriate in the earlier study.

The relative conformations of the trifluoromethyl groups can be inferred from the radial distribution curve in the region 3·8—4·7 Å, where the longest F···F distances occur. The shape of the curve is generally consistent with a staggered model, as shown in (I), which, for the values of the other geometrical parameters obtained, has 4 F···F distances at *ca.* 4·1 Å ($F_a\cdots F_a'$, $F_b\cdots F_c'$ *etc.*) and one F···F distance at *ca.* 4·5 Å ($F_c\cdots F_c'$). We have considered the effects of rotating both trifluoromethyl groups about their three-fold axes by an angle θ, where θ has a value of 0° when the CF_3 groups are completely staggered, as in (I). Two molecular models were investigated; one (A) in which C_2 symmetry is maintained for the $(CF_3)_2N$ group, the other (B) in which C_s symmetry is maintained for the $(CF_3)_2NO$ group. Extensive trials revealed only one minimum for each model, at *ca.* $\theta = 5°$ (model A) and $\theta = 7°$ (model B). We prefer model A for two reasons: (i) the fit achieved by model A is better at the 99·5% confidence level[9] than that by model B [R_G (model A) = 0·080, R_G (model B) = 0·095; $R_G = (\mathbf{U'WU/I'WI})^{1/2}$ where **U** is the vector of residuals, **I** the vector of intensities, and **W** the weight matrix]; (ii) the shortest F···F

TABLE 1

Weighting functions, correlation parameters, and scale factors

Height/ cm	Δs	$s_{min.}$	s_1	s_2	$s_{max.}$	p/h	k
100	0·100	1·00	2·00	5·00	7·90	0·4960	0·761 ±0·004
50	0·200	3·20	4·70	10·20	15·60	0·4894	0·818 ±0·009
25	0·400	5·20	9·30	20·00	30·40	0·4740	0·794 ±0·010

R factors

R_G	0·080
R_D	0·049

TABLE 2

Distances and amplitudes/Å with estimated standard deviations in parentheses

	Distance	Amplitude	Parameter no.
(*a*) Independent distances			
r(N–O)	1·399(24)	0·050 *	r_1
r(C–N)	1·435 *	0·045 *	
r(C–F)	1·322(2)	0·048(6)	r_3 and u_3
Z	0·95(5)		r_4
(*b*) Dependent distances			
$r(C\cdots C')$	2·50(2)	0·065(6)	u_{21}
$r(F_a\cdots F_b)$	2·162(4)		
$r(C\cdots O)$	2·339(14)		
$r(N\cdots F_a)$	2·249(12)	0·08 *	
$r(N\cdots F_b)$	2·248(12)		
$r(N\cdots F_c)$	2·244(12)		
$r(F_a\cdots F_a')$	2·645(14)	0·126(14)	u_5
$r(C'\cdots F_a)$	2·841(12)		
$r(C'\cdots F_b)$	2·927(8)		
$r(F_a\cdots O)$	2·77(3)		
$r(F_c\cdots O)$	2·625(12)		
$r(F_a'\cdots O)$	2·87(3)		
$r(F_c'\cdots O)$	2·54(2)		
$r(C'\cdots F_c)$	3·592(14)	0·087(10)	u_6
$r(F_a\cdots F_b')$	3·56(2)		
$r(F_c\cdots F_c')$	4·48(2)		
$r(F_a'\cdots F_b)$	3·25(2)		
$r(F_b\cdots O)$	3·484(14)		
$r(F_b'\cdots O)$	3·46(2)		
$r(F_a\cdots F_c')$	4·062(6)	0·119(8)	u_{14}
$r(F_b\cdots F_c')$	4·047(8)		

* Parameter not refined.

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[7] S. Shibata and L. S. Bartell, *J. Chem. Phys.*, 1965, **42**, 1147.

[8] L. S. Bartell and H. K. Higginbotham, *Inorg. Chem.*, 1965, **4**, 1346.

[9] W. C. Hamilton, 'Statistics in Physical Science,' Ronald Press, New York, 1964.

distance between CF_3 groups in model B, 2·53 Å, is unreasonably short [*cf.* model A, 2·65 Å; $(CF_3)_2N{\cdot}N(CF_3)_2$,[8] 2·70 Å; $(CF_3)_2NO$,[1] 2·61 Å; van der Waals contact 2·70 Å]. It is possible that the deviation from the completely staggered conformation arises from a torsional shrinkage effect; further, the C_2 model may simply provide a better representation than the C_s model of the concerted torsional motion of the two CF groups.

TABLE 3

Angles/° with estimated standard deviations in parentheses

	Angle	Parameter no.
F–C–F	109·8(0·4)	<1
θ	5·4(0·7)	<2
φ	0·2(0·9)	<3
C–N–C	120·6(1·3)	<4
O–N–C	111·3(0·8)	
Δ	43·0(2·0)	

Δ Is the angle between the CNC plane and the NO bond.

TABLE 4

Least-squares correlation matrix multiplied by 1000

*r*1	*r*3	*r*4	<1	<2	<3	<4	*u*3	*u*5	*u*6	*u*14	*u*21	*k*1	*k*2	*k*3
1000	−690	666	717	−711	−390	670	−710	612	421	−121	519	87	220	232
	1000	−314	−774	447	399	−701	413	−430	−147	38	−687	−100	−271	−312
		1000	193	−338	159	142	−522	687	464	−235	150	−4	1	49
			1000	−465	−490	838	−502	234	85	−86	689	66	174	139
				1000	535	−574	508	−563	−284	−101	−315	−52	−131	−168
					1000	−778	239	−235	249	−271	−376	−79	−196	−158
						1000	−481	358	−95	20	604	81	166	92
							1000	−441	−254	167	−208	0	38	153
								1000	227	−26	213	2	28	147
									1000	−214	115	47	159	252
										1000	21	35	113	187
											1000	132	383	494
												1000	270	120
													1000	358
														1000

The effect of tilting the threefold axes of the CF groups in the CNC plane was also investigated. This tilt is defined by a parameter φ; positive values of φ indicate that the angle between the two local three-fold axes is greater than the C–N–C angle. φ Could be refined successfully, but the final value does not differ significantly from zero.

Table 1 gives the weighting functions, correlation parameters, and scale factors for the three sets of data. The distances, amplitudes of vibration, and angles obtained in the final least-squares cycle, when the C–N bond length was fixed and a C_2 model A assumed, are presented in Tables 2 and 3. The estimated standard deviations quoted in the Tables are based on those obtained in the least-squares refinement, but they have been increased in order to reflect our subjective judgement of the systematic errors, and errors introduced by the correlation between parameters [in the correlation matrix (Table 4) there are 6 elements numerically greater than 0·7], by the geometrical constraints imposed in the final refinement, and by the uncertainties in the electron wavelength.

DISCUSSION

Experimental values for the N–O bond length in nitroxyls and hydroxylamines cover a large range.[1,10] However, it is expected that in a similar chemical environment the 2-electron bond in $R_2N{-}OH$ would be longer than the 3-electron bond in $R_2N{-}O{\cdot}$; this is observed here for the CF_3-derivative, although neither value is very precise (Table 5). The C–F bond lengths and the F–C–F and the C–N–C angles in $(CF_3)_2NO$ and $(CF_3)_2NOH$ do not differ significantly. The O–N–C angle is appreciably smaller in the hydroxylamine. This difference is consistent with the expected change in hybridisation of the N atom when the partial double-bond character of the three-electron N–O bond is eliminated. Alternatively, this change can be attributed to steric factors, which have been invoked[8,1] to rationalise the relatively large X–N–C angles (X = N, O) found in $(CF_3)_2N{\cdot}N(CF_3)_2$ and $(CF_3)_2NO$. In the molecules $(CF_3)_2N{\cdot}N(CF_3)_2$, $(CF_3)_2NO$, and $(CF_3)_2NOH$ the shortest F(C) · · · (N)X distance is about 0·2 Å shorter than the sum of the van der Waals radii. In the present case, the combination of an N–O bond longer and an O–N–C angle smaller than the values found for $(CF_3)_2NO$ has resulted in essentially the same shortest F · · · O contact for the two molecules.

TABLE 5

Comparison of bond lengths/Å, angles/°, and non-bonded distances/Å; estimated standard deviations in parentheses

	$(CF_3)_2NOH$ [a]	$(CF_3)_2NO$ [b]	$(CF_3)_2N{\cdot}N(CF_3)_2$ [c]
r(C–F)	1·322(2)	1·320(4)	1·325(5)
r(C–N)	1·435 [d]	1·441(8)	1·433(7)
r(N–X) [e]	1·399(24)	1·26(3)	1·40(2)
Z [f]	0·95(5)	0·47(5)	0·22(10) [g]
F–C–F	109·8(4)	109·8(1·0)	108·2(0·5)
C–N–C	120·6(1·3)	120·9(2·0)	121·2(1·5)
C–N–X [e]	111·3(0·8)	117·2(0·6)	119·0(1·5)
Δ [h]	43·0(2·0)	21·9(3·0)	9(5) [g]
F · · · X [i]	2·54(2)	2·53(2)	2·59(2) [g]
F · · · F [j]	2·645(14)	2·61(2)	2·70(2) [g]

[a] This work. [b] Ref. 1. [c] Ref. 8. [d] Parameter not refined. [e] X = O or N. [f] *Z* Is the distance of the X atom from the CNC plane. [g] Estimated by the authors from the values in ref. 8. [h] Δ Is the angle between the CNC plane and the N–X bond. [i] The shortest distance between an F atom and the X atom. [j] The shortest distance between F atoms in different CF_3 groups.

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[10] 'Molecular Structures and Dimensions,' ed. O. Kennard and D. G. Watson, A. Oosthoek's Uitgevers Mij, Utrecht, 1970.