The Molecular Structure of Benzotrifluoride as Studied by Gas Electron Diffraction

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In memoriam Prof. Dr. Werner Zeil

The molecular structure of benzotrifluoride has been studied by electron diffraction. The geometry of the carbon ring is essentially regular hexagonal. The bond configuration of the trifluoromethyl group considerably departs from the regular tetrahedral arrangement. The following values were obtained for bond lengths (r_g) and bond angles: $r(\text{C–C})_{\text{ring}} = 139.7 \pm 0.3$ pm (mean value), $r(\text{C}_{\text{methyl}}\text{–C}_{\text{phenyl}}) = 150.4 \pm 0.4$ pm, $r(\text{C–F}) = 134.5 \pm 0.3$ pm, $r(\text{C–H}) = 109.9 \pm 0.5$ pm and $\sphericalangle$ C–C–F $= 111.9 \pm 0.1°$. The electron diffraction data are in agreement with nearly free rotation of the $-\text{CF}_3$ group around the $\text{C}_{\text{methyl}}\text{–C}_{\text{phenyl}}$ axis.

Introduction

Recent studies of the molecular geometries of mono- and disubstituted benzene derivatives have provided interesting information on the substituent effects for the ring deformation (cf., e. g. [1 – 6]). The CCC bond angle (α) adjacent to the substituent is the most sensitive geometrical parameter characterising the ring deformation. This angle may change by several degrees depending on the nature of the substituent. Very electronegative substituents substantially increase this bond angle, thus, e. g. it is 121.7° in chlorobenzene [4] and 123.4° in fluorobenzene [7]. A recent study [8] on group electronegativities (χ) empirically estimated χ_{CF_3} to be in between χ_{F} and χ_{Cl} (*viz.* 3.3, 4.0 and 3.0, respectively). This would suggest a considerable ring deformation in benzotrifluoride. On the other hand, Domenicano et al. [5] observed empirical correlations between the α angle and the substituent electronegativity indicating a systematic difference between the changes generated by second row and third row elements. This is shown in Figure 1. According to these correlations, very little ring deformation may be expected in benzotrifluoride.

As an extension of the earlier studies it was decided to investigate the molecular geometry of benzotrifluoride in the gaseous state by electron diffraction. Although better suited for more symmetrical molecules [3, 4], electron diffraction has already proved to be able to provide information on the ring deformation in toluene. This has been shown recently [3] while it is true that originally the ring deformation in toluene has not been examined [9]. The electron diffraction results [3, 9] have been in good agreement with *ab initio* calculations

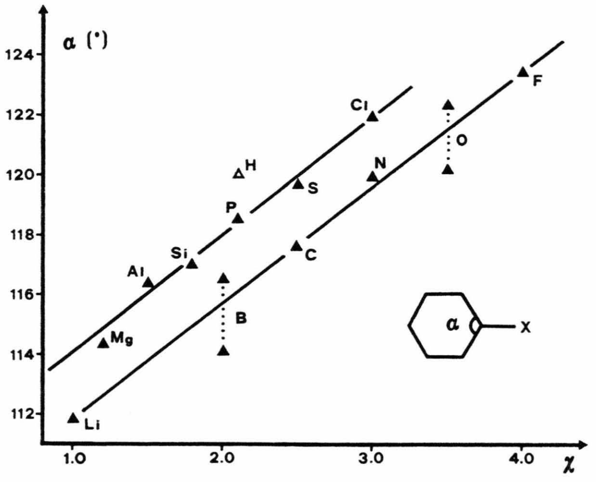

Fig. 1. Empirical correlations between the α angle and electronegativity of the substituent (χ). Separate correlations exist for elements belonging to the second and third rows of the periodic table. After Domenicano et al. [5].

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[10] as well as available microwave spectroscopic [11, 12] and low-temperature X-ray diffraction [13] results. It was anticipated that benzotrifluoride would be a better subject for electron diffraction due to the higher scattering power of fluorine than that of hydrogen. It was also expected that structural information could be gained about the influence of the phenyl group on the geometry of the trifluoromethyl moiety.

The molecular geometry of benzotrifluoride has not been studied before, but a recent microwave spectroscopic investigation [14] yielded accurate B and C rotational constants and a barrier height $V_0 = 42.7 \pm 1.3$ J/mol.

Experimental

The sample was a Fluka (Buchs, Switzerland) product. The Balzers KD-G2 unit of the Oslo laboratory was used for the experiments with the following data:

	50 cm camera range	25 cm camera range
Nozzle temperature (°C)	23	23
Electron wave-length (pm)	5.869	5.869
Number of plates analysed	5	5
Range of data (pm^{-1})	0.0125–0.15125	0.0300–0.2975
Δs (pm^{-1})	0.00125	0.0025

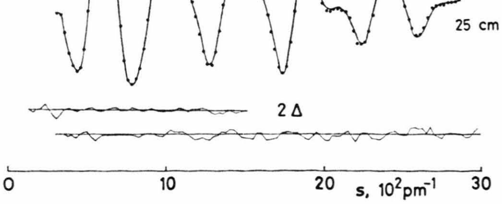

Fig. 2. Molecular intensity curves for the two camera ranges (E, experimental; T, theoretical), Δ = experimental-theoretical.

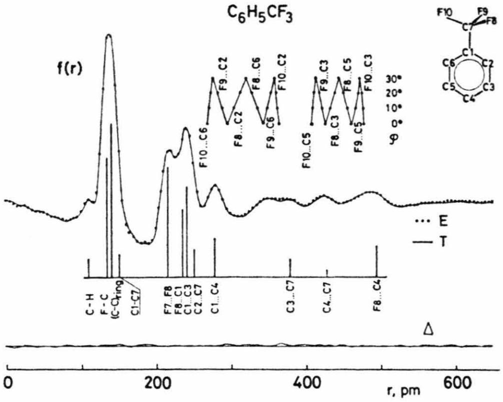

Fig. 3. Radial distribution curves (E, experimental; T, theoretical) and their difference (Δ). The positions of most important interatomic distances are indicated (the vertical lines mark the rotation independent distances, the possible positions of rotational dependent F ... C distances as function of rotational angle (φ) are also shown). The numbering of atoms is presented.

The data treatment and further analysis was similar to our earlier practice [3, 4, 9]. The experimental molecular intensities and radial distribution are shown in Figs. 2 and 3 together with theoretical ones calculated for the final model. As is indicated, some direct structural information could be read off the experimental radial distribution.

Structure Analysis and Results

The phenyl group and the trifluoromethyl groups were assumed to have C_{2v} and C_{3v} local symmetries, respectively. All C – H bonds were taken equal and it was also assumed that they bisect the respective CCC bond angles. The structural parameters have been refined by least-squares procedure based on the molecular intensities [15]. In most calculations a mean ring C – C bond distance has been refined. The results are collected in Table 1. The treatment of the mean amplitudes of vibration is also clarified in this Table. The correlation coefficients exceeding 0.5 in absolute value are given in Table 2. The deviations of the bond angles C6 – C1 – C2 and C1 – C2 – C3 from the regular 120° is about one standard deviation. Removel of the constraint concerning the equality of the ring C – C bond lengths led to unreasonable results. The ring bond angles themselves indicate very small ring deformation, if any, and this should correspond to very small differences between the ring C – C bond lengths.

As regards the trifluoromethyl rotation, three models have been considered in this analysis. A semi-rigid model with a well-determined angle of rotation and fairly small amplitudes of vibration for the rotation-dependent F ... C distances could be easily eliminated. Another model corresponding to unrestricted rotation or to rotation with very small barrier was set up by summing a series of rotational forms with appropriate weights to be determined. Attempts to determine these weights, however, proved unsuccessful. The third model was also based on non-rigidity of this molecule: it allowed for large vibrational amplitudes of the rotation-dependent F ... C distances (see Table 1) and an effective average angle of rotation as a result of the large-amplitude motion (cf. [15]).

Table 1. The molecular parameters (r_a) of benzotrifluoride from least-squares refinement. Parenthesized values are standard deviations. The symbols i through iv indicate vibrational amplitudes coupled with fixed differences in the refinements. Bracketted values were assumed.

Atomic pair	Multi-plicity	r_a/pm ∢/°	l/pm	
Independent geometrical parameters				
C–H	5	109.5 (3)	7.1 (3)	
F–C	3	134.34 (9)	4.8 (1)	
$(C–C)_{ring}$	6	139.51 (9)	[4.6]	
C1–C7	1	150.2 (2)	[5.0]	
∢ C1–C7–F		111.89 (9)		
φ		14.0 (5)		
∢ C6–C1–C2		119.7 (3)		
∢ C1–C2–C3		120.4 (3)		
Dependent geometrical parameters				
F8 ... F9	3	215.91 (8)	5.91 (8)	
F8 ... C1	3	235.9 (2)	6.9 (2)	
C1 ... C3	2	242.1 (3)	[5.4]	
C2 ... C6	1	241.2 (4)	[5.4]	
C2 ... C4	2	240.9 (4)	[5.4]	
C3 ... C5	1	242.5 (4)	[5.4]	
C2 ... C7	2	251.2 (2)	[6.7]	
C6 ... F10	1	272.1 (4)	10.6 (10)	i
C1 ... C4	1	278.6 (5)	[5.7]	
C2 ... C5	2	279.2 (3)	[5.7]	
F9 ... C2	1	286.9 (5)	10.6	i
F8 ... C2	1	308.1 (5)	14.3 (23)	
F8 ... C6	1	333.9 (5)	15.6 (24)	
F9 ... C6	1	352.3 (3)	8.0 (7)	ii
F10 ... C2	1	363.8 (2)	8.0	ii
C3 ... C7	2	379.7 (3)	[6.7]	
F9 ... C5	1	411.0 (4)	7.2 (6)	iii
F9 ... C3	1	421.0 (4)	7.2	iii
C4 ... C7	1	428.8 (4)	[6.5]	
F8 ... C3	1	435.8 (4)	7.2	iii
F8 ... C5	1	454.5 (5)	7.0 (9)	iv
F9 ... C5	1	468.3 (4)	7.0	iv
F10 ... C3	1	477.1 (4)	7.0	iv
F8 ... C4	3	494.9 (4)	10.1 (5)	
∢ F–C–F		106.9 (1)		
∢ C2–C3–C4		119.4 (3)		
∢ C3–C4–C5		120.7 (4)		

Table 2. Elements of correlation matrix (x) exceeding 0.5 in absolute value.

Parameters i	j	x_{ij} ($i \neq j$)
$r\,(C–C)_{ring}$	r (F–C)	− 0.769
∢ C–C–F	r (F–C)	0.816
∢ C–C–F	$r\,(C–C)_{ring}$	− 0.556
∢ C1–C2–C3	∢ C6–C1–C2	− 0.941
l (F–C)	$r\,(C–C)_{ring}$	− 0.814
l (F8 ... C1)	r (F–C)	0.577
l (F8 ... C1)	$r\,(C–C)_{ring}$	− 0.746
l (F8 ... C1)	l (F–C)	0.654
l (F9 ... C2)	l (F8 ... C2)	0.837
l (F8 ... C6)	l (F8 ... C2)	0.774
l (F8 ... C6)	l (F9 ... C2)	0.608
l (F8 ... C6)	l (F10 ... C2)	0.626
l (F8 ... C4)	l (F10 ... C3)	0.687
S_2[a]	r (C1–C7)	0.523

[a] Scale factor for the long camera distance data set.

The refinements have been carried out using various initial values for the rotational angle φ ($\varphi = 0°$ when one of the C – F bonds coplanar with the benzene ring). The results were invariant to the initial φ values. The refined φ value (Table 1) is close to the average of the two possible extreme φ values (0 and 30°) and may be regarded as an effective value corresponding to practically free rotation of the CF_3 group around the C – C bond. Assuming the potential of this rotation to have the form $V(\varphi) = \frac{1}{2} V_0 (1 - \cos 6\varphi)$, where V_0 is the barrier height, the average value of the angle of rotation is given as

$$\varphi_{av} = \int_0^{\pi/6} \exp(-V/RT)\,\varphi\, d\varphi \Big/ \int_0^{\pi/6} \exp(-V/RT)\, d\varphi .$$

Assuming that $\varphi = 0°$ corresponds to the potential minimum, the value of $\varphi_{av} = 14°$ suggests a barrier about 1 kJ/mole. Considering the uncertainty of this result, the agreement with the much more accurate data is satisfactory.

The results on the molecular geometry of $C_6H_5CF_3$ in terms of bond distances and bond angles with estimated total errors are collected in Figure 4. The bond lengths here are given as average distances ($r_g \approx r_a + l^2/r_a$). The total errors were estimated considering an 0.2% experimental systematic error and the standard deviations of the least-squares refinement which were increased by a factor of $\sqrt{2}$ to

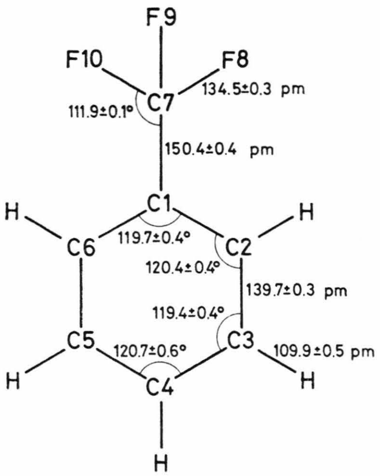

Fig. 4. Molecular geometry of benzotrifluoride molecule. Bond distances (r_g) are given in pm, angles in degrees. The estimated total errors are also given.

take account of possible correlation among the experimental intensities (cf. [17]).

As regards the assumptions for the local symmetries, in view of this investigation the phenyl group of $C_6H_5CF_3$ has indeed at least $\mathbf{C}_{2v}$ symmetry: as the benzene ring is practically undistorted, even $\mathbf{D}_{6h}$ symmetry would not be a very crude assumption. The practically freely rotating CF_3 group is not expected to distort the $\mathbf{C}_{2v}$ symmetry of the benzene ring. This nearly free rotation again is consistent with the $\mathbf{C}_{3v}$ symmetry assumed for the trifluoromethyl group.

Discussion

The small, non-significant ring deformation and the benzene-like mean C – C bond distance (C_6H_6: $r_g = 139.9 \pm 0.1$ pm [18]) in benzotrifluoride shows a very limited influence of the CF_3 group on the phenyl structure. This is in agreement with the empirical α vs. χ plot cited in Figure 1.

The bond configuration in the trifluoromethyl group considerably departs from the regular tetrahedral arrangement (F – C – F $106.9 \pm 0.1°$). The C – F bond here is much longer than that in CF_4 (131.7 pm) [19]. However, the F...F distance (215.8 pm) is the same as in a large series of molecules containing a CF_3 group. The remarkable stability of the F...F non-bond distance has recently been noted [20]. Similarly, we call attention, to the stability of the C...F distances in molecules containing $\succ$C – CF_3 or $\gg$C – CF_3 moiety. Thus, e. g.

CF_3CH_3	r_0	236.4 pm [21],
CF_3CF_3	r_g	235.2 pm [22],
CF_3CCl_3	r_0	234.7 pm [23],
CF_3CF_2H	r_0	235.2 pm [24],
$C_6H_5CF_3$	r_g	236.2 pm [present work].

Shorter C...F distances occur, however, in $\gg$C – CF_3 and $\equiv$ C – CF_3 moieties.

The rotational constants determined from the microwave spectra [7] and calculated from the present geometry are compared in Table 3. The agreement is good taking into account the uncertainties of the electron diffraction results and the difference in the physical meaning of the parameters originating from the two techniques. Of the three rotational constants, A' is the most sensitive to angular ring deformations. Thus the good agreement between the microwave and electron diffraction A' values gives further support to the essentially undistorted ring in benzotrifluoride.

Table 3. The experimental and calculated rotational constants of $C_6H_5CF_3$ molecule in MHz.

	A'	B	C
Microwave spectra [7]	5701.2 ± 5.0	946.31 ± 0.08	810.63 ± 0.04
Electron diffraction geometry	5675	942	808
Model a C6C1C2 122° C1C2C3 119°	5593	955	819
Model b C6C1C2 118° C1C2C3 121°	5796	931	802

A' does not contain the contribution of the CF_3 group. Models a and b were calculated from the geometrical data of Table 1 but with angularly distorted benzene rings.

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