Microwave Investigation of Tertiary Butyl Fluoride

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Determinations of the molecular structure of tertiary butyl chloride, bromide, and iodide have earlier been made by means of electron-diffraction technique [1] and microwave measurements [2]. All three molecules are symmetric tops, the threefold axis of symmetry being the carbon-halogen bond.

The electron-diffraction studies resulted in a model in which the carbon-halogen bond length was "normal", *i. e.* the same as in the methyl halides, while the angle C—C—C was found to be about 2° greater than the tetrahedral (109° 28′). The microwave measurements seemed, however, to indicate that the valence angles did not deviate from 109° 28′ and that the carbon-halogen bond length was "normal" inspite of the "tertiary" position of the halogen. In order to see whether the well-known differences in chemical reactivity of primary and tertiary bonded halogen may be partly or wholly contributed to a difference in bond length the present investigation of *tertiary butyl fluoride* was undertaken. In so doing one has, of course, abandoned to say anything definitely about the halides hitherto investigated, but probably the result for the fluoride does not deviate essentially from the correct configuration of other halides. It was decided to investigate the *fluoride* because its microwave spectrum to be expected is far more simple than the spectra of the other halides. The nuclear spin of chlorine (3/2), bromine (3/2), and iodine (5/2) deviates from 0 and $\frac{1}{2}$ which gives rise to a complicated hyper-fine structure in the molecular microwave-spectra. A detailed interpretation of these spectra has, therefore, not yet been possible. Furthermore, molecules in low-lying, torsionally excited states (rotation of the methyl groups) contribute with several extra lines, each with their hyperfine structure. As a result it is somewhat uncertain exactly what microwave absorption frequency should be used at the calculation of the moment of inertia [2]. Since the spin of the fluorine nucleus is $\frac{1}{2}$ the only complication left is the appearance of lines corresponding to molecules in vibrationally excited levels. Among the lines thus to be expected the absorption corresponding to molecules in the ground state must be by far the largest.

THE MICROWAVE SPECTRUM. MOLECULAR STRUCTURE

Experience fully confirmed the above expectations. The microwave absorption spectrum of tertiary butyl fluoride (TBF) consists of one strong line. and three weaker satellites the frequencies of which are given below in order of decreasing intensity.

18 849.8 Mhz ("main" line)
18 836.3 »
18 825.3 »
18 817.5 »

Relative intensities are given in the paragraph "internal rotation". Consequently the line at 18 849.8 Mhz must correspond to a transition for molecules in their ground state. By means of the formula

$$E_{rot} = \frac{h^2}{8\pi^2 c\, I_B}\, J\ (J+1)$$

and the Bohr frequency rule (E_{rot} is the rotational energy, h is Planck's constant, c the velocity of light, J the rotational quantum number, and I_B the moment of inertia about the principal axis perpendicular to the C—F bond) one calculates for the transition $J = 1 \rightarrow 2$

$$I_B = 107.25 \text{ A.M.U. } \text{Å}^2 = 178.03\ 10^{-40} \text{ gcm}^2.$$

Of course this information is insufficient for a determination of the five geometrical parameters of the molecule. Therefore, the electron-diffraction pattern was studied simultaneously in a collaboration with the Chemical Department of the University of Oslo, Blindern [3]. This part of the investigation is reported in the following paper by Bastiansen, and Smedvik [4]. If the reasonable assumption is made that the length of all the C—C bonds is 1.54 Å and that 1.093 Å is the length of all C—H bonds the following combinations of the geometrical parameters are compatible with the observed microwave absorption frequency at 18849.8 Mhz:

CCF-angle	CCH-angle	C—F Å
107°28′	107°28′	1.311
107°28′	109°28′	1.339
107°28′	111°28′	1.367 *
109°28′	107°28′	1.321
109°28′	109°28′	1.349
109°28′	111°28′	1.377 *
111°28′	107°28′	1.331
111°28′	109°28′	1.359
111°28′	111°28′	1.389

This shows that if the valence angles are assumed to be 109° 28' the C—F distance (1.349 Å) will deviate significantly from the distance in CH_3F (1.384 Å).

From the electron-diffraction pattern it follows, however, that the C—F distance is 1.38 ± 0.02 Å and that the CCF-angle is 108° ± 1.5°. The only combinations of the table above which agree with this are the two marked with an asterisk. The agreement between these two combinations is very satisfactory. It is, therefore, concluded, that the geometrical parameters of tertiary butyl fluoride are as given in Table 1.

Table 1. Geometrical parameters of tertiary butyl fluoride.

	Distances in Å	Angles
Found	C—F: 1.37 ± 0.01	CCF: 108° ± 1.5° CCH: 111°.5 CCC: 111° ± 1°.5
Assumed	C—C: 1.54 C—H: 1.093	

The result is independent of whether an 'eclipsed' or 'staggered' position of the methyl groups is assumed — and consistent with the electron-diffraction work by Beach and Stevenson [1] for the other halides.

INTERNAL ROTATION. POTENTIAL BARRIER

Since no hyperfine structure due the nuclear spin is to be expected and since the so-called K-type splitting is negligible at the low J-values involved it is necessary to interpret the lines other than 18 849.8 Mhz as due to molecules in vibrationally excited states. Due to its intensity the line at 18 836.3 Mhz could be due to molecules in the first vibrationally excited level, the line at 18 825.3 to molecules in the second vibrationally excited level etc. If all energy levels were non-degenerate this interpretation would be self-evident. Since this is not the case for TBF further evidence is necessary for this assignment.

In a molecule like TBF several low-lying, torsionally excited vibrational levels (rotation of the methyl groups) exist and two or three of these levels must be expected to lie lower than any other vibrationally excited level. According to this we shall show that the microwave lines at 18 836.3 and 18 825.3 Mhz may be interpreted as originating from molecules in the first and

second torsionally excited level, respectively. To check the validity of this, relative intensity measurements were carried out at 297° K and 213° K. Due to experimental conditions this latter temperature is not too well-defined.

Intensity ratios.

	18 836.3/18 849.8	18 825.3/18 836.3
At 297° K	0.54	0.61
» 213° K	0.35	0.38

Since one torsional vibrational quantum may be introduced in three ways (there are three methyl groups) and two torsional quanta may be introduced in six ways the ratios of the statistical weights of the ground level, the first and the second torsionally excited level are 1:3:6. The situation is pictured in Fig. 1.

	Concentration of molecules:	Statistical weights:
Second torsionally excited level	$\overline{\quad\Delta E_{21}\quad}$ c_2	6
First » » »	$\overline{\quad\Delta E_{10}\quad}$ c_1	3
Ground »	$\underline{\quad\Delta E_{10}\quad}$ c_0	1

Fig. 1. Showing statistical weights and 'population density' of ground and torsionally excited levels. Energy differences ΔE_{10} and ΔE_{21}.

From Boltzmann statistics it follows that

$$\frac{c_1}{c_0} = \frac{3}{1} \ \exp. \left(\frac{-\Delta E_{10}}{kT} \right) \text{ and } \frac{c_2}{c_1} = \frac{6}{3} \ \exp. \left(\frac{-\Delta E_{21}}{kT} \right)$$

At 297° K, $c_1/c_0 = 0.54$ while $c_2/c_1 = 0.61$. It follows that

$$\Delta E_{10} = 352 \text{ cm}^{-1} \text{ and } \Delta E_{21} = 245 \text{ cm}^{-1}.$$

At 213° K, $c_1/c_0 = 0.35$ while $c_2/c_1 = 0.38$. It follows that

$$\Delta E_{10} = 316 \text{ cm}^{-1} \text{ and } \Delta E_{21} = 246 \text{ cm}^{-1}.$$

Considering the difficulties involved in cooling the wave-guide with the gas in a well-defined way and the usual difficulties in accurate determinations of intensity the agreement between the two values of ΔE_{10} is satisfactory (the agreement in the two ΔE_{21}-values is accidental). It is, therefore, concluded that the torsional frequency, ν_t, of TBF is approximately $\dfrac{316 + 352}{2} =$ 334 cm^{-1}.

It seemed reasonable first to try to verify this directly by photographing the Raman spectrum of TBF which is particularly valuable for the identification of low-lying levels. This proved to be impossible due to the readiness with which the reaction

$$(CH_3)_3CF \rightarrow CH_2 = C(CH_3)_2 + HF$$
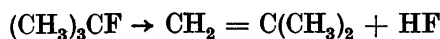
takes place. The infrared absorption spectrum was recorded in the region from 3 to 15 μ but, as one would expect, the spectrum was too complicated and the region investigated too narrow to permit any assignment of the torsional frequency. As a substitute for this, the Raman spectrum of the more stable $(CH_3)_3CCl$ was photographed. Here, a non-polarized line appeared at 305 cm^{-1} (medium intensity).

Since a direct verification of the assumption that the torsional frequency is 334 cm^{-1} proved impossible an indirect method was attempted. The height of the barrier, hindering the internal rotation, was estimated and compared with other estimated barrier heights.

Any moment of inertia, I, can be associated with a *rotational constant*, R, given by

$$R = \frac{h}{8 \; \pi^2 \; cI} = \frac{27.9865 \; 10^{-40}}{I \; (\text{gcm}^2)} \; \text{cm}^{-1}.$$

If a cosine form of the barrier hindering the rotation is assumed its height, V_0, is given by

$$V_0 = \frac{R^{CC}_{TBF}}{R^{CC}_{CH_3} \; R^{CC}_{FC(CH_3)_2}} \; \frac{\nu_t^2}{9}$$

Here, R^{CC}_{TBF} means the rotational constant corresponding to rotation of the entire molecule about the C—C bond while the quantities in the denominator correspond to rotations of the methyl and the $FC(CH_3)_2$ groups, respectively, about the same C—C bond.

In polar coordinates the equation of the inertial ellipsoid of TBF is

$$r^2 = \frac{1}{I_B \sin^2 \Theta + I_C \cos^2 \Theta}$$

Here, I_B is the magnitude of the two 'small' moments of inertia, I_C the magnitude of the great moment. Θ is the angle between radius vector, r, and the C—F bond. In A.M.U.Å^2, $I_B = 107.25$ and $I_C = 113.89$. TBF is, therefore, almost a spherical top. Its center of mass is close to the central carbon atom. An approximately correct value of the moment of inertia about the C—C bond is, therefore, found by setting $\Theta = 109°28'$ and ignoring that the axis

so considered deviates a little from the C—C bond. It is calculated that this moment of inertia is 107.99 A.M.U.Å², so that $R_{TBF}^{CC} = 0.1561$ cm⁻¹. Since $I_{CH_3}^{CC} = 5.40$ gcm² and $I_{TBF}^{CC} = 179.25$ gcm², $I_{FC(CH_3)_3}^{CC} = 173.85$ gcm². Consequently, $R_{CH_3}^{CC} = 5.21$ cm⁻¹ and $R_{FC(CH_3)_3}^{CC} = 0.1610$ cm⁻¹. The height of the barrier, V_0, is therefore

$$V_0 = 2\ 100 \text{ cm}^{-1} \text{ or } 6\ 000 \text{ cal/mole}$$

The height of corresponding barriers in $(CH_3)_3CH$, $(CH_3)_4C$, and $(CH_3)_3N$ has been estimated to 3 870, 4 200, and 4 270 cal/mole, respectively. It seems as if such barriers increase if fluorine is introduced, since the barrier height in CH_3CH_3 and CH_3CF_3 is 2 750 and 3 450 cal/mole [5], respectively. From these numbers it is estimated that the barrier height in TBF should be about 5 000 cal/mole. Considering the assumption made (cosine form of potential curve) and the above-mentioned experimental imperfectness the agreement with the value found is not unsatisfactory.

As further evidence for the above interpretation of the lines at 18 836.3 and 18 825.3 Mhz it can be mentioned that both lines definitely split into two components when observed under conditions of maximum resolving power, *i. e.* at low temperature and pressure. The splitting is due to the tunneling effect to be expected in such cases. The smallness was taken as a sign that hindered rotation takes place but that the barrier must be high.

The line at 18 817.5 Mhz probably belongs to the third torsionally excited level but the line was too weak and diffuse to be of value at the calculations of the torsional frequency.

DIPOLE MOMENT

In the case of TBF it is particularly important that the dipole moment can be found by microwave technique. Due to the instability of the molecule the ordinary methods meet with serious difficulties. Actually an attempted determination has had to be abandoned [10]. In the spectroscope, isobutylene and hydrofluoric acid do not interfere with the measurements of the displacements of the Stark components at various field intensities.

In the electric field (intensity F abs.volt cm⁻¹) a rotational energy level of a symmetric top is displaced and split according to the equation

$$\Delta E_{rot}(\text{cm}^{-1}) = \frac{-\mu E}{hc} \frac{KM}{J(J+1)} + \frac{E^2\mu^2}{2Bh^2c^2} \left[\frac{(3K^2 - J(J+1))(3M^2 - J(J+1))}{J^2(J+1)^2(2J-1)\ (2J+3)} - \frac{M^2K^2}{J^3\ (J+1)^3} \right]$$

μ is the dipole moment, J the rotational quantum number, K is the component of J in the direction of the C—F bond, M is the magnetic quantum number, and B is the rotational constant (0.15721 cm^{-1}). Since the selection rules are $\Delta J = 1$, $\Delta K = 0$, $\Delta M = 0$ we get that the Stark displacement, ΔS(cm^{-1}), corresponding to $(K,M) = (1.0)$ or (0.1) for the transition $J = 1 \rightarrow 2$, is

$$\Delta S(\text{cm}^{-1}) = \frac{E^2\mu^2}{2B\ h^2c^2}\left(\frac{6 \times 3}{4 \times 9 \times 3 \times 7} - \frac{-2}{1 \times 4 \times 1 \times 5}\right) = \frac{13E^2\mu^2}{210Bh^2c^2}$$

$$\Delta S(\text{Mhz}) = \frac{13E^2\mu^2}{210Bh^2c}$$

For the Stark component corresponding to $(K, M) = (0.0)$ one derives

$$\Delta S(\text{Mhz}) = \frac{-16E^2\mu^2}{105Bh^2c}$$

Thus the latter Stark component falls on the low-frequency side of the main line where all the satellites and their Stark components are situated while the former component lies at the high-frequency side where its observation is undisturbed. Measurements of the Stark displacement have, therefore, been carried out on this component. Table 2 gives the experimental results.

Table 2. Measurements of the transition $(J, K, M) = (1, 1, 0) \rightarrow (2, 1, 0)$ at various field intensities.

Field intensity F (abs.volts cm^{-1})	F^2	ΔS Mhz Undisplaced line at 18 849.8 Mhz
2.357	5.555	7.6 $\pm$ 0.1
2.525	6.375	8.7 $\pm$ 0.1
2.693	7.252	10.0 $\pm$ 0.1

From this it follows that the dipole moment of the molecule in its ground vibrational state in the ideal gas phase (the pressure being 0.003 mm at the measurements) is 2.15 ± 0.02 D. In Table 3 the dipole moments of the methyl and the tertiary *iso*-butyl halides are summarized.

Table 3. Dipole moments of methyl halides and tertiary butyl halides (D.U.).

	Fluoride	Chloride	Bromide	Iodide
Methyl halides	1.83 [6]	1.87 [7]	1.80 [8]	1.66 [7]
Tertiary butyl halides	2.15 [9]	2.04 [10]	2.17 [10]	2.20 [10]

PREPARATION

The procedure followed was a modification of the method given by Cooper and Hughes [11]. 55 g tertiary butanol (0.75 mole) and 30 g 40 % hydro-fluoric acid (0.60 mole) was heated in a platinum container on a water-bath for 1 hour during which period the temperature was raised from 20 to 100° C. The gases liberated were lead through a copper tube, partly filled with a mixture of finely powdered NaF and coarse CaF_2 for removal of excess hydrofluoric acid, and finally condensed in a glass trap at $-10°- -15°$ C. After cooling in a dry-ice-ether mixture the condensed gases were treated with bromine (about 16 g) which was added dropwise until the bromine color no more disappeared. In this way unsaturated compounds (such as *iso*-butylene) were converted into high-boiling liquids. After three fractionations at 0° C where low- and high-boiling fractions were discarded, 10 g of a sample boiling at 465—468 mm Hg was obtained. Yield: 22 %. The fractionations were carried out in a glass apparatus. TBF may be kept in glass containers at dry-ice temperature for months without any serious decomposition. At atmospheric pressure the' boiling point is 12° C.

SUMMARY

Because of the simplicity of its microwave spectrum TBF was chosen as an object for a combined electron-diffraction and spectroscopic investigation in order to decide whether the distances from carbon to primary and tertiary bonded halogen in simpler organic compounds differ. It was found that the C—F distance in TBF does *not* deviate significantly from the C—F distance in methyl fluoride. Small deviations from the regular tetrahedral value (109°28′) were found in the valence angles of TBF. The deviations are in the direction to be expected [12]. Observations of intensity relationships at two temperatures for lines corresponding to molecules in torsionally excited levels permitted the torsional frequency to be calculated. The interpretation was verified by calculation of the approximate height of the barrier, hindering the internal rotation of the methyl groups. The barrier height proved to be of the order of magnitude to be expected. The dipole moment of the molecule in its ground level was measured in the ideal gas state.

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