Short communication

THE MOLECULAR CONFORMATION OF BENZENE SULPHONYL CHLORIDE

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The molecular geometry and conformation of benzene sulphonyl chloride from electron diffraction were reported by Brunvoll and Hargittai in this journal a few years ago [1]. Recently Boggia et al. [2] recorded the microwave spectrum of this compound. From the a-type band spectrum they concluded that the molecule has a C_s structure with the chlorine atom in the plane of the benzene ring (dihedral angle $\tau = 0°$). This is in evident contrast to the results of the electron diffraction investigation [1] in which it was possible to exclude this form while the experimental data could be approximated equally well by either a model in which the benzene plane is perpendicular to the plane containing the sulphur—chlorine bond and the line bisecting the O=S=O angle ($\tau = 90°$) or an asymmetric model with $\tau = 75 \pm 5°$. In the former of these two models the mean vibrational amplitudes associated with some of the rotation-dependent distances were considerably larger than in the latter model. It is the purpose of the present communication to show that the microwave spectroscopic data are not really in disagreement with the electron diffraction structure.

From the electron diffraction bond lengths and bond angles the rotational constants A_0, B_0 and C_0 were calculated for the isotopic species $C_6H_5SO_2{}^{35}Cl$ as functions of τ. To allow a comparison with the observed low-resolution parameter $B + C$, the calculated quantity $B_0 + C_0$ was corrected according to the formula suggested by Farag and Bohn [3]. The results are given below,

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together with the asymmetry parameter κ and the isotopic shift Δ which occurs in $B + C$ when ^{35}Cl is substituted by ^{37}Cl:

τ (degrees)	κ	$B_0 + C_0$ (MHz)	$B + C$ (MHz)	Δ (MHz)
0	−0.806	1341	1347	−15.7
15	−0.812	1340	1346	−15.7
30	−0.830	1338	1344	−15.7
45	−0.859	1335	1340	−15.7
60	−0.896	1333	1336	−15.7
75	−0.939	1331	1333	−15.7
90	−0.969	1330	1331	−15.7

From the data in ref. 2, $B + C$ is extracted as 1354 MHz and Δ as −16 MHz. Superficially this seems to indicate a τ-value around 0°, but when the error limits of the electron diffraction geometry are taken into account, the calculated $B + C$ values are found to have an uncertainty of about 20 MHz. Therefore these values must be considered to be compatible with the microwave results for each value of τ, especially when one remembers that the two techniques should not be expected to agree much better than within 1% unless corrections for vibrational effects are applied. To determine the conformation from the microwave spectrum alone, a full set of rotational constants would be required, preferably for both chlorine isotopic species.

Two further arguments are presented by Boggia et al. [2] in favour of the conformation with $\tau = 0°$. One is the occurrence of b-type lines (which should be absent for τ around 90°). However, the evidence for b-type lines in Fig. 2 of ref. 2 is rather unconvincing. The other argument is the results of some standard CNDO/2 calculations. Boggia et al. [2] have obtained the energy minimum at $\tau = 0°$ and a maximum at $\tau = 90°$ with a barrier height of 17 kJ mol^{-1}. It is known, however, that for molecules with second-row atoms the standard CNDO/2 method in many cases fails to predict even qualitatively the relative stability of the conformers. Often, especially if the molecule contains strongly polarizing groups [4], the correct conformer can be obtained only by using the sp instead of the spd basis, i.e. by omitting the d-orbitals which are included in the basis of the standard CNDO/2 method. Therefore the CNDO/2 results cannot be considered to be reliable for making a choice between the rotational forms. In fact, according to our calculations* the standard CNDO/2 method (spd basis) gives, in agreement with the results of Boggia et al., the minimum energy at $\tau = 0°$ and the maximum at $\tau = 90°$, with a barrier height of 14 kJ mol^{-1}. When, however, the sp basis is used, the

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*Note that the OSCl angle of 54.9° used by Boggia et al. in their calculations involves an unrealistically short distance of 164.6 pm between the non-bonded Cl and O atoms. In our calculations the bond lengths and bond angles were taken from the electron diffraction structure analysis [1].

minimum is at $\tau = 90°$, the maximum at $\tau = 0°$ and the barrier height is 7 kJ mol^{-1}. The differences may be connected with the fact that the standard CNDO/2 method strongly exaggerates the population of the d-orbitals; in our calculations the sulphur d-population was 1.97 for all angles, which is quite close to the values obtained for some other sulphonyl chloride molecules [5].

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