Geometry of the Molecules CH3Cl and CH3Br

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Geometry of the Molecules CH₃Cl and CH₃Br

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IN organic-chemical problems one often meets with the question to what extent the substitution of one or more hydrogen atoms by so-called "electronegative" groups alters the original stereochemistry of the compound. The simplest case which can be studied in this respect is the substitution of one of the hydrogen atoms of methane by a halogen atom. Among the methyl halides conditions for studying the geometry are most favorable in the case of CH_3Cl and CH_3Br. Here, comparatively exact spectroscopic and interferometric data are available, which, in connection with thermodynamic data, give the best possible information on intramolecular distances and angles.

Penney[1] has given an approximative quantum-mechanical treatment of the bond energies and the valency angles of the methyl halides. To quote Penney, the result is that "if some or all of the hydrogen atoms in methane are replaced by other monovalent groups, the resulting deviations from the tetrahedral angle are remarkably small and can hardly exceed a few degrees."

If the greatest moment of inertia of a methyl halide is denoted by I_A, the small one by I_C, the C–X distance by a (X being a halogen atom), the C–H distance by d, the valency angle H–C–X by α and the mass of the atom or molecule Y by m_Y, we have:

$$I_C = 3m_H d^2 \sin^2 \alpha \tag{I}$$

$$(I_A - \tfrac{1}{2}I_C)m_{CH_3X} = a^2 m_X m_C + 3(a - d \cos \alpha)^2 m_X m_H + 3d^2 \cos^2 \alpha m_C m_H. \tag{II}$$

The quantities to be determined are a, d, and α. Sutherland[2] has discussed the matter from the point of view that the methyl group of the methyl halides has the same shape as in methane, e.g., that $d = 1.09A$ and $\alpha = 110°$. In the case of CH_3Cl, I_A and I_C were known from spectroscopic work. Thus, Sutherland could calculate a, the C–Cl distance. He found $a = 1.66A$ with a maximum possible error of 0.05A. However, from electronic diffraction experiments[3] a had been found to be $1.77A \pm 0.02A$. A serious discrepancy seemed to exist. As is easily seen this dis-

crepancy will vanish if we assume that the methyl group of the methyl halides and of methane may have a different shape. Indeed, new experimental data, published since the paper of Sutherland, seem to support this point of view.

In the case of CH_3Cl we can take $I_A = 57.9 \cdot 10^{-40}$ gcm² from the paper by Nielsen.[4] The value is good to 1–2 percent. $I_C = 5.44 \cdot 10^{-40}$ gcm² is good to about 5 percent.[5,6] Setting $a = 1.77 \pm 0.02A$ we get:

$I_A \cdot 10^{40}$	$I_C \cdot 10^{40}$	a A	$\alpha°$	d A	<HCH°
57.9	5.44	1.77	93	1.05	118
59.0	5.17	1.75	102	1.04	114
Val. for CH₃ group in CH₄:			110	1.09	110

$\alpha = 93°$ is the value obtained by using middle numbers of all experimental data. $\alpha = 102°$ is the maximum possible value. To some extent a similar result can be established in the case of CH_3Br. Taking $I_C = 5.37 \cdot 10^{-40}$ gcm² ± 5 percent[5,6] and $a = 1.91 \pm 0.06A$[7] we only miss a value for I_A to be able to calculate α and d. Egan and Kemp[8] have determined the standard entropy of CH_3Br at 276.66°K. Besides being a function of a number of quantities, such as the vibrational frequencies of the molecule, which are all known practically exact, the entropy is a function of $I_A^2 \cdot I_C$. We get:

$$I_A^2 I_C = 33,400 \cdot 10^{-120} \text{ g}^3 \text{ cm}^6 \pm 10 \text{ percent}.$$

Substituting $I_C = 5.37 \cdot 10^{-40}$ we get $I_A = 78 \cdot 10^{-40} \pm 8$ percent. Another estimate of I_A can be obtained from the doublet separation, $\delta\nu$, of the ‖ bands in infra-red. Taking the average value of the $\delta\nu$'s which have been determined by several authors,[5,9–11] as 25.0 cm⁻¹ ± 1 cm⁻¹ we get: $I_A = 82 \cdot 10^{-40} \pm 10$ percent.

In a paper to be published the author[12] has studied the equilibrium $CH_3Br + HCl \lessgtr CH_3Cl + HBr$ in a temperature interval from 70°C to 335°C. The exact knowledge of the equilibrium constant at different temperatures permits of calculating the ratio $I_A(CH_3Br):I_A(CH_3Cl)$, as $I_C(CH_3Br)$ to a good approximation is equal to $I_C(CH_3Cl)$. The result is that $I_A = 76.0 \cdot 10^{-40} \pm 4$ percent. From these three determinations we conclude that $I_A = 77.5 \cdot 10^{-40}$ gcm² ± 4 percent. The corresponding values of α and d are given below.

$I_A \cdot 10^{40}$	$I_C \cdot 10^{40}$	a A	$\alpha°$	d A	<HCH°
77.5	5.37	1.91	90	1.04	120
80.5	5.11	1.85	111	1.08	110
Val. for CH₃ group in			110	1.09	110

$\alpha = 90°$ is the value obtained using middle numbers of all experimental data. $\alpha = 111°$ is the maximum possible value.

For CH_3Cl it thus seems firmly established that α deviates considerably from the tetrahedral angle. For CH_3Br the same is very probably the case. The methyl group in CH_3Cl and CH_3Br thus seems to be considerably more 'flat' than in CH_4.

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