DET KGL. DANSKE VIDENSKABERNES SELSKAB
MATEMATISK-FYSISKE MEDDELELSER, BIND XXIV, NR. 10

GEOMETRY OF THE MOLECULES METHYL CHLORIDE AND METHYL BROMIDE

BY

B. BAK

KØBENHAVN
I KOMMISSION HOS EJNAR MUNKSGAARD
1947

Printed in Denmark.
Bianco Lunos Bogtrykkeri

1. Introduction.

The determination of the exact geometrical shape of the methyl halides is of more general interest. It has long been realized that numerous chemical problems which hitherto could only be treated empirically or half-empirically, as e. g. the Walden inversion, should be studied by means of the methods of quantum mechanics. A first step which should enable us to perform such calculations is, of course, the study of the geometrical configuration of the molecule.

In organic-chemical problems we often meet with the question to what extent the substitution of one or more hydrogen atoms by so-called "electro-negative" atoms or groups, such as the halogens, will alter the original stereochemistry of the compound. In this respect the simplest cases are the methyl halides, and conditions are most favourable in the case of CH_3Cl and CH_3Br. Here, comparatively exact spectroscopical and interferometrical data are available which, in connection with thermodynamical data, offer the best possible information on the geometrical properties of the molecules.

PENNEY[1] has given a quantum mechanical treatment of the bond energies and the valency angles of the methyl halides. The treatment, of course, is only approximative, To quote PENNEY, the result is that "if some or all of the hydrogen atoms in methane are replaced by other mono-valent groups, the resulting deviations from the tetrahedral angle are remarkably small, and can hardly exceed a few degrees". Beside this theoretical treatment, a contribution based upon spectroscopical results was later given by SUTHERLAND[2]. However, since the paper of SUTHERLAND was

[1] PENNEY, Trans. Far. Soc. **31**, 734 (1935).
[2] SUTHERLAND, ibid. **34**, 325 (1938).

published, many new important spectroscopical and thermodynamical data have been found which make a new treatment interesting.

2. Relations Between the Intramolecular Distances and Angles in the Methyl Halides and the Two Principal Moments of Inertia. Numerical Calculations.

In Fig. 1, X is the halogen atom, C the carbon atom, and H a hydrogen atom. T is the center of gravity, d is the distance C—H, and a the distance C—X. The supplementary angle to

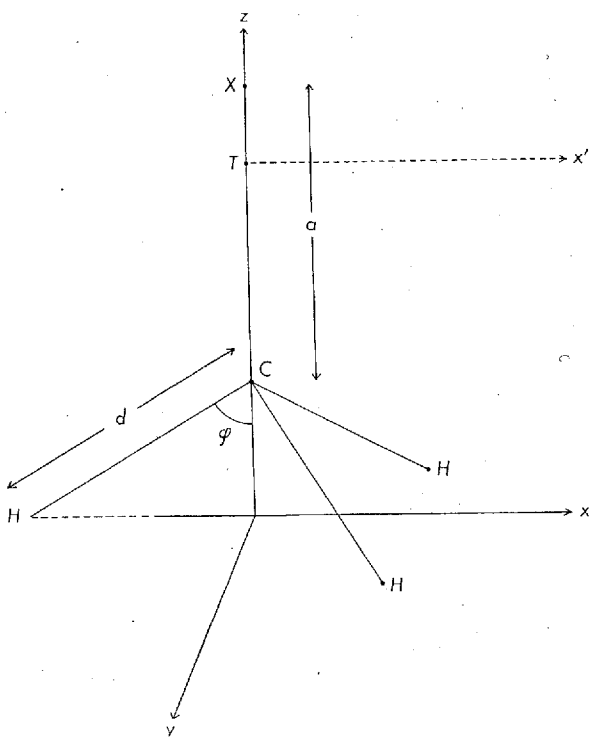

Fig. 1.

H—C—X is denoted by φ. I_C is the moment of inertia around the z-axis and I_A the corresponding quantity around the x'-axis. Then, the following relations hold:

$$I_C = 3\, m_H\, d^2 \sin^2 \varphi. \qquad (1)$$

$$I_A - \frac{1}{2} I_C = a^2 \frac{m_X\, m_C}{m_{CH_3X}} + 3\,(a + d\cos\varphi)^2 \frac{m_H\, m_X}{m_{CH_3X}} + 3\, d^2 \cos^2\varphi \frac{m_C\, m_H}{m_{CH_3X}}. \qquad (2)$$

Here, m_H is the mass of the hydrogen atom, etc.

The quantities to be determined are a, d and φ. a, the distance between the carbon and the halogen atom, has been determined by electron scattering experiments.

	a Å.	
CH_3Cl	1.77 ± 0.02	SUTTON and BROCKWAY[1].
CH_3Br	1.91 ± 0.06	LEWY and BROCKWAY[2].

It is to be expected that these values are rather reliable since in the electronic scattering experiments the molecule practically acts as if it was diatomic owing to the small scattering effect of the hydrogen atoms. Thus, the additional knowledge of I_A and I_C will enable us to calculate d and φ by means of (1) and (2).

Our present knowledge of I_A and I_C for CH_3Cl is mainly based upon a work of NIELSEN[3] and papers by BENNETT and MAYER[4] and JOHNSTON and DENNISON[5]. Studying the fine structure of the infrared band at 1355 cm^{-1} NIELSEN was able to show that $I_A = 57.9\ 10^{-40}$ gcm^2. Utilizing the measurements of BENNETT and MAYER, JOHNSTON and DENNISON could show that $I_C = 5.44\ 10^{-40}$ gcm^2. NIELSEN's value of I_A is probably exact within 1—2 per cent*, while I_C is uncertain to 5 per cent.

The present values of I_A and I_C for CH_3Br were communicated and discussed by the author in a previous paper[6]. $I_C = 5.37\ 10^{-40}$ $gcm^2 \pm 5$ per cent and $I_A = 77.5\ 10^{-40}$ $gcm^2 \pm 4$ per cent, values which are equally well consistent with spectroscopical[7], heat capacity[8], and equilibrium[9] data.

[1] Journ. Am. Chem. Soc. **57**, 473 (1935).
[2] Ibid. **59**, 1662 (1937).
[3] NIELSEN, Phys. Rev. **56**, 847 (1939).
[4] BENNETT and MAYER, Phys. Rev. **32**, 888 (1928).
[5] JOHNSTON and DENNISON, Phys. Rev. **48**, 868 (1935).
[6] B. BAK, D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd. XXIV, 9 (1948).
[7] BENNETT and MAYER, loc. cit.
[8] EGAN and KEMP, Journ. Am. Chem. Soc. **60**, 2097 (1938).
[9] B. BAK, loc. cit.
* Compare, however, the note added in proof.

	$I_A \cdot 10^{40}$	$I_C \cdot 10^{40}$
CH_3Cl	57.9	5.44
CH_3Br	77.5	5.37

By means of these values the following figures for d and φ are calculated:

	$I_A\,10^{40}$	a Å	$I_C\,10^{40}$	φ	d Å
CH_3Cl	57.9	1.77	5.44	87°	1.05
CH_3Br	77.5	1.91	5.37	90°	1.04
Tetrahedral angle:				70°	
C—H distance in CH_4:					1.09

The figures given here are, of course, not exact, as the experimental data on which they are based have a given uncertainty. Considering equation (2) we see that the least possible value of φ is obtained by using the highest possible value of I_A and, at the same time, minimum values of a and I_C. When carrying through the calculations as above we find:

	$I_A\,10^{40}$	a Å	$I_C\,10^{40}$	φ	d Å
CH_3Cl	59.0	1.75	5.17	78°	1.04
CH_3Br	80.5	1.85	5.11	69°	1.08
Tetrahedral angle:				70°	
C—H distance in CH_4					1.09

In the case of CH_3Cl it seems firmly established that φ deviates considerably from the tetrahedral angle. For CH_3Br it is necessary to assume a maximum deviation from the experimental average in order to get a model with $\varphi = 70°$. It seems thus unevitable to draw the conclusion that the methyl group of CH_3Cl and CH_3Br is far more "flat" than that of CH_4, in contrast to the result obtained by PENNEY.

Note added in proof: In a letter to Phys. Rev. 72, 344 (1947) GORDY, SIMMONS and SMITH have reported $I_A(CH_3Cl^{35}) = 63.1 \cdot 10^{-40}$ gcm^2 and $I_A(CH_3Br) = 87.5 \cdot 10^{-40}$ gcm^2. A serious discrepancy thus exists between this microwave value and $I_A(CH_3Cl) = 57.9 \cdot 10^{-40}$ gcm^2 given by NIELSEN (loc. cit.), which is hardly explanable by experimental uncertainty. Should the values found by means of the new microwave technique be confirmed by future experiments, they will mean a confirmation of PENNEY's viewpoint:

	$I_A\,10^{40}$	a Å	$I_C\,10^{40}$	φ	d Å
CH_3Cl	63.1	1.77	5.44	69°	1.10
CH_3Br	87.5	1.91	5.37	67°	1.12
Tetrahedral angle:				70°	
C—H distance in CH_4					1.09

Universitetets kemiske Laboratorium.
Copenhagen.

Indleveret til Trykkeriet d. 6. August 1946.
Færdig fra Trykkeriet d. 31. December 1947.