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THE CONFORMATION OF OPEN-CHAIN COMPOUNDS I. DIPOLE MOMENTS AND VICINAL PROTON SPIN COUPLING CONSTANTS OF 1,1,2-TRICHLORO- AND 1,1,2-TRIBROMOETHANE

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In previous work (1,2) the correlation between the dipole moments and the vicinal proton spin coupling constants of trans-1,2-dihalogenocyclohexanes and -cyclopentanes was discussed. The present paper deals with a comparable relationship between the dipole moments and the vicinal proton coupling constants of 1,1,2-trichloroethane (I) and 1,1,2-tribromoethane (II), in benzene and in carbon tetrachloride. In the conformational equilibrium two conformers differing in polarity (anti (a) and gauche (g)) are predominant. In the anti form, which has double probability, the torsional angle ψ (see Fig. 1) is 70° (3).

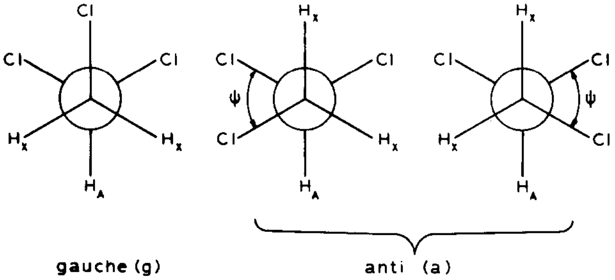

FIG. 1. The conformers of 1,1,2-trichloroethane.

The proton coupling of interest is that between H_A and H_X (AX_2-type). As J_{HH} is a function of the torsional angle between the protons according to the modified Karplus equation (2,4):

$$J_{\psi} = A\cos^2\psi_{HH} - B\cos\psi_{HH} + C \qquad (1)$$

we write J_{AX} of the gauche form as J_{60}, of the anti form as $1/2(J_{70} + J_{170})$. The observed $J = J_{AX}$ is given by the expression:

$$J = (1 - x_a)\, J_{60} + 1/2\, x_a\, (J_{70} + J_{170}) \qquad (2)$$

where x_a is the molar fraction of the anti form (5). Similarly, the squares of the dipole moments are related by the expression:

$$\mu^2 = (1 - x_a)\ \mu_g^2 + x_a\, \mu_a^2 \qquad (3)$$

Combining (2) and (3) it is seen that a linear relation between J and μ^2 should hold with a slope:

$$H = d\mu^2/dJ = (\mu_a^2 - \mu_g^2)/(1/2\ (J_{70} + J_{170}) - J_{60}) \qquad (4)$$

H can be expressed in terms of the Karplus constants and the partial electric moment along the C-halogen bond (μ_p) with the aid of eq.(1) and the usual vector calculation of dipole moments. We obtain (cf. ref. 2):

$$\mu_g = 1.78\ \mu_p\ ;\quad \mu_a = 0.79\ \mu_p \qquad (5)$$

$$H = -8.5\ \mu_p^2/(A + 2.75B) \qquad (6)$$

μ_p is the partial electric moment along the C-X bond in the CH_2X-moiety. The partial moments along the C-X bonds in the CHX_2-moiety are taken 15% lower than μ_p (6).

Results

Dipole moments at 25°C and J_{AX} for compounds I and II in benzene and in carbon tetrachloride are collected in Table I. A plot of μ^2 against J gives a straight line (Fig.2), which obeys the relation:

$$\mu^2 = -1.4\ J + 11.0 \qquad (7)$$

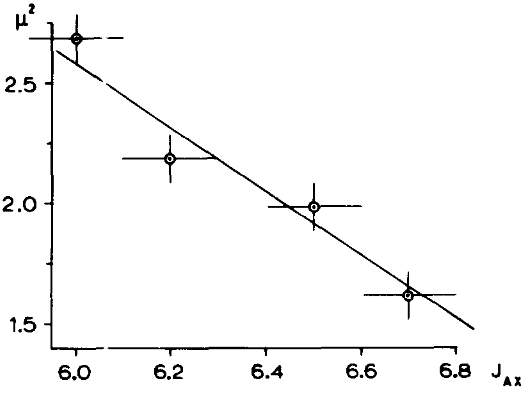

FIG. 2. Plot of μ^2 against J for compounds I and II in benzene and in carbon tetrachloride.

Now the dipole moments of the two conformers can be calculated in two different ways: (i) Sheppard et al. (8) derived $J_g = 3$ c/s and $J_a = 6.8$ c/s from a direct infrared measurement of the proportions of the isomers of compound I in different solvents. Substituting these values in eq.(7), we get $\mu_g = 2.6$ D, $\mu_a = 1.2$ D. Abraham et al.(9) calculated $J_g = 2.2$ c/s and $J_a = 6.83$ c/s from the observed J_{AX} of compound I in a number of solvents. Using eq.(7) this yields $\mu_g = 2.8$ D, $\mu_a = 1.2$ D.

(ii) From the slope with eqs. (5) and (6), using the theoretical Karplus constants (4) A = 9, B = 1/2, which are in good agreement with those experimentally found from Sheppard's J-values (8). Then we find: μ_p = 1.4 D, μ_g = 2.5 D, μ_a = 1.1 D. These values agree well with those found by method (i).

The value of μ_p (1.4 D) is appreciably lower than the moment of ethyl chloride (7): 2.04 D. The decrease of the partial moment of the C-halogen bond is ascribed to mutual induction. Introduction of additional chlorine atoms decreases μ_p still further, cf. the electric moment of pentachloroethane : 0.9 D (7).

With the aid of eq.(3) the molar fractions x_g and the free energy differences at 25°C, ΔH^o_{a-g}, can be calculated for the two compounds. The results, taking μ_g = 2.5 D and μ_a = 1.1 D, are collected in Table I.

TABLE I

Compound	Solvent	μ (D)	J_{AX}	x_g	ΔH^o_{a-g}(kcal/mole)
I	C_6H_6	1.64	6.0	0.71	-0.1
	CCl_4	1.48	6.2	0.81	-0.4
II	C_6H_6	1.41	6.5	0.85	-0.6
	CCl_4	1.27	6.7	0.92	-1.0

Remarkably, there is a characteristic 'benzene' effect, favouring the anti form to the extent of0.3-0.4 kcal/mole. This benzene effect, that had been observed earlier with the trans-1,2-dihalogenocyclohexanes (10,11) and -cyclopentanes (1), thus seems to occur generally with alicyclic and aliphatic vicinal halogeno compounds. Its origin forms an object of special study in this laboratory.

Experimental

The dipole moments were measured at 25°C as described previously (1). The NMR spectra were obtained from solutions (10 mole %) on a Varian HA 100 spectrometer.

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5) The assumption of trigonal projection symmetry implicit in eq.(2) is justified by calculation of the projected valency angles from the bond angles in ref. (3). The maximum deviation is of the order of 2°.

6) cf. the dipole moments of chloroethane and 1,1-dichloroethane (7).

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