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THE CONFORMATION OF NON-AROMATIC RING-COMPOUNDS—XXVII

THE DIPOLE MOMENTS OF TRANS-aa-DIHALOGENO-4-t-BUTYLCYCLOHEXANES*

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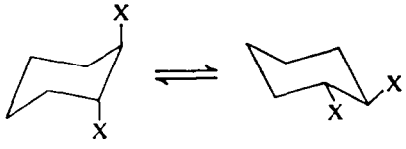
Abstract—Some *trans*-diaxial-1,2-dihalogeno-4-t-butylcyclohexanes have been synthesized and the dipole moments determined in carbon tetrachloride and in benzene at 25°. It is concluded that the diaxial conformer of *trans*-1,2-dibromo(chloro)cyclohexane probably has a dipole moment of 1·20 D.

INTRODUCTION

THE conformational analysis of *trans*-1,2-dihalogenocyclohexanes in solution by means of physical methods such as IR, Raman and NMR spectroscopy and dielectric measurements, has been reported in a number of papers.[1–9] The conformational



equilibria of these compounds in solution as well as in the vapour state[1–4,6,8] have been calculated using the expression for the mean square moment of the equilibrium mixture

$$\mu^2 = X_{aa}\mu_{aa}^2 + X_{ee}\mu_{ee}^2$$

in which X_{aa} and X_{ee} denote the molar fractions and μ_{aa} and μ_{ee} the dipole moments of the diaxial and the diequatorial conformers respectively. In the older calculations the dipole moment of the diaxial conformer was provisionally assumed to be zero. The moment of the diequatorial conformer was estimated to be 3·13 D, equal to that of the *cis*-1,2-dihalogenocyclohexanes. In 1960 Wessels[10] applying Winstein and Holness'[11] method for obtaining conformational homogeneity by introducing a

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t-butyl group into the cyclohexane ring, found the dipole moment of *trans*-aa-1,2-dibromo-4-t-butylcyclohexane to be 1·1 D and the moment of the *trans*-ee compound to be 3·3 D. These results are consistent with those of van der Linden,[12] who has effected conformational homogeneity by the attachment of a second cyclohexane ring in *trans* junction (e.g. *trans*-aa-2,3-dibromo-*trans*-decalin; $\mu = 1{\cdot}1$ D).

In a study of the addition reaction of bromine chloride to alkyl-substituted cyclohexenes[13,14] a number of *trans*-aa-1,2-dihalogeno-4-t-butylcyclohexanes were prepared. The dipole moments were determined in carbon tetrachloride as well as in benzene. The values are represented in Table 1.

TABLE 1.—DIPOLE MOMENTS OF *trans*-aa-1,2-DIHALOGENO-4-t-BUTYLCYCLOHEXANES IN CARBON TETRACHLORIDE AND IN BENZENE AT 25°

X_1	X_2	μ(D) CCl_4	μ(D) Benzene
Cl	Cl	1·21	1·20
Cl	Br	1·22	1·21
Br	Cl		
Br	Br	1·19*	1·23

* A sample from Dr. E. C. Wessels[10] was also found to have a moment of 1·19 D in carbon tetrachloride. The small difference with his results (1·1 D) can probably be attributed to the difference in the apparatus used.

DISCUSSION

As can be seen from Table 1 the dipole moments are independent of the solvent. From spectroscopic evidence[14] it is known that these compounds are not contaminated with the diequatorial isomers. Therefore, the value of ~1·20 D is to be attributed entirely to the diaxial isomer. Geise *et al.*[15] recently reported the dipole moments of *trans*-2,3- and *trans*-5,6-dihalogenocholestanes. The moments of the diaxial dihalides (1·11–1·40 D) were explained partly by the fact that the angle between the two C-Hal bonds (ca. 155°) differs considerably from 180°, and partly by inductive effects. These effects also operate in the case of simple cyclohexane derivates. Table 1 shows that there is no change in moment in the sequence dichloride → bromochloride → dibromide. This would suggest that the X_1-C_1-C_2-X_2 angle is approximately constant in the series, a conclusion that is supported by the results obtained by Altona,[16] who performed X-ray analyses of some 2,3-dihalogeno-1,4-dioxans.

In using these *trans*-1,2-dihalogeno-4-t-butylcyclohexanes as conformationally homogeneous model compounds for the conformers of *trans*-1,2-dihalogenocyclohexanes, it has to be assumed that the t-butyl group does not introduce additional effects of polar and/or steric nature. The absence of polar effects is supported by a comparison of the dissociation constants of *trans*-4-t-butylcyclohexanecarboxylic

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acid and of cyclohexanecarboxylic acid.[17] From a study of the IR and Raman spectra of a number of *trans*-1,2-dihalogeno-alkylcyclohexanes[18] it is concluded that a small steric effect due to the t-butyl group cannot be ruled out. Nevertheless, the most probable value of the dipole moment of the diaxial conformer of the *trans*-1,2-dibromo (chloro)cyclohexanes seems to be 1·20 D. For the moment of the diequatorial conformer the value of 3·30 D given by Wessels[10] for *trans*-ee-1,2-dibromo-4-t-butylcyclohexane (3·28 D in carbon tetrachloride and 3·33 D in benzene) seems to be representative.

EXPERIMENTAL*

4-t-Butylcyclohexene was obtained by the method described by Sicher *et al.*[19] in 85% yield; b.p. 61·5–62·5°/18 mm; n_D^{20} 1·4587 (reported:[19] b.p. 54–55°/10 mm; n_D^{20} 1·4587).

trans-aa-1,2-Dichloro-4-t-butylcyclohexane was obtained by chlorinating 4-t-butylcyclohexene employing sulphuryl chloride;[20] b.p. 78–80°/1·5 mm; n_D^{20} 1·4856. (Found: Cl, 33·9. Calc. for $C_{10}H_{18}Cl_2$: Cl, 33·9%.) This dichloride was also prepared by chlorinating 4-t-butylcyclohexene with lead tetraacetate–hydrogen chloride, a method described elsewhere.[21]

trans-aa-1,2-Bromochloro-4-t-butylcyclohexane was prepared by the addition of bromine chloride to 4-t-butylcyclohexene employing N-bromosuccinimide–hydrogen chloride as described elsewhere,[13,14] b.p. 84–86°/1·5 mm; n_D^{20} 1·5050. (Found: Hal, 46·3. Calc. for $C_{10}H_{18}BrCl$: Hal, 45·5%.)

trans-aa-1,2-Dibromo-4-t-butylcyclohexane was synthesized by the addition of Br_2 to 4-t-butylcyclohexene in methylene chloride at −70°; b.p. 81–82°/0·4 mm; n_D^{20} 1·5273 (reported:[10] b.p. 105–106°/2·75 mm; n_D^{20} 1·5277). (Found: Br, 53·9. Calc. for $C_{10}H_{18}Br_2$: Br, 53·6%.)

Benzene (analytical grade, Merck) was refluxed over Na-wire and fractionated through a Widmer column from Na-wire before use. CCl_4 (analytical grade, Merck) was dried over $CaCl_2$ and finally fractionated through a Widmer column from P_2O_5 prior to use.

The dipole moments were determined by measuring dielectric constants of a set of 5 solutions of each compound in CCl_4 and in benzene and of the pure solvents at 25°. From these data the dipole moments were calculated by the method of Halverstadt and Kumler.[22] The R_D values were obtained by addition of atomic and group refractions. The quantities α', β', ε_1, and v_1 were all evaluated by the method of least squares.

The dielectric measurements were carried out by means of a low-frequency Schering-bridge (General Radio, type 716c) and a measuring cell similar to those described previously;[23,24] densities were measured with 5, 6 and 7 ml pyknometers calibrated with water. The results are summarized below.

trans-aa-1,2-Dichloro-4-t-butylcyclohexane

In carbon tetrachloride				In benzene			
x_2	ε	v		x_2	ε	v	
0·00000	2·2282	0·63124	$\alpha' =$ 1·82	0·00000	2·2789	1·14462	$\alpha' =$ 1·98
0·00264	2·2330	0·63234	$\beta' = +0·39$	0·00255	2·2846	1·14333	$\beta' = -0·65$
0·00532	2·2377	0·63340	$P_{20} =$ 85·67	0·00376	2·2868	1·14187	$P_{20} =$ 85·36
0·00745	2·2417	0·63428	$R_D =$ 55·92	0·00507	2·2894	1·14108	$R_D =$ 55·92
0·00979	2·2459	0·63520	$\mu =$ 1·21 D	0·00714	2·2931	1·14021	$\mu =$ 1·20 D
0·01252	2·2510	0·63615					

* The analyses were carried out by Miss E. C. van Duijn of this laboratory.

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trans-aa-1,2-Bromochloro-4-t-butylcyclohexane

In carbon tetrachloride				In benzene			
x_2	ε	v		x_2	ε	v	
0·00000	2·2349	0·63081	$\alpha' =$ 1·85	0·00000	2·2800	1·14462	$\alpha' =$ 1·87
0·00217	2·2389	0·63166	$\beta' = +0·27$	0·00210	2·2841	1·14241	$\beta' = -1·10$
0·00439	2·2433	0·63223	$P_{20} =$ 89·02	0·00370	2·2872	1·14022	$P_{20} =$ 88·84
0·00648	2·2472	0·63272	$R_D =$ 58·87	0·00574	2·2907	1·13820	$R_D =$ 58·87
0·00887	2·2516	0·63334	$\mu =$ 1·22 D	0·00806	2·2950	1·13568	$\mu =$ 1·21 D
0·01094	2·2549	0·63388		0·00999	2·2989	1·13362	

trans-aa-1,2-Dibromo-4-t-butylcyclohexane

In carbon tetrachloride				In benzene			
x_2	ε	v		x_2	ε	v	
0·00000	2·2349	0·63115	$\alpha' =$ 2·01	0·00000	2·2800	1·14462	$\alpha' =$ 2·08
0·00191	2·2389	0·63136	$\beta' = +00·07$	0·00191	2·2829	1·14128	$\beta' = -1·71$
0·00377	2·2425	0·63148	$P_{20} =$ 90·70	0·00332	2·2859	1·13887	$P_{20} =$ 92·54
0·00530	2·2460	0·63151	$R_D =$ 61·75	0·00514	2·2898	1·13576	$R_D =$ 61·75
0·00709	2·2493	0·63166	$\mu =$ 1·19 D	0·00677	2·2930	1·13408	$\mu =$ 1·23 D
0·00914	2·2532	0·63185		0·00879	2·2982	1·12901	

trans-aa-1,2-Dibromo-4-t-butylchclohexane*

In carbon tetrachloride			
x_2	ε	v	
0·00000	2·2362	0·63114	$\alpha' =$ 1·88
0·00374	2·2429	0·63135	$\beta' = +0·15$
0·00549	2·2467	0·63162	$P_{20} =$ 90·93
0·00712	2·2496	0·63182	$R_D =$ 61·75
0·00921	2·2534	0·63266	$\mu =$ 1·19 D

* Sample from Dr. E. C. Wessels.[10]