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[Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, New Jersey]

Microwave Absorption and Molecular Structure in Liquids. XXXVI. The Relaxation of the Methylene Chloride Group in Three Aromatic Molecules[1,2]

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The dielectric constants and losses at wave lengths of 1.25, 3.22, 10, 25 and 50 cm. and 300 m. have been measured for benzyl chloride and α,α'-dichloro-*p*-xylene in benzene solution at 20, 40 and 60°, and bis-(chloromethyl)-durene has been measured in benzene solution at 20°. The data have been used to calculate the dielectric relaxation times of the molecules. The benzyl chloride absorption curve has been resolved into two peaks corresponding to over-all molecular and group relaxation. The short relaxation time for benzyl chloride is compared with the relaxation time of α,α'-dichloro-*p*-xylene, which should be associated primarily with intramolecular rotation. The durene compound has only one absorption region, that corresponding to molecular rotation. The moment measured for bis-(chloromethyl)-durene is analyzed and found to be consistent with the moments previously found for benzyl chloride and α,α'-dichloro-*p*-xylene.

Because of its possession of two rotatable polar groups, CH_2Cl, on opposite sides of a benzene ring, α,α'-dichloro-*p*-xylene offers a particularly good model for the study of intramolecular rotation by means of dielectric relaxation measurements. Measurements of dielectric loss or dielectric constant and loss have been carried out at megacycle frequencies, far below the region of maximum absorption, and the results have been discussed.[4–6] The present paper presents measurements in the kilomegacycle region on three compounds containing the CH_2Cl group with different structural factors producing very different effects of the group upon the observed relaxation times.

Experimental Methods

Apparatus.—The apparatus and the various methods of measurement have been described in previous papers.[7–9]

A Varian 4300 B apparatus equipped with a flux stabilizer was used by Mr. I. D. Kuntz to take the nuclear magnetic resonance spectrum of bis-(chloromethyl)-durene in benzene solution. The measurements were made at 25° using the side band technique.[10]

Purification of Materials.—Benzyl chloride, obtained from Eastman Kodak Co., was fractionally distilled.

α,α'-Dichloro-*p*-xylene, obtained from Eastman Kodak Co., was recrystallized twice from benzene and dried under vacuum in an Abderhalden pistol.

Bis-(chloromethyl)-durene, obtained from Shell Development Co., was recrystallized three times from benzene and dried under vacuum in an Abderhalden pistol, m.p. 197.0–198.0.

Benzene, obtained from Allied Chemical Corp., was used without further purification.

Experimental Results

The experimental results were treated in the manner previously described.[11] The slopes of the straight lines thus obtained, a', corresponding to ϵ', and a'', corresponding to ϵ'', were plotted in Cole–Cole arcs[12] in the usual fashion[11] for α,α'-dichloro-*p*-xylene and bis-(chloromethyl)-durene to obtain the critical wave lengths λ_m, the corresponding relaxation times τ, the distribution coefficients α and the arc intercepts at infinite frequency a_∞. The concentration range in mole fraction is given in parentheses for each set of solutions in Table I.

Table I

Slopes for the Dependence of the Dielectric Constant and Loss of Benzene Solutions upon Mole Fraction of Solute

Wave length (cm.)	20°		40°		60°	
	a'	a''	a'	a''	a'	a''
Benzyl chloride (0–0.0425)						
0.435	1.25	1.30				
1.24	2.24	1.43	2.34	1.47	2.32	1.38
3.22	3.40	1.54	3.52	1.28	3.32	1.05
10	4.55	0.90	4.36	0.62	4.02	0.44
25	5.03	0.39				
300	4.98		4.58		4.10	
α,α'-Dichloro-*p*-xylene (0–0.035)						
1.24	4.50	2.31	4.75	2.03	4.90	1.67
3.22	6.17	1.52	5.90	1.11	5.51	0.84
10	6.80	0.45	6.25	0.36	5.90	.21
25	6.90	0.25	6.33	0.15	5.80	.10
300	7.05		6.45		5.79	
Bis-(chloromethyl)-durene (0–0.0057)						
1.20	0.5	0.5				
3.22	2.05	1.85				
10	3.5	2.2				
25	5.6	1.4				
50	6.5	0.8				
300	6.5					

[a] Measurements made by Mr. W. E. Vaughan.

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(3) Allied Chemical Corporation Fellow, 1959-1960.

(4) A. Budó, *Physik. Z.*, **39**, 706 (1938).

(5) E. Fischer, *Z. Naturforsch.*, *9a*, 909 (1954).

(6) A. Aihara and M. Davies, *J. Coll. Sci.*, **11**, 671 (1956).

(7) H. L. Laquer and C. P. Smyth, This Journal, **70**, 4097 (1948).

(8) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

(9) D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, 582 (1959).

(10) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(11) A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P Smyth, This Journal, **72**, 3447 (1950).

(12) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

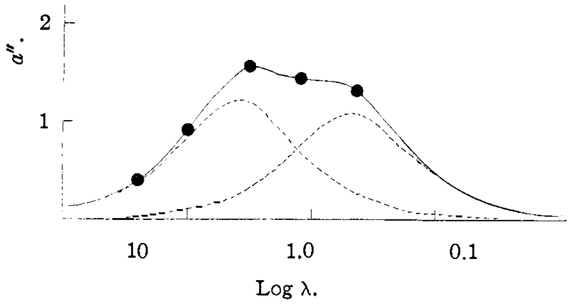

Fig. 1.—Absorption curve (a'' against log λ) for benzyl chloride at 20° in benzene solution: solid curve, experimental; broken curves, calculated.

The benzyl chloride results were treated differently, owing to the complexity of the relaxation mechanism, and will be discussed later.

The moment of bis-(chloromethyl)-durene measured in benzene solution at 20° is reported in Table III. Both the Halverstadt–Kumler[13] and Guggenheim[14] methods of calculation yield the value 2.08×10^{-18}. To make possible the moment calculation by the Halverstadt–Kumler method, solution densities were measured to obtain a slope $\beta = 0.002773$ for the density–weight fraction curve at 20°. The moments of the other two molecules are taken from the literature.[15]

TABLE II

SLOPES FOR THE DEPENDENCE OF SQUARE OF REFRACTIVE INDEX a_D UPON MOLE FRACTION, WITH INFINITE FREQUENCY INTERCEPTS a_∞, CRITICAL WAVE LENGTHS λ_M, RELAXATION TIMES τ AND DISTRIBUTION PARAMETERS α IN BENZENE SOLUTION

t, °C.	a_D	a_∞	λm (cm.)	τ(10^{-12} sec.)	α
			α,α′-Dichloro-*p*-xylene		
2					
20	0.33	0.88	0.700	3.72	0.16
40	.33	.82	.565	3.00	.12
60	.33	.85	.509	2.70	.06
			Bis-(chloromethyl)-durene		
20	0.46	0.54	8.19	43.5	0.19

TABLE III

MOLECULAR AND COMPONENT MOMENTS

	μ($\times 10^{18}$)	m($\times 10^{18}$)
Benzyl chloride[15]	1.83	1.57
α,α′-Dichloro-*p*-xylene[15]	2.20	1.56
Bis-(chloromethyl)-durene	2.08	1.47

Discussion of Results

Cole–Cole arcs[12] were not plotted for the benzyl chloride results because a plot of a'' against log λ_0, where λ_0 is the wave length used, indicated two absorption regions. The problem was, therefore, one of resolving the broadened experimental curve (solid curve, Fig. 1) into two absorption curves.

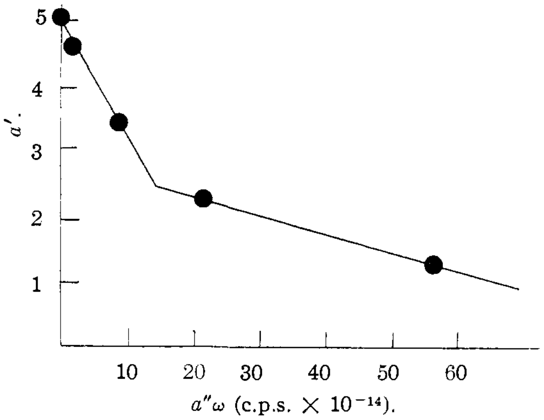

Fig. 2.—Plot of a' against $a''\omega$ for benzyl chloride at 20° in benzene solution.

When ϵ' is plotted[16] against $\epsilon''\omega$, where ω is the angular frequency, the slope is $-\tau$. A plot of a' against a'' ω for benzyl chloride (Fig. 2) gives two straight lines with relaxation times, τ_1 and τ_2, corresponding to the two slopes. The values thus obtained are $\tau_1 = 18.7 \times 10^{-12}$ sec. and $\tau_2 = 2.9 \times 10^{-12}$ sec. This value of τ_1 is presumably low, while τ_2 is high because of the effect of the overlap of the two absorption regions on the slopes of the two lines. A second method of analysis[17] gives $\tau_1 = 23.7 \times 10^{-12}$ and $\tau_2 = 2.3 \times 10^{-12}$ sec., values which are probably somewhat more accurate, although still approximate. Using mean values and replacing the ϵ terms in the Debye equation[18] by their corresponding slopes, two absorption curves were calculated for benzyl chloride (broken curves, Fig. 1). Each experimental point has an a'' value which is equal to the sum of the two absorption curves at that point. τ_1 must be the relaxation time for molecular rotation and τ_2, that for rotation of the CH_2Cl group.

The symmetry of the α,α′-dichloro-*p*-xylene molecule is such that there is no fixed moment in the molecule, the considerable molecular moment, 2.20×10^{-18}, being the resultant of the components of the two CH_2Cl moments perpendicular to their axis of rotation. The single absorption peak for the benzene solutions of the substance shown in Fig. 3 and the very low relaxation times in Table II show that the principal relaxation mechanism is the rotation of the two CH_2Cl groups around their bonds to *para* positions of the ring. However, the appreciable values of the distribution parameter α and the fact that the relaxation time 3.7×10^{-12} at 20° is considerably higher than the values of $\tau_2 =$ 2.3 or 2.9×10^{-12} calculated for the rotation of the CH_2Cl group in benzyl chloride suggest a small contribution from over-all molecular rotation resulting from momentary restriction of CH_2Cl groups to rotatory oscillation in potential energy troughs and, possibly, to the presence of a small mesomeric moment in the molecule.

For bis-(chloromethyl)-durene, in which the rotation of each CH_2Cl group is normally restricted

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(13) I. J. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

(14) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

(15) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, Chap. X. XI.

(16) R. H. Cole, *J. Chem. Phys.*, **23**, 493 (1955).

(17) K. Bergmann, D. M. Roberti and C. P. Smyth, *J. Phys. Chem.*, **64**, 665 (1960).

(18) Ref. 15, p. 56.

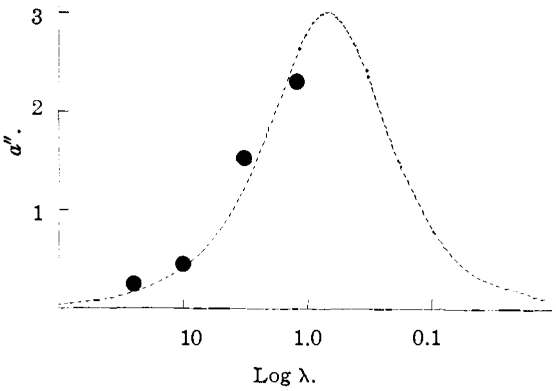

Fig. 3.—Calculated absorption curve for α,α'-dichloro-*p*-xylene at 20° in benzene solution; solid circles, experimental points.

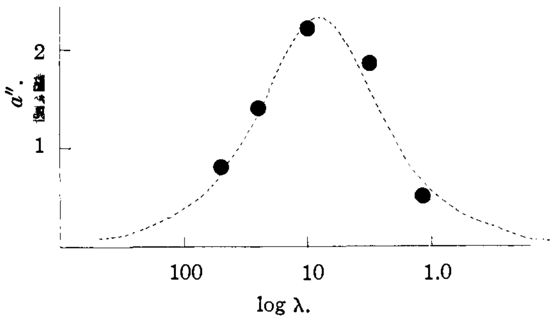

Fig. 4.—Calculated absorption curve for bis-(chloromethyl)-durene at 20° in benzene solution; solid circles, experimental points.

to a slight rotatory oscillation by the adjacent methyl groups, the single absorption peak (Fig. 4) and the large relaxation time, more than ten times that for α,α'-dichloro-*p*-xylene, show that the principal relaxation process is over-all molecular rotation. The value of the distribution parameter, $\alpha = 0.19$, is a little large even for this somewhat large disk-shaped molecule, but, like most values of α, may contain a considerable experimental error. It is possible that a slight rotation of the CH_2Cl groups in their potential energy troughs also contributes to the dipole orientation, but its contribution is too small to be apparent in a plot of a' against $a''\omega$, which gives a single straight line, in contrast to the two found for benzyl chloride (Fig. 2). The Stuart–Briegleb models show strong steric repulsion between the CH_2Cl groups and the methyl groups on each side of them, so that the molecules should exist only in *cis* and *trans* forms. Only the *cis* forms should have appreciable molecular dipole moments and thereby contribute to the molecular relaxation process. The probabilities of occurrence of the two forms appear to be practically equal. The n.m.r. spectrum of bis-(chloromethyl)-durene yielded two extremely sharp peaks having an area ratio of 3:1. The larger peak corresponds to the methyl protons, of which there are twelve, and the smaller peak corresponds to the methylene protons, of which there are four. The two sharp peaks are attributable to a rapid exchange (about 1000 times per sec. estimated) between the *cis* and *trans* forms.[19]

The molecular dipole moments of α,α'-dichloro-*p*-xylene and bis-(chloromethyl)-durene are dependent only on the moment component m of each CH_2Cl group perpendicular to the axis around which each group rotates. If all positions of rotation of each group around the axis are equally probable in α,α'-dichloro-*p*-xylene, the observed molecular moment is[15] $\mu = 2^{1/2}m$. The same equation applies to bis-(chloromethyl)-durene if the *cis* and *trans* forms are equally probable. The slightly lower value of m obtained for the latter compound in Table III might arise from a slightly greater stability of the *trans* form, which has almost zero moment, but is probably due to a slight opposing moment induced by the C–Cl dipole in each of the two adjacent methyl groups.[20] In benzyl chloride there should be a tendency toward a slight shift of electronic charge from the methylene group to the ring analogous to that from the methyl group to the ring in toluene. The moments due to such shifts cancel each other in α,α'-dichloro-*p*-xylene and bis-(chloromethyl)-durene, but, in benzyl chloride, it is reasonable to assign to it a moment value 0.37×10^{-18} equal to the moment of toluene. Using this moment value and 110° for the C–C–Cl valence angle, the value $m = 1.57$ (Table III) is calculated by simple geometry from the observed moment of benzyl chloride. The excellence of the agreement of this value of m with that obtained for α,α'-dichloro-*p*-xylene supports the validity of the assumptions made concerning the structures of these three molecules. The dipole moment values show that the very low frequency rotational jumps of the CH_2Cl groups in bis-(chloromethyl)-durene would not be distinguishable in the dielectric measurements from the molecular rotation in the liquid.

The results reported in this paper give a consistent picture of three molecules containing polar CH_2Cl groups which can rotate in benzyl chloride and in α,α'-dichloro-*p*-xylene but are restricted by strong steric hindrance to relatively infrequent rotation in bis-(chloromethyl)-durene.

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(19) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 223.

(20) Ref. 15, p. 235.