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THE DIPOLE MOMENTS AND MOLECULAR STRUCTURE OF CHLORAL AND BROMAL HYDRATES

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Abstract—The dipole moment of chloral hydrate is 2·07 D and 2·65 D at 35° in benzene and dioxane solutions respectively. Bromal hydrate has a moment of 2·56 D in benzene solution. The moments observed can reasonably be accounted for on the scheme of Smith *et al.* and the results have been discussed in terms of the possible structures of these molecules.

INTRODUCTION

CHLORAL and bromal hydrates are of theoretical interest being two of the few stable compounds containing two OH groups attached to the same carbon atom. When the electron cloud of the carbon atom of a carbonyl group is attracted towards a strongly electron attracting group by the inductive effect, the positive charge on the carbon atom stabilizes the compound with its two (*gem*-C)—OH bonds. Chloral and bromal hydrates may, therefore, not contain water of crystallization as is evidenced by their inability to react with the Schiff's reagent. By a variety of physical measurements such as X-ray diffraction,[1,2] IR spectra,[3] Raman spectra[4] and nuclear quadrupole resonance,[5] it has been established that chloral hydrate in the solid state does not contain water of crystallization. A knowledge of the detailed structures of these compounds is desirable because of their important role as soporific agents and an investigation of the dipole moments has been undertaken so as to obtain information regarding the structure and the position occupied by the two hydroxyl groups.

EXPERIMENTAL

Materials. Benzene and dioxane used as solvents in this investigation were purified by standard methods.[6] Both chloral and bromal hydrates were pure products; m.ps chloral hydrate 55°, and bromal hydrate, 53·5°.

Apparatus and methods of measurements. The dielectric constant measurements were made with an a.c. mains operated heterodyne beat apparatus as described earlier.[7] Densities of the solutions were obtained using an Ostwald–Sprengel pyknometer with ground-in caps at both ends. The polarization of the solute at infinite dilution was obtained using the mean values of Hedestrand constants α and β.[8] Electronic polarization of the solute was calculated by bond refraction values.[9] Atomic polarization was taken as 5% of the electronic polarization. Mol. wt. of chloral hydrate was determined in benzene by the freezing point method.

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TABLE 1. DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AT 35° ± ·01°

Mole fraction	Dielectric constant	Density
	Chloral Hydrate in Benzene	
·001510	2·2518	·86426
·003041	2·2603	·86539
·004346	2·2666	·86635
·006479	2·2786	·86800
	Chloral Hydrate in Dioxane	
·005071	2·2639	1·01420
·007178	2·2840	1·01584
·009234	2·3061	1·01755
·01581	2·3679	1·02264
	Bromal Hydrate in Benzene	
·000769	2·2646	·86462
·001087	2·2667	·86525
·002171	2·2757	·86735
·002775	2·2803	·86850
·003697	2·2886	·87046

TABLE 2

	Chloral hydrate		Bromal hydrate
	in benzene	in dioxane	in benzene
Hedestrand α	2·442	4·35	3·743
Hedestrand β	0·8911	0·7818	2·266
Molar refraction (cm^3)	28·60	28·60	37·27
Total polarization (cm^3)	115·13	169·46	168·24
Orientation polarization (cm^3)	85·1	139·43	129·11
Dipole moment (Debye)	2·07	2·65	2·56

TABLE 3. PARAMETERS USED IN CALCULATING THE CHARGE DISTRIBUTION AND DIPOLE MOMENTS BY THE SMITH *et al.* METHOD

Bond	β_{ab}	ν_{ab}[a]	Bond distance[b] in Å
H—C	0·13	0	1·09
F—C	0·25	−1·44	1·332
Cl—C	0·71	−1·49	1·82[3]
Br—C	0·906	−1·44	1·939
I—C	1·288	−1·73	2·18
O—C	*	*	1·44[3]
H—O	0·169	2·097	0·96
O═C	0·45	−2·32	1·15
C—C	$\beta_c^c - 0·718$	$\alpha_{cc} = 0$	

[*] The parameters needed are $\beta_C{}^O = 0·346$ and $\beta_O{}^C = 0·472$ as tabulated by Smith *et al.* and $\alpha_{OC} = 1·628$ calculated from the dipole moment of dimethyl ether.[10]

[a] The parameters β_{HO} and ν_{HO} are derived from H—O bond refraction[9] and dipole moment of water[11] respectively. $\nu_{O=C}$ from that of formaldehyde.[12] All other parameters needed are derived from the Tables given by Smith *et al.*[13]

[b] All the bond distances except Cl—C and O—C are taken from Sutton's Tables of interatomic distances[14] and in calculation of dipole moments of the hydrates all the bond moments are assumed to be tetrahedral and ${}_{COH} = 110°$.

TABLE 4. FORMAL CHARGE DISTRIBUTION AND DIPOLE MOMENTS

Atom	Fluoral hydrate	Chloral hydrate	Bromal hydrate	Iodal hydrate
C	1·1115	0·883	·814	·7918
C(methyl)	2·0744	1·326	1·106	1·0316
H	·1445	·1148	·1058	·1029
H(alcohol)	1·753	1·745	1·7426	1·7416
O	−2·035	−2·084	−2·097	−2·103
X(halogen)	−0·9214	− ·549	−0·44	−0·402
Dipole moments (Debyes)				
* Calculated	2·11, 3·58, 2·29.	2·18, 3·31, 2·11.	2·23, 3·16, 2·03	2·23, 3·17, 2·036
Observed		2·07 (B), 2·65 (D),	2·56 (B)	

* Dipole moments calculated in various positions of O—H bonds, (1) when both hydrogens are in *cis* position i.e. towards halogens, (2) when both hydrogens are in *trans* position i.e. away from halogens and (3) when one hydrogen is towards and other away from halogens respectively.

TABLE 5. FORMAL CHARGE DISTRIBUTION AND DIPOLE MOMENTS

	Fluoral	Chloral[12]	Bromal[12]	Iodal
C (aldehyde)	1·712	1·457	1·386	1·354
C (methyl)	2·248	1·4328	1·1977	1·104
H (aldehyde)	·2225	·1894	·1801	·1760
O	−1·5497	−1·6642	−1·6967	−1·7106
X (halogen)	−0·8782	−0·4718	−0·3556	−0·308
Dipole moments (Debyes)				
Calculated	1·40	1·82	1·86	1·88
Observed	—	1·58(15)	1·68(15)	—

RESULTS AND DISCUSSION

Absorption spectra studies of chloral hydrate in dioxane,[16] carbon tetrachloride, carbon disulphide and in chloroform[3] does not indicate any dissociation, although contradictory results have been obtained in carbon tetrachloride[17] and benzene.[2,17] A determination of the molecular weight of chloral hydrate in benzene by the freezing point method shows it to be undissociated in solution (Mol wt, calc. = 165·4, observed, 169) in agreement with the earlier observation by Brunner.[18] The molecular weight determination of bromal hydrate in benzene by the cryoscopic method is not possible due to the low solubility. However, the dependence of the dielectric constant on the mole fraction of the solute was found to be linear in benzene within the experimental error. The dipole moment of bromal hydrate in dioxane solution was not determined as the compound decomposes giving bromine.

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The observed dipole moments of chloral hydrate in benzene (2·07 D) and in dioxane (2·65 D) and of bromal hydrate in benzene (2·56 D) definitely prove that they are not molecular compounds of chloral and bromal with water but normal covalent compounds as described by the formula $CH(OH)_2CX_3$.

The expected resultant dipole moments of these molecules calculated from the characteristic bond moments as tabulated by Smyth[19] are not equal to the observed values due to the fact that the inductive effect of halogens plays a major role in these molecules. However, Smith *et al.*[18] have proposed a method of evaluating the modification of bond moments due to induction along polarizable bonds. According to this scheme, dipole moments of these hydrates have been calculated for the three extreme positions of OH groups, with both the C—O and O—H bonds lying in the same plane.

The observed dipole moment of chloral hydrate (2·07 D) agrees well with the two calculated values i.e. 2·18 and 2·11 D; corresponding to the two configurations: one in which both O—H bonds point towards the chlorine and the other in a staggered gauche form with the one O—H bond towards and the second away from chlorine. Consequently it is difficult to draw conclusions regarding the positions of the OH groups from the observed dipole moment; however, a tentative conclusion can probably be drawn from a comparative study of the calculated and observed dipole moments of the hydrates of this series. The higher dipole moment observed for bromal (1·69 D) as compared with chloral (1·58 D) has been explained by Coomber and Partington[16] to be due to the lower moment of $—CBr_3$ as compared with the $—CCl_3$ moment. Similarly, bromal hydrate has a higher dipole moment (2·57 D) than chloral hydrate (2·07 D) in benzene and this increment is to be expected if they have a similar structure. A comparison of the calculated moments of the series (Table 4) shows that the gradual increment from fluoral hydrate to bromal hydrate is observed only when the two OH groups are in the *cis* position to the $—CX_3$ radical. This conclusion is in agreement with the IR study of chloral hydrate by Davies[3] and Novak and Whalley.[20]

Further, the moment of bromal hydrate might be accounted for by a *cis* position or to some extent by a *trans* position of the OH groups with respect to the $—CBr_3$ radical but not by a *cis-trans* position, for which the calculated moment is much lower than the observed value. However, Davies[3] has pointed out that chloral hydrate is stable because both the OH groups are locked in the *cis* position and the hydrogens are not free to rotate about the C—O bonds; if they do so they might approach one another very closely with the consequent elimination of water. In this sense, in bromal hydrate the two OH groups do not occupy a *trans* position with respect to the $—CBr_3$ radical.

The moment of chloral hydrate in dioxane is higher than in benzene which is probably due to the formation of intermolecular hydrogen bonds.

Values of formal charges for each atom in these hydrates and their parent trihalogenated aldehydes have been given in Tables 4 and 5. The formal positive charge on carbon (methyl) gradually decreases from fluoral hydrate to the hypothetical iodal hydrate; while charge on oxygen increases in the same order. The stability of these hydrates also appear to decrease in the same order i.e. fluoral hydrate > chloral hydrate > bromal hydrate > iodal hydrate and it is interesting to note that the iodal hydrate has not been prepared so far. A similar trend is observed in the case of fluoral to iodal.

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