POLARIZATION AND APPARENT DIPOLE MOMENTS OF SOME SYMMETRICAL MOLECULES

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Polarizations and apparent dipole moments of a series of symmetrical molecules were determined by the standard method in three solvents: benzene, *p*-xylene, and mesitylene. Their explanation by complex formation with solvent applies only in the case of 1,4-dicyanobenzene and 4,4'-dicyanobiphenyl since the apparent orientation polarizations ($P_{O,app}$) are large and depend strongly on solvent. On the other hand, 1,4-dihalogenbenzenes do not form any complexes and $P_{O,app}$ is virtually zero. 1,4-Dihalogenbicyclo[2,2,2]octanes reveal also considerable $P_{O,app}$ which is attributed mainly to enhanced atomic polarization but — in the case of heavier halogens — also partly to complexes of unknown structure.

Some undoubtedly symmetrical molecules (e.g. symmetry groups C_{2h}, C_{3h}, $D_{\infty h}$) exhibit nevertheless non-zero apparent dipole moments (μ_{app}) in solution[1]. This phenomenon may cause difficulties in practice when one has to distinguish symmetrical and unsymmetrical molecules on the basis of their dipole moments. Several explanations have been advanced:

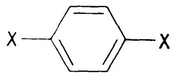
A) The atomic polarization P_A may be abnormally high[2-4] in molecules containing strongly polar bonds of opposite direction. The usual correction[5,6] for P_A, 5% or 7% of the molar refraction (R_D), may then be insufficient and an apparent dipole moment comes into existence.

B) Donor–acceptor complexes may be formed with the solvent benzene[7-10], some interactions of different nature are possible even with other solvents[11,12]. The apparent dipole moment is than the moment of the complex, for instance in the complexes with benzene it is oriented perpendicularly to the ring plane.

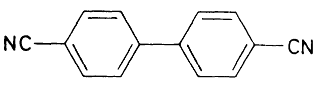
C) Some molecules need not possess actually as high symmetry as might be suggested by the topology of their formula[12-15]. This means that in this case the original assumption was wrong.

D) Some apparent solvent effects may have their actual origin in the imperfection of the underlying Debye theory.

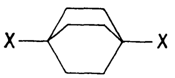
The problem cannot be considered as solved: it is probable that different explanations apply for different compounds. In this work we measured the polarizations and apparent dipole moments in three aromatic solvents: benzene, *p*-xylene, and mesitylene, which all are nonpolar but have variable donor ability. Such measurement should reveal complex formation even in cases when data in inert solvents are not available due to low solubility. We investigated compounds with guaranteed symmetry: simple aromatic derivatives *I* and *II* whose μ_{app} in benzene were already reported[2,16,17], and in addition derivatives of bicyclo[2,2,2]octane *IIIa*–*IIIc* which have also opposite polar bonds but cannot form complexes of similar structure. Our goal was thus mainly to decide between complex formation with solvent (explanation sub *A*) and abnormally large atomic polarization (*B*) while explanation sub *C* was a priori excluded by the structure of the solutes. If the task is to distinguish between small and zero dipole moments, the measurement of dielectric absorption is the method of choice[18] but it does not help in understanding the apparent dipole moment.



Ia, X = Cl
Ib, X = Br
Ic, X = I
Id, X = CN



II



IIIa, X = Cl
IIIb, X = Br
IIIc, X = I
IIId, X = CN

EXPERIMENTAL AND RESULTS

1,4-Dihalogenbicyclo[2,2,2]octanes[19,20]: *IIIa* m.p. 234°C, *IIIb* m.p. 256°C, *IIIc* m.p. 242°C. 4,4'-Dicyanobiphenyl[2] m.p. 234°C.

Solution dipole moments were measured by the standard method[21], some details were described[22]. The orientation polarization defined in the usual way is denoted in this paper as apparent, $P_{\mathrm{O,app}}$. From it the apparent dipole moment is calculated $\mu_{\mathrm{app}} = 0{\cdot}7390\,\sqrt{P_{\mathrm{O,app}}}$. The results are listed in Table I. We preferred to express our results in terms of apparent values $P_{\mathrm{O,app}}$ (based on the standard assumption[5] $P_{\mathrm{A}} = 0{\cdot}05R_{\mathrm{D}}$) instead of in terms of variable P_{A} calculated for each compound. The reason is that our expression is general and purely formal, not involving any explanation.

The attainable experimental accuracy is critical in the region of small dipole moments (below $3 \,.\, 10^{-30}$ C m) since their error depends inversely on their value[23]. In this region the density measurements (slope β in Table I) are most important and our previous results[24] were not quite consistent. We have now carefully detected the data deviating from linear relationships, repeated some measurements, and compared measurements on the same compound in different solvents. Unless strong complexes are formed, β in the three solvents are very close. The reliability of the total polarization P_2^0 should by in general approximately 1 cm^3 while that of R_D (calculated from increments[23]) is much better, say 0·3 cm^3. The best estimate of the possible error is a comparison with previous literature for some compounds *I* (see

TABLE I

Polarization data and apparent dipole moments of some symmetrical molecules (298 K)

Compound	Solvent[a]	α^b	β^b	$P_2^{0\,c}$	$R_D^{\,c}$	$P_{O,app}^{\;c,d}$	$\mu_{app}^{\;d,e}$
Ia	Bz	0·14	−0·35	38·7[f]	36·2	0·7	0·62
	Xy	0·12	−0·37	38·1		0·1	0·20
	Ms	0·18	−0·37	40·0		2·0	1·04
Ib	Bz	0·17	−0·62	44·5[g]	42·0	0·4	0·44
	Xy	0·14	−0·62	43·9		0	0
	Ms	0·13	−0·63	43·6		0	0
Ic	Bz	0·22	−0·74	53·5[h]	52·4	0	0
	Xy	0·20	−0·77	51·5		0	0
	Ms	0·12	−0·75	48·5		0	0
Id	Bz	0·19	−0·14	43·0[i]	37·0	4·1	1·50
	Xy	0·46	−0·27	45·4		6·5	1·89
	Ms	0·78	−0·32	51·5		12·6	2·63
II	Bz	1·14	−0·34	92·8[j]	61·4	28·3	3·93
IIIa	Bz	0·30	−0·33	53·6	44·4	7·0	1·96
	Xy	0·23	−0·35	51·2		4·6	1·59
	Ms	0·15	−0·35	48·8		2·1	1·08
IIIb	Bz	0·13	−0·52	56·5	50·2	3·8	1·43
	Xy	0·22	−0·54	61·1		8·4	2·14
	Ms	0·36	−0·60	63·7		11·0	2·45
IIIc	Bz	0·28	−0·69	68·1	60·7	4·1	1·49
	Xy	0·30	−0·71	69·9		6·2	1·84
	Ms	0·38	−0·71	75·6		11·9	2·55
IIId	Bz	—	—	47·0[k]	43·7	1·1	0·77

[a] Bz benzene, Xy p-xylene, Ms mesitylene; [b] slopes of the plots ε_{12} and d_{12}^{-1}, respectively, versus the weight fraction w_2; [c] cm^3 mol^{-1}; [d] The apparent orientation polarization $P_{O,app} = P_2^0 - 1{\cdot}05R_D$, the apparent dipole moment $\mu_{app} = 0{\cdot}7390\sqrt{(P_{O,app})} \cdot 10^{-30}$ C m. [e] 10^{-30} C m; [f] literature gives 37·7, 37·4, 38·0, 38·0, refs[16,25–27], respectively; [g] ref.[16] gives 43·8, ref.[28] gives 41·7; [h] ref.[16] gives 54·1; [i] ref.[17] gives 45·8, from the original data of ref.[29] one gets according to the present method 43·5; [j] ref.[2] gives 97, loaded with a small calculation error; [k] ref.[30].

notes to Table I). The mean square difference in P_2^0 is 1·5 cm^3 (mean of nine values calculated or even measured by different methods). If our data and those from the literature were assumed – very cautiously – to be of equal precision, an estimate of the standard deviation in P_2^0 would be 1·0 cm^3.

DISCUSSION

To be quite sure, we deal in the following discussion only with values of $P_{O,app}$ which are larger than 4 cm^3. The values of μ_{app} are less telling since they are sensitive just in the region of small values.

The most striking feature in Table I is the difference between halogen derivatives of benzene *Ia–Ic* and of bicyclooctane *IIIa–IIIc*. The latter possess larger apparent dipole moments which must be ascribed to the greater flexibility of the molecule and larger atomic polarization. In addition, there might be some interaction with the solvent, forming complexes of unknown structure in the case of compounds *IIIb* and *IIIc*. Its main experimental support is the dependence on solvent: μ_{app} increases with the solvent donor ability, similarly as observed for stronger acceptors as solutes[9,10].

Actual donor–acceptor complexes are observed with the cyano derivatives, *Id* and particularly *II*. Since the acceptor power of *II* cannot be greater as compared to *Id*, its apparent dipole moment must be due partly also to enhanced atomic polarization in the long molecule[2]. Among benzene 1,3,5-tris-derivatives complex formation was encountered[8,10] only in the presence of strong acceptor substituents, CN or NO_2. We have not confirmed the originally assumed[24] steric hindrance of complex formation by bulky halogen atoms: It is true that *Ib* and *Ic* do not form complexes at all but even with *Ia* the complex is at best very weak. In the bicyclooctane series (*III*), the interaction with the solvent is evidently stronger just in the case of bulkier halogens.

In conclusion, the complex formation with aromatic solvents is restricted to strong acceptors as solutes. Since such structures (tetracyanoethylene, 1,3,5-trinitrobenzene) can be easily recognized, the phenomenon does not seem to jeopardize the common practice of measuring dipole moments in benzene. The apparent dipole moments of the remaining symmetrical molecules are, in our opinion, most often due to anomalous atomic polarization of some molecules. This is in agreement with recent findings on some metalorganic compounds[4]. In general, the common methods of measuring dipole moments in solution are not quite satisfactory for small values. When studying steric arrangement or electron distribution of a certain functional group it is therefore recommended to avoid compounds with low dipole moments; this can be almost always achieved by proper substitution.

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