DIPOLE MOMENTS INDUCED IN LARGER MOLECULES. TRIPHENYLMETHYL DERIVATIVES

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Dipole moments of triphenylmethyl derivatives *I—VI* with electron attracting functional groups were measured in benzene solution. Comparison with respective methyl and tert-butyl derivatives revealed the moments induced in the phenyl group which are possibly somewhat greater than those induced in an alkyl group. These moments should be accounted for when determining mesomeric dipole moments of acceptor groups from benzene derivatives; however, a quantitative evaluation is not yet possible.

Dipole moments of monofunctional derivatives are in the first approximation attributed to the functional group as expressed explicitly by the bond moment scheme[1]. In fact their values are virtually constant only in homologous series beginning with propyl derivatives, but usually distinctly lower for methyl derivatives, and higher for branched compounds[1−3]. Variations of this kind can be accounted for in terms of induced moments arising either by successive polarization of bonds[4], or by direct polarization through space[5]. The results of such calculations are semiquantitative in character and can be viewed as the second order approximation at best. On the other hand, the differences between aliphatic and aromatic derivatives have been always discussed in terms of the theory of resonance (or mesomerism) and served to define the mesomeric dipole moments[3,6,7]. There is, however, no reason to believe that polarization within the benzene nucleus is negligible; due to the mobility of π-electrons it could be even greater than in alkyl groups. Therefore, it was argued that the values of mesomeric dipole moments are doubtful in the case of acceptor substituents[8]. For instance, the difference between experimental dipole moments of nitrobenzene and nitromethane cannot be equated with the mesomeric contribution, before a correction for induction is made. An attempted calculation[8] of the induced moments was evidently oversimplified; a more promising approach might refer to model compounds, *e.g.* those containing benzene rings not directly conjugated with the functional group.

In this communication we report the results obtained on triphenylmethyl derivatives with acceptor groups (*I—VI*, Table I). Dipole moments of triphenylmethyl halides

and triphenylmethanol were reported[9] to be somewhat greater than those of corresponding aliphatic derivatives. Note still that deviations of another kind were observed for certain large molecules[10] and ascribed tentatively to violation of basic assumptions of the theory if dielectrics. If these effects were encountered with our compounds, they would make the evaluation of induced moments impossible.

TABLE I

Dipole moment data of triphenylmethyl derivatives $(C_6H_5)_3CX$ (benzene, 25°C)

Compound	X	α^a β^a	P_2^0 cm³ R_D	$\mu(5)^b$ $\mu(15)^b$	μ_{ind}^c
I	CCl_3	1·66 −0·396	193·5 99·3	7·0 6·6	2·3
II	CN	5·67 −0·286	355·8 84·1	12·1 11·9	1·5
III	$COCH_3$	3·57 −0·290	265·0 89·1	9·7 9·4	1·4[d]
IV	$COOCH_3$	1·28 −0·303	148·6 90·5	5·4 4·9	0·5[d]
V	COCl	2·70 −0·380	225·5 89·3	8·5 8·2	1·2[d]
VI	SO_2CH_3	6·35 −0·470	449·3 93·0	13·9 13·7	0·7[d]
VII	F	—	151·8[e] 79·5	6·1[f] 5·7[f]	1·4
VIII	Cl	—	165·4[e] 84·5	6·5[f] 6·1[f]	1·8
IX	Br	—	179·9[e] 87·4	6·9[f] 6·6[f]	2·1
X	I	—	163·0[e] 92·6	5·9[f] 5·5[f]	2·1
XI	OH	—	147·5[e] 81·2	5·8[f] 5·4[f]	1·3[d]

[a] Slopes of the plots ε_{12} vs w_2 and d_{12}^{-1} vs w_2, respectively; [b] correction for the atomic polarization 5% or 15%, respectively, of the R_D value; [c] difference against the dipole moment of the corresponding methyl derivative[23] plus a correction of $1 . 10^{-30}$ C m for the dipole moment of triphenylmethane; [d] simple scalar difference instead of the vector difference; [e] ref.[9]; [f] recalculated from P_2^0 and R_D as given in the preceding column.

EXPERIMENTAL AND RESULTS

Materials. The compounds $I-V$ were prepared according to the literature[11-14], their purity was checked by TLC, ^{1}H NMR and m.p. determination. Methyl triphenylmethyl sulphone (VI) was obtained by one-step formation and rearrangement of triphenylmethyl methanesulphinate as proposed for the synthesis of analogous compounds[15]. To a solution of triphenylchloromethane (5·57 g; 0·02 mol) in dimethyl sulphoxide (50 ml), sodium methanesulphinate[16] (2·04 g; 0·02 mol) was added. The mixture was stirred at $50-60$°C for 4 h, poured into water and the separated product collected, yield 68%, m.p. 191—192°C (acetic acid), for $C_{20}H_{18}O_2S$ (322·4) calculated: 74·5% C, 5·62% H, 9·94% S; found: 74·5% C, 5·53% H, 9·72% S. IR spectrum in nujol: 1 130, 1 300 cm^{-1}; ^{1}H NMR spectrum in CDCl$_3$ solution: $\delta_{Ph} = 7·33$, $\delta_{CH_3} = 2·80$ ppm (tetramethylsilane as internal standard).

All attempts to prepare triphenylnitromethane failed. Thus, treatment of triphenylchloromethane with nitrogen peroxide or trichloronitromethane with benzene according to literature methods[17,18] and under a variety of different conditions afforded only mixtures containing triphenylmethanol as the main component. Similar results were obtained even when working under dry nitrogen atmosphere.

Physical measurements. The technique of dipole moment measurements in benzene solution was described in some detail[19]. The molar refraction R_D was calculated from increments[20], the increment of the SO$_2$ group was 8·67 cm^3, see ref.[1]. With respect to the size of molecule the correlation for atomic polarization is not negligible; in addition to the recommended[21] value of 5% of R_D we calculated also the values with a 15% correction as possible limit. The experimental results for compounds $I-VI$ are listed in Table I, together with the results of Nazarova[9] recalculated with the said corrections (compounds $VII-XI$).

DISCUSSION

Arylaliphatic hydrocarbons show small finite dipole moments[23] which can be formally attributed either to the bond between two differently hybridized carbon atoms, or to different bond moments H—C(sp^2) and H—C(sp^3). The latter possibility has been adopted in the bond moment system currently used by us[1]. Accordingly, a moment of 1·0 would be envisaged for triphenylmethane. (All dipole moments are given in 10^{-30} C m). A direct experimental determination[22] did not allow distinguishing between this value and zero, the upper limit seems more probable with respect to measurements on toluene and diphenylmethane[23]. Hence the dipole moments of triphenylmethyl derivatives would be approximately by 1 lower compared to respective methyl derivatives if there were no polarization. The differences against this value can be attributed to induced moments. According to Table I these are perceptible, in general somewhat higher than in the case of tert-butyl derivatives[23], but differences between individual compounds are marked. The highest induced moments are found for trichloromethyl derivative and halogen derivatives, smaller values occur with unsymmetrical molecules $III-VI$. For the latter the induced moment should be actually calculated as a vector difference but such more sophisticated treatment is useless due to the negligible resulting value. The most relevant results were expected from triphenylnitromethane, but unfortunately it was not possible to obtain a sample of this compound.

We conclude that dipole moments induced in the benzene nucleus are demonstrable but not much greater as compared to aliphatic alkyl groups. Nevertheless, they can affect the values of mesomeric dipole moments in particular if these are calculated as a mere difference between the phenyl and methyl derivative; tert-butyl derivatives would be a better reference. It follows that the mesomeric moments for acceptor groups as commonly given[3,7] are too high[8]. The approach used in this paper did not allow to separate quantitatively the contributions of the induced moment and of conjugation; one can still doubt[8] whether the latter is significantly different from zero for certain groups, *e.g.* NO_2, SO_2X, CN. Recent *ab initio* calculations[24] have not revealed any conjugation of the named groups with the benzene nucleus unless the electron density on it is enhanced by another substituent. This finding agrees fully with previous conclusions from dissociation constant measurements[25]. Hence the mesomeric dipole moments of these groups are still doubtful.

On the other hand, Table I does not reveal any particularly enhanced values (as compared with tert-butyl derivatives) which could be connected with the unusual size of the molecule. Such effects have not yet been found with other compounds[26] except diamantane derivatives[10] and their explanation will still need further observations.

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