DIPOLE MOMENTS INDUCED IN LARGER MOLECULES. 1- AND 4-SUBSTITUTED DIAMANTANES

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Received February 22nd, 1980

Dipole moments of fourteen monofunctional diamantane derivatives were measured in benzene solution. The values found are almost equal for 1-substituted (*IIa*—*IIg*) and 4-substituted (*IIIa* to *IIIg*) isomers but both are distinctly higher than those of the corresponding adamantane derivatives (*I*). This trend is not accounted for in terms of the classic Smith–Eyring theory of induced moments which works reasonable well for smaller molecules. Probably some basic assumptions of the theory of dielectrics (a spherical molecular cavity with a dipole in its centre) are no more fulfilled for diamantane derivatives.

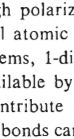
It is a long known fact that dipole moments of monofunctional saturated derivatives depend primarily on the functional group and vary but little with the size of the hydrocarbon chain[1-3]. For example, in the homologous series of 1-halogenoalkanes the dipole moments are virtually constant beginning with the propyl derivatives, and the only salient difference is between methyl and ethyl[2]. Somewhat more significant is the increase within the series of branched derivatives from methyl to tert-butyl[2]. Nevertheless, the system of bond moments commonly used[3] neglects even these differences and attributes equal dipole moments to all aliphatic derivatives. In a more sophisticated approach the observed pattern is explained by electrostatic induction raised by the carbon–halogen dipole within the polarizable alkyl groups[3]; this effect drops rapidly with the distance. The classic semiquantitative theory of Smith and Eyring[4-6] is based on successive polarization of bonds, each of them acting simultaneously as polarizable and polarizing as well. The charges on the atoms induce a moment (μ_{AB}) in the respective bond which is represented as having its poles in the two end atoms. The charges which come into existence in this way are summed up in each atom and constitute its net charge q_A:

$$q_A = -\sum_i (\mu_{ABi}/r_{ABi}) \,. \qquad (1)$$

The summation relates to all atoms B_i adjoining to A. The Smith–Eyring theory has been applied in several classes of compounds with a relative success[7-11], new numerical constants were determined[8,9] and the original ones amended[10,11]. Even a modified form was presented[12] which takes into consideration the polarization by all bonds not only by the neighbouring ones. The electrostatic induction is certainly operative even in aromatic compounds[13] and responsible for a great part of the so-called mesomeric moments[14].

Alternative explanations were also advanced. Attention was drawn to the fact that in solution measurement the basic model of a spherical cavity does not conform with the actual shape of larger molecules[1]. However, the solution and gas phase measurements yield an essentially similar pattern[2]. In the case of branched isomers even the intrinsic polarity of C—H and C—X bonds need not be uniform[2] and a bond moment scheme has been elaborated distinguishing bonds to primary, secondary, tertiary, and quaternary atoms[15].

The experimental data were recently extended to 1-adamantyl derivatives[16-18] (*I*). Their dipole moments, still enhanced compared *e.g.* to tert-butyl derivatives, were assigned to high polarizability of the hydrocarbon residue[17,18], or, less probably, to an abnormal atomic polarization[16]. In this paper we report the results on two still larger systems, 1-diamantyl (*II*) and 4-diamantyl derivatives (*III*) which have been made available by recent synthetic work[19-22]. We believed that these compounds can contribute significantly to the problem outlined since the successive polarization of bonds can hardly reach up to the remote end of the molecules. In this respect compounds *II*, *III* can be viewed as a marginal case of a large rigid molecule.



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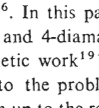

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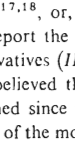

III

EXPERIMENTAL

Materials. The synthesis of diamantane derivatives *IIa,d,g* and *IIIa,d,f,g* has been described in another place[22], the remaining ones were prepared according to the literature (ref.[19] for *IIb*, *IIIb*, ref.[20] for *IIf*, and ref.[21] for *IIc,e*, *IIIc,e*). Their purity was checked by TLC and by ^{1}H-NMR spectra. Adamantane derivatives *Ia,b* were from the laboratory stock, the m.p.'s agreed with the material used by previous workers[18].

Physical measurements. The method of dipole moment measurement was described in some detail previously[23]. The values of R_D were based on the molar refraction of 1-ethyladamantane determined experimentally: $n_D^{25} = 1{\cdot}4915$, $d^{25} = 0{\cdot}9379$, $R_D^{25} = 50{\cdot}99\ \mathrm{cm}^3$, calculated from Vogel's increments[24] $R_D^{20} = 51{\cdot}65\ \mathrm{cm}^3$. The negative increment $-0{\cdot}66\ \mathrm{cm}^3$ for the adamantane system is in accord with the value[24] $-0{\cdot}15$ for one cyclohexane ring. We thus adopted increments of $-0{\cdot}66\ \mathrm{cm}^3$ for adamantane and $-1{\cdot}0\ \mathrm{cm}^3$ for diamantane, the remaining increments according to Vogel[24]. The calculated R_D values are given in Table I together with the polarization data.

The dipole moments were calculated according to Halverstadt and Kumler[25] as in our previous work[23], and in addition also using the equation of Sagnes and Casadevall[26]. The latter equation was rearranged by substituting for $(\varepsilon_1')_0$ and by introducing the symbols α and β as used in the Halverstadt–Kumler[25] approach. The final form

$$\mu^2 = \frac{9kTM_2}{4\pi N}\left[\frac{\alpha v_1(2\varepsilon_1 + 1)^2}{27\varepsilon_1^2} + \frac{(\varepsilon_1 - 1)(2\varepsilon_1 + 1)(\beta + v_1)}{9\varepsilon_1} - \frac{P_D}{M_2}\right] \cdot \left[\frac{2\varepsilon_1 + 1}{2\varepsilon_1 + 1 + (2\varepsilon_1 - 2)\,P_D/M_2(\beta + v_1)}\right]^2 \qquad (2)$$

reveals the relation to the Halverstadt–Kumler equation

$$\mu^2 = \frac{9kTM_2}{4\pi N}\left[\frac{3\alpha v_1}{(\varepsilon_1 + 2)^2} + \frac{(\varepsilon_1 - 1)(\beta + v_1)}{\varepsilon_1 + 2} - \frac{P_D}{M_2}\right]. \qquad (3)$$

As usual, the subscripts 1, 2 refer to solvent and solute, respectively. For the distortion polarization P_D we substituted into either equation the molar refraction R_D with 5% or 15% added as an allowance for the atomic polarization. As in our previous work[23], we believed that the right value is between these limits.

Calculations. The Smith–Eyring calculations were carried out according to the original concept[4–6], but several symbols were modified[28] in order to avoid confusion. (In particular ε should denote only the permittivity.) The induced dipole μ_{AB} in Eq. (*1*) is expressed through the longitudinal bond polarizability b_{AB}, the effective charges Z_A and Z_B, and the covalent radii r_A, r_B of the respective atoms. The effective charges are in turn resolved into the nuclear charge Z^0 and the net charge q, the latter multiplied by the Slater shielding factor S:

$$q_A = -\sum_i\left[\frac{eb_{ABi}}{r_{ABi}}\left(\frac{Z_A^0}{r_A^2} - \frac{Z_{Bi}^0}{r_{Bi}^2}\right)\right] - q_A\sum_i\left[\frac{S_A b_{ABi}}{r^2 r_{ABi}}\right] + \sum_i\left[\frac{b_{ABi}S_{Bi}}{r_{ABi}r_{Bi}^2}\right]q_{Bi}\,.$$

The terms in brackets represent numerical coefficients and are replaced by simple symbols α and β:

$$q_A = \left(\sum_i \alpha_{A-Bi} + \sum_i \beta_{Bi(A)}q_{Bi}\right)/\left(1 + \sum_i \beta_{A(Bi)}\right). \qquad (4)$$

The charge on a given atom q_A is thus expressed as a function of the charges q_{Bi} on all its neighbours and it is necessary to solve a set of as many equations as is the number of non-equivalent atoms in the molecule. A further simplification is possible in the case of atoms bonded only

to one neighbour. For example, the equations for halogen atoms and for hydrogen (bonded to C) are simplified as follows:

$$q_{Hal} = \alpha_{Hal-C}/(1 + \beta_{Hal(C)}) + [\beta_{C(Hal)}/(1 + \beta_{Hal(C)})]\, q_C = \eta_{Hal-C} + \vartheta_{Hal-C} q_C \qquad (5a)$$

$$q_H = \alpha_{H-C}/(1 + \beta_{H(C)}) + [\beta_{C(H)}/(1 + \beta_{H(C)})]\, q_C = \eta_{H-C} + \vartheta_{H-C} q_C \,. \qquad (5b)$$

The number of equations as well as of necessary constants is thereby reduced. If for instance only halogenated hydrocarbons are concerned, the set of equations is reduced to as many as there are different C atoms since for q_{Hal} and q_H one can directly substitute from Eqs (*5a,b*). The constants needed are in this simple case: η_{Hal-C} and ϑ_{Hal-C} for F, Cl, Br, I, in addition η_{H-C}, ϑ_{H-C}, and $\beta_{C(C)}$; α_{C-C} is zero by definition. The original values were several times modified[7], *e.g.* on the basis of more recent polarizability data. However, we treated the whole theory as a semiempirical one and retained the figures suggested by its founders[4-6]: $\beta_{C(C)} = 0{\cdot}43$ (empirically corrected[6]), $\vartheta_{H-C} = 0{\cdot}13$, $\vartheta_{Cl-C} = 0{\cdot}71$, $\vartheta_{Br-C} = 0{\cdot}91$, $\vartheta_{I-C} = 1{\cdot}29$, $\eta_{H-C} = 0$ (arbitrarily chosen and empirically verified[5]), $\eta_{Cl-C} = -1{\cdot}49$, $\eta_{Br-C} = -1{\cdot}44$, $\eta_{I-C} = -1{\cdot}42$ (redetermined in ref.[6]); the three latter values were adjusted[4,6] to match the experimental dipole moments of the corresponding methyl halides in the gas phase. While β and ϑ are dimensionless, η is given originally in 10^{10} e.s.u.

The calculations were programmed for the HP 9820 calculator using the standard program for solving a set of linear equations. With one given halogen atom, only the incidence matrix of the carbon framework is given on the input. It is of great advantage if equivalent carbon atoms are given the same numbering, but it is possible only if they are not directly connected to each other. On the output the net charges q of all atoms are obtained. In the next step, the total dipole moment is calculated from these charges, either in the cartesian coordinates or, as we preferred, after converting them into bond moments. The latter are summed in each of the four directions, it means that tetrahedral angles were assumed throughout and, as far as possible, each molecule was localized into the diamond lattice. If the moments in four directions ($\mu_1 - \mu_4$) are known, their vector sum is given by the formula:

$$\mu^2 = \tfrac{4}{3} \sum_{i=1}^{4} \mu_i^2 - \tfrac{1}{3} \Big(\sum_{i=1}^{4} \mu_1 \Big)^2 \,.$$

The resolution into bond moments is not unambiguous with each structure but the final dipole moment is single-valued. In the case of highly symmetrical structures (tert-butyl, adamantyl) the calculation is considerably simplified. For the same reason as with parameters β, ϑ, η we retained also the originally used values[6] of bond lengths (in pm): C—C 154, C—H 109, C—Cl 178, C—Br 194, C—I 214.

RESULTS AND DISCUSSION

An inspection of Table I reveals that the dipole moments of isomeric 1- and 4-substituted diamantanes (*II*, *III*) are very close, in average those of 4-derivatives (*III*) are higher only by 0·1. (All dipole moment values are given in units 10^{-30} C m.) Compared to the corresponding adamantane derivatives[16-18] the (*I*) dipole moments of *II*, *III* are higher by some 0·4. Since this comparison is very important and in previous work partly a different solvent was used[16,17], we redetermined dipole moments

TABLE I

Polarization Data of Diamantane Derivatives (benzene, 25°C)

Compound Substituent	α^a β^a	P_2^0	R_D	μ, 10^{-30} Cm H.K. (5)[b] H.K. (15)[b]	 S.C. (5)[b] S.C. (15)[b]
IIa	2·46	149·3	55·6	7·0	7·4
1-F	—0·268			6·8	7·2
IIIa	3·18	178·0	55·6	8·1	8·4
4-F	—0·254			7·9	8·2
IIb	3·85	217·8	60·6	9·2	9·5
1-Cl	—0·291			9·0	9·2
IIIb	3·94	220·9	60·6	9·3	9·5
4-Cl	—0·300			9·1	9·3
IIc	3·09	209·3	63·5	8·8	9·0
1-Br	—0·464			8·6	8·8
IIIc	3·14	211·7	63·5	8·9	9·1
4-Br	—0·466			8·7	8·8
IId	2·68	215·9	68·8	8·9	9·1
1-I	—0·528			8·6	8·8
IIId	2·67	214·2	68·8	8·8	9·0
4-I	—0·540			8·6	8·7
IIe	2·77	159·0	57·4	7·3	7·7
1-OH	—0·279			7·1	7·4
IIIe	2·92	163·4	57·4	7·5	7·8
4-OH	—0·302			7·3	7·5
IIf	2·02	133·5	59·2	6·2	6·6
1-NH_2	—0·216			6·0	6·4
IIIf	2·10	139·7	59·2	6·5	6·9
4-NH_2	—0·164			6·3	6·7
IIg	7·82	398·2	61·5	13·5	13·7
1-NO_2	—0·346			13·4	13·4
IIIg	6·84	355·0	61·5	12·6	12·7
4-NO_2	—0·350			12·5	12·5
Ia	4·28	182·2	46·5	8·5[c]	8·8
Cl	—0·260			8·4[c]	8·6
Ib	9·17	355·8	47·4	12·9[d]	13·1
NO_2	—0·336			12·8[d]	12·9

TABLE I
(*Continued*)

Compound Substituent	α^a β^a	P_0^2	R_D	μ, 10^{-30} Cm H.K. (5)^b H.K. (15)^b	 S.C. (5)^b S.C. (15)^b
2-Chloro-2-methyl-propane	5·11 +0·024	121·1	25·5	7·2^c 7·1^e	7·6 7·4

^{a} Slopes of the Halverstadt–Kumler[25] plots, ε_{12} *vs* w_2 and d_{12}^{-1} *vs* w_2, respectively; ^{b} calculated according to Halverstadt–Kumler[25], or according to Sagnes–Casadevall[26], correction for the atomic polarization 5% or 15%, respectively, of the R_D value; ^{c} the literature gives the values of 7·7 (Hederstrand method. ref.[17]), and 8·0 or 8·4 (Guggenheim method in tetrachloromethane, ref.[18,16]); ^{d} ref.[13] gives 11·9, ref.[18] 12·7 in tetrachloromethane (Guggenheim method); ^{e} the median value of five published values[27] is 7·14.

TABLE II
Dipole Moments of Some Halogeno Derivatives R—X Calculated by the Smith–Eyring Procedure

R	μ, 10^{-30} C m X = Cl	 X = Br	 X = I
CH_3	6·19^a	5·94	5·51^a
C_2H_5	6·74^b	6·49^b	6·06^b
$(CH_3)_2CH$	7·17^b	6·93^b	6·53^c
$(CH_3)_3C$	7·51^b	7·28^b	6·92^b
$(CH_3)_3CCH_2$	7·06	6·76	6·32
e-Cyclohexyl	7·57	7·28	6·85
a-Cyclohexyl	7·16	6·92	6·53
1-Adamantyl	8·07	7·79	7·38
4-Diamantyl	8·11	7·83	7·41
1-Diamantyl	8·25	8·01	7·49
1-Adamantyl-CH_2	6·93	6·65	6·22
1-Adamantyl-$(CH_3)CH$	7·30	7·06	6·66
1-Adamantyl-$(CH_3)_2C$	7·63	7·39	7·02

^{a} Taken originally as reference value[4]; ^{b} these values agree with previous calculations[6] within the limits of rounding; ^{c} the value of 6·70 is listed in ref.[6] although the same parameters were used for the calculations.

of two adamantane derivatives (*Ia*,*b*) at comparable conditions (Table I, at the bottom). We confirmed that there is a real difference between *II* or *III* on the one hand and *I* on the other. At the same time all these compounds have distinctly higher dipole moments than corresponding simple open-chain derivatives, see 2-chlor-2-methylpropane in Table I and further tabulated data[1,27]. We can conclude that the molecule of adamantane derivatives is not yet sufficiently large to yield the upper limiting value of the dipole moment but we believe that diamantane derivatives should be already near to this limit.

For a comparison of experimental results with the Smith–Eyring theory[4-6] we selected a series of derivatives with an unambiguous conformation and without any appreciable angle or torsional strain. As described in detail in Experimental, we applied this classic theory with the original parameters. The choice of parameters is not critical since the main question is whether the general trend is correctly reproduced. The results of calculation for three series of halogeno derivatives (Table II) reveal a close parallelism; with respect also to the mathematical procedure we believe that the same picture would be obtained for any other functional group. Hence the comparison with experiments is restricted to chloro derivatives (Fig. 1), for which most data are available[27]. When evaluating the fit, we must first of all take into consideration the experimental error which is rather high compared to the dif-

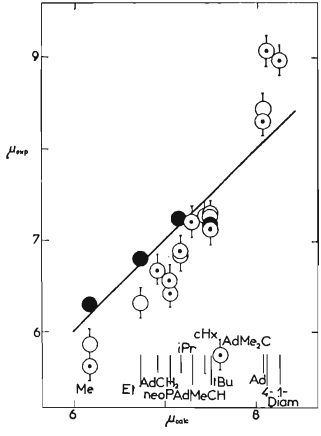

FIG. 1

Comparison of Calculated and Experimental Dipole Moments of Chloro Derivatives

● Gas phase values[27], ⊙ benzene solution ref.[17,27] and this work), ○ other solutions[16,27]; calculated according to Smith–Eyring[4-6], the line has unity slope. Ad for adamantyl, Diam for diamantyl.

ferences between individual compounds; in solution measurements it is still higher than in the gas phase. In addition some values have been reported only once and a big error is not quite excluded, see in particular 2-chloro-2-(1-adamantyl)propane[17]. The agreement with theory is best for simple alkyls in the gas phase since some of them served as reference compounds in the optimization of parameters[6]. The dipole moments determined in solution are systematically lower than calculated, but the trend is maintained from methyl to tert-butyl. It is true that the main difference is between primary, secondary, and tertiary derivatives, but even within each class the dipole moments are not uniform. Hence a bond moment scheme based on different types of bonds[15] cannot account for the whole observed pattern. In our opinion the simple classic picture of successive bond polarization appears to be essentially correct and can serve as a first approximation at least.

The behaviour of adamantane (*I*) and diamantane (*II*, *III*) derivatives is apparently anomalous (Fig. 1). While the calculated dipole moments are already approaching a limiting value and would not further increase, *e.g.* by an alkyl substitution, the experimental values are higher than calculated and in particular, they increase still from *I* to *II* and *III*. We do not see any reason why the electrostatic induction in the adamantane nucleus should proceed along different lines than in simpler aliphatic and alicyclic compounds. It is true that correlations of dipole moments with inductive substituent constants were reported in the adamantane series[17,18] and believed to evidence concentration of the positive charge close to the centre of the molecule[17]. However, these correlations were made possible only by arbitrary assumptions and/or by very restricted choice of substituents.*

An alternative explanation in terms of an extraordinary atomic polarization[16] – instead of an induced dipole – was disproved in a convincing manner by dielectric measurements on adamantane itself[18]. The total polarization of 42·8 ($cm^3\ mol^{-1}$) was but slightly higher than the estimated electronic polarization (41·4). We can con-

* We have argued[29] that correlations of dipole moments with substituent constants σ should be extremely limited in scope, practically only to monoatomic substituents. The main reason is that the dipole moment belongs to the whole substituent while the σ constant expresses only the effect of the substituent on the rest of the molecule and is rapidly attenuated with the distance. (For instance, the substituents Br and CH_2Br have almost equal dipole moments but very different σ constants.) For monoatomic substituents the correlation is somewhat improved and acquires more physical meaning if a correction for the length of the dipole is introduced[29]. However, in one reported correlation of the adamantane series[17] this length was arbitrarily defined from the centre of the molecule to the substituent, as it would be required perhaps for the induced dipole only but not for the gross dipole moment. In this way the differences between substituents Br and CH_2Br are diminished but the physically meaningless correlation is disclosed by the intercept which is very different from zero[17]. In the second correlation described in the literature[18] a geometrical factor $\cos \Phi$ was arbitrarily introduced. In this way the dipole moment of the CH_2Br substituent is projected into the C—C direction without any apparent ground, even the dipole length as defined has no physical meaning.

firm this reasoning on the basis of our measurement on 1-ethyladamantane, which implies the molar refraction of 41·7 for adamantane itself.

In our opinion the observed facts may be understood if one takes into consideration a fundamental assumption of the theory of dielectrics[1]: a spherical cavity with the dipole situated at its centre. This assumption might be met for very small molecules or even for molecules with a long aliphatic chain, which can be wound round the dipole. It is, however, clearly violated in the case of large rigid molecules. We also attempted to calculate the dipole moments according to a more sophisticated method than the Halverstadt–Kumler[25] method used by us hitherto. The equation of Sagnes and Casadevall[26], based ultimately on the Onsager theory[30], yielded results (Table I), which are uniformly higher than the convential ones and could be considered as an estimate of gas phase values. However, the general pattern is not changed, see in particular the relation of tert-butyl, adamantyl, and diamantyl derivatives. This result is in fact not surprising since even the Onsager theory[30] assumes a spherical molecule. From the literature data we may quote the dipole moment of 3β-chloro-5-cholestene[31] ($7{\cdot}8 \cdot 10^{-30}$ C m), which is distinctly higher compared with chlorocyclohexane. A calculation according to Smith–Eyring would be, however, less reliable in this case due to the presence of a double bond. We conclude that the conventional determination of dipole moments in solution is restricted in scope by several factors, also by the size and shape of the molecule. This restriction may cause but small inconsistencies as far as common molecules are considered. However, it can – in our opinion – manifest itself if an exact comparison is made between similar compounds with less common structures.

Thanks are due to Mrs M. Kuthanová for skilful technical assistance.

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Translated by the author (O. E.).