

PRINCIPLE OF ADDITIVITY OF DIPOLE MOMENTS: HALOGEN DERIVATIVES OF ADAMANTANE

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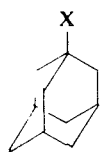
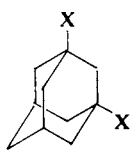
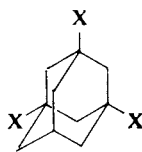
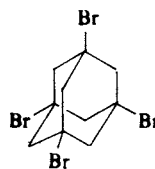
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Dipole moments of halogenated adamantanes *II–IV* were measured in two solvents using the Guggenheim–Smith method. The reliability of the method was checked on non-polar symmetrical compounds *I, V*. The dipole moments of 1,3-dihalogen and 1,3,5-trihalogen derivatives reveal small but real deviations from the additive behaviour: the experimental values are less than those calculated by vector addition from the moments of monoderivatives, assuming tetrahedral geometry. This fact can be explained by mutual induction of dipole rather than by angle deformation, although both effects can contribute. The deviations from the additive behaviour are qualitatively represented by CNDO/2 calculations with fixed geometry. However, even the greatest deviations observed amount only several percent in relative values and do not impair the general applicability of the bond moment approach.

Interpretation of dipole moments in terms of structure assumes that their expected values can be predicted with a reasonable reliability. Quantum chemical methods in their present state of development do not fulfil this requirement¹. Semiempirical methods are not sufficiently accurate^{1–3} although for particular simple molecules the agreement may be very good⁴. Even the present *ab initio* methods yield commonly too low results both with a contracted basis⁵ and with the double zeta plus polarization function basis⁶. Still most popular is the empirical approach which expresses the expected dipole moment as a vector sum of bond moments situated in the direction of the respective bond¹. The contributions of some functional groups need not be resolved and a gross group moment can be used instead. The approach has been widely applied to stereochemical problems¹. It is nowadays quite familiar and is explained in many textbooks – very often on the example of isomeric benzene derivatives. Nevertheless, it has never been systematically tested. The opinion finds general acceptance^{1,7} that its precision is variable and depends on the similarity of molecules from which the bond moments have been derived and to which they are applied. (In particular the corresponding bond angles should be rather close, indicating similar degree of hybridization⁸.) Much attention has been also given to molecules for which the additivity principle is evidently violated. This is due mostly to conjugation^{1,8,9} or intramolecular hydrogen bonds², less evident are smaller deviations connected with the polarization effects in larger molecules^{10,11}.

On the contrary, our intention in the present work is to test with which accuracy the additivity is fulfilled in standard structures when all mentioned effects are excluded. To this purpose one needs rigid model molecules with known geometry and well separated functional groups. Since the expected deviations may approach the experimental error, careful measurements are necessary and the results must be evaluated on a whole series of compounds together. In this first communication we report on the dipole moments of halogenated adamantanes *I*–*V*. The unsubstituted adamantane (*I*) and 1,3,5,7-tetrabromoadamantane (*V*) the dipole moments of which are zero have been included for testing the experimental accuracy. Previous measurements on adamantane monoderivatives^{11–14} revealed that their dipole moments are enhanced compared to simple aliphatic derivatives. Hence the additivity test must be based on bond moments derived from adamantane derivatives themselves. In this conception, the term bond moment means exactly the difference of the C—X and C—H bond moments, the latter being actually unknown.

*I*; X = H*IIa*; X = Cl*IIb*; X = Br*IIIa*; X = Cl*IIIb*; X = Br*IVa*; X = Cl*IVb*; X = Br*V*

EXPERIMENTAL AND RESULTS

Materials. Adamantane (*I*), 1-bromoadamantane (*IIb*) and 1,3-dibromoadamantane (*IIIb*) were commercial products, 1,3,5-Tribromoadamantane (*IVb*) was prepared by further bromination¹⁵. In the case of 1,3,5,7-tetrabromoadamantane (*V*) the work in an open vessel¹⁶ was preferred to a sealed tube¹⁵ but the yield given¹⁶ could not be reached even by prolonging the reaction time to 15 h. 1-Chloroadamantane (*IIa*) and 1,3-dichloroadamantane (*IIIa*) were prepared from the corresponding bromo derivatives *via* the hydroxy derivatives¹⁷. 1,3,5-Trichloroadamantane (*IVa*) was kindly provided from the stock of Laboratory of Synthetic Fuels, Institute of Chemical Technology, Prague. All samples were purified by repeated sublimation and their purity checked by m.p. determination, GLC, and mass spectrometry.

Physical measurements. The dipole moments were determined at 25°C in tetrachloromethane and benzene solutions. The method of Guggenheim-Smith^{18,19} was applied, the experimental details were as previously described². The physical constants of tetrachloromethane were: $d_4^{25} = 1.4930$, $n_D^{25} = 1.4740$, $n_D^{20} = 1.4710$. The results are given in Table I. In addition to the resulting dipole moment and the slopes α and γ , also the orientation polarization P_0 is given to allow comparison to compounds with zero dipole moment.

Calculations. The dipole moments of polyderivatives expected according to the additive scheme were calculated using the bond moment derived from the pertinent monoderivative

measured in the same solvent. Tetrahedral geometry was assumed throughout. The results are given in Table I, last column. The CNDO/2 calculations were carried out with the standard parametrization²⁰, for chlorine and bromine participation of the *d*-orbitals was accounted for and expressed by the parameters advanced^{20,21}. The tetrahedral bond angles and standard bond lengths were not optimized. The results are given in Table II.

DISCUSSION

Before discussing the minute differences between calculated and experimental dipole moments, a check of the experimental accuracy is advisable. The Guggenheim-Smith method¹⁸ is based on the assumed proportionality of atomic polarization and molar volume. This approximation need not be good for compounds of all structures²². Particularly for adamantane derivatives it was suggested²³ that atomic polarization P_A might be abnormally high. This view was disproved¹² by mea-

TABLE I
Dipole moments of halogen derivatives of adamantane (25°C)

Substituents (m.p., °C)	Solvent	α^a	γ^a	P_0 cm ³	μ^b	$\mu_{add}^{b,c}$
H	CCl ₄	0.23	0.185	0.5	0	—
(268)	C ₆ H ₆	0.32	0.260	1.4	0	—
1-Cl	CCl ₄	7.08	0.516	117.5	8.0 ^d	—
(164)	C ₆ H ₆	4.00	0.043	126.9	8.3 ^e	—
1,3-Cl ₂	CCl ₄	7.20	0.320	148.2	9.0	9.2
(132)	C ₆ H ₆	4.35	0.170	161.1	9.4	9.6
1,3,5-Cl ₃	CCl ₄	4.55	0.428	103.4	7.5	8.0
(102)	C ₆ H ₆	2.62	0.056	115.4	7.9	8.3
1-Br	CCl ₄	6.40	0.425	134.8	8.6 ^f	—
(116)	C ₆ H ₆	3.75	0.145	145.7	8.9 ^g	—
1,3-Br	CCl ₄	5.89	0.410	169.0	9.6	9.9
(112)	C ₆ H ₆	3.56	0.204	185.3	10.0	10.3
1,3,5-Br ₃	CCl ₄	3.32	0.385	114.5	7.9	8.6
(125)	C ₆ H ₆	2.00	0.153	129.3	8.4	8.9
1,3,5,7-Br ₄	CCl ₄	0.20	0.220	— 1.5	0	—
(246)	C ₆ H ₆	0.23	0.230	— 0.3	0	—

^a Slopes of the plots ϵ_{12} vs w_2 and n_{12}^2 vs w_2 , respectively; ^b units 10^{-30} C m; ^c calculated from bond moments, see Experimental; ^d in agreement with ref.¹¹, gives 8.4; ^e our previous value¹⁰ was 8.5 (Halverstadt-Kumler method), ref.¹³ gives 7.7; ^f the values obtained by two methods in two laboratories^{11,12} are 8.3, 8.7, 8.6, 8.6; ^g ref.¹³ 8.3.

asuring the total polarization within the framework of the Halverstadt-Kumler method: after subtracting the electronic polarization P_E the remaining P_A would represent only 3% of P_E . Within the framework of the Guggenheim-Smith method the orientation polarization is obtained directly and its value should equal zero for symmetrical molecules with zero dipole moment. Our measurements afforded small positive values for adamantane, and negative ones for its tetrabromo derivative V. We can assume that these values are completely random, indicating the inherent inaccuracy of the method. In this case the limit of this inaccuracy could be approximately 2 cm^3 in P_O , resulting in an uncertainty less than 0.1 in μ . (All dipole moment values are given in 10^{-30} C m). Another possibility is that these values of P_O are not random but really positive for the hydrocarbon and negative for its tetrabromo derivative. In this case mono-, di- and tri-halogen derivatives should exhibit deviations in P_O in magnitude between these limits. The resulting uncertainty in μ would be much less than 0.1.

The reliability of our results can be further estimated from the differences between the corresponding bromo and chloro derivatives (six values from 0.4 to 0.6, mean 0.55) or between measurements in the solvents benzene and tetrachloromethane for the same compound (six values from 0.3 to 0.5, mean 0.38). These differences are evidently real but fairly constant, indicating the maximum error of our values to be less than 0.2. In conclusion, the dipole moments of Table I are consistent and their experimental accuracy is as high as attainable in solution measurements. Comparison with the scarce literature data is also favourable, only the values of ref.¹⁴ are definitely shifted towards the others. Data of Table I also confirm the previous finding¹¹⁻¹⁴ that the dipole moments of 1-substituted adamantanes are by more than a unit

TABLE II
CNDO/2 calculations of dipole moments of halogenated adamantanes^a

Substituents	μ CNDO/2	μ_{add} CNDO/2 ^b	Difference
1-Cl	25.8 (8.3)	—	—
1,3-Cl ₂	28.9 (9.0)	29.8 (0.6)	1.8 (0.6)
1,3,5-Cl ₃	23.4 (7.1)	25.8 (8.3)	2.4 (1.2)
1-Br	7.7	—	—
1,3-Br ₂	8.3	8.9	0.6
1,3,5-Br ₃	5.6	7.7	2.1

^a Calculated with the participation of *d*-orbitals as given in Experimental, except the values in parentheses which were obtained without *d*-orbitals; ^b calculated according to the additive scheme the value for the pertinent monoderivative as obtained by CNDO/2.

higher than of the corresponding aliphatic tertiary derivatives. This feature was discussed in connection with still higher moments of diadamantanes, but not explained unambiguously¹¹.

The simplest test of the additive behaviour can be obtained on 1,3,5-trihalogen derivatives whose dipole moments should be equal as for the corresponding monoderivative in the same solvent, provided the ideal tetrahedral geometry. Our experimental results reveal that trihalogen derivatives have definitely smaller moments, the differences being from 0.4 to 0.7, mean value 0.52. According to the above discussion this difference is to be considered real. For 1,3-dihalogen derivatives one can calculate the anticipated dipole moments from monoderivatives, assuming again the tetrahedral geometry. Comparison with experiment reveals smaller differences: from 0.2 to 0.3, mean 0.25. These values are already close to experimental errors and could be actually doubted if considered separately. However, one must take into account that all four differences are fairly constant and in the same sense which agrees with 1,3,5-derivatives. We thus believe that even these minute deviations are real.

There are two plausible interpretations of the observed facts: either in terms of distorted geometry or of electrostatic interaction of dipoles. The first explanation assumes that the bond angles in substituted adamantanes are somewhat deformed with respect to the tetrahedral values since the original T_d symmetry of adamantane is reduced to C_{2v} in *III* and C_{3v} in *IV*. We can calculate the deformations necessary to meet the experimental dipole moments. In *IIIa,b* the angle of the two C—X bonds should be widened by 1.3° or 2.4° , respectively, with respect to the ideal tetrahedral values. In *IVa,b*, the angle of the C—X and $C_{(7)}$ —H bonds should be reduced by 1.1° or 1.4° , the change of the angle between two C—X bonds being virtually the same in the opposite sense. Distortion of this order of magnitude could be detected only by very accurate X-ray crystallographic studies or by statistical evaluation of many results²⁴ which are not available for adamantane derivatives. X-Ray studies of 1-chloroadamantane²⁵ and 1-fluoro-adamantane²⁶ did not allow a more exact determination of the $X-C_{(1)}-C_{(2)}$ angle but distortions up to 2° are in any case admitted. It seems also *a priori* reasonable that the distance of halogen atoms should be always extended. It follows that deformations of bond angles could explain the observed dipole moments, both in the absolute values of the deviations and in their sense. Significant are also the comparable deformations required for di- and trihalogen derivatives, further virtually equal effects of chlorine and bromine. Systematic analysis of benzene derivatives²⁴⁻²⁶ revealed deformations of the bond angles, not exceeding 2° except for the most powerful electron attracting substituents. Even in this case the effects of bromine²⁷ and chlorine²⁴ were equal.

The second explanation assumes unchanged geometry and mutual lowering of bond moments by electrostatic interaction (inductive effect). It has been used already

in classical discussions of dipole moments of halogenated methanes²⁸ and expressed in a more quantitative manner by the topological theory of Smith-Eyring²⁹ and its non-topological extension³⁰. Comparison to di- and tri-halogenomethanes may be of relevance since these compounds bear the C-Hal dipoles at the same angles as compounds *III*, *IV* but at a shorter distance. Dipole moments of dichloromethane and chloroform are by 1.9 and 2.8 (in the gas phase³¹) less than the additive tetrahedral values. For dibromomethane and bromoform this makes³¹ 2.3 and 2.7, respectively. There is again little difference between chlorine and bromine but compared to adamantane derivatives the deviations from additivity are much larger. The angles Cl—C—Cl are 111.78° in dichloromethane³² and 111.3° in chloroform³³. Introduction of these values into the calculation can account only for a lesser part of the deviations: 0.2 and 0.6, respectively. The rest, 1.7 in CH₂Cl₂ and 2.2 in CHCl₃, must be due to induction. In adamantane derivatives the inductive effect is smaller as it decreases with the third power of the distance of point dipoles. As far as this oversimplified picture is applicable at all, we can place the point dipoles tentatively into the middle of each C—Cl bond. Then the inductive effect would be reduced to 5%, when going from methane to adamantane derivatives, and would become unimportant in the latter. If, however, the point dipoles are placed nearer to the chlorine atom, say in seven eighths of the C—Cl distance²⁸, the reduction is only to 11% and the induction might account for the effect observed in adamantane derivatives.

The aforementioned problem might be attacked by several theoretical approaches, calculating either the optimized geometry of adamantane derivatives or mutual influence of bond dipoles. We applied the CNDO/2 calculations with fixed tetrahedral geometry. We can not expect that the calculated dipole moments should agree well with the experiments in solution. However, they could reproduce at least the relative deviations due to dipole interactions. The data of Table II reveal that the calculations using *d*-orbitals are acceptable for bromo derivatives while they overestimate badly the dipole moments of chloro derivatives. For the latter the calculations without the participation of *d*-orbitals are much more suitable. Irrespective of the disagreement in absolute values, all calculations agree with the general trend of the experimental values: all polyderivatives show reduced dipole moments, triderivatives more than bisderivatives. Since the calculations were carried out with fixed geometry, the results can be understood only in terms of electrostatic induction.

According to the foregoing discussion, both the angle distortion and induction provide acceptable explanations of the observed dipole moments and their deviations from additivity. A decision is not possible at present on the basis of adamantane derivatives only; even an X-ray study on one, two compounds would be probably not sufficient. It is also possible that the two effects are operating simultaneously and are of comparable magnitude. In our opinion, however, the induction is at least more important. This conclusion is based on model compounds with a well known

geometry and with greater observed effects: halogenated methanes discussed above and various *meta* derivatives of benzene investigated in the accompanying paper³⁴. The merit of adamantane derivatives consists in yielding the first evidence of deviations from the additive behaviour in the case a non-conjugated system and non-adjacent polar bonds.

It is to be stressed that the deviations just discussed amount at most 6% of the measured value and exceed but slightly the common experimental error. They can be thus detected only by accurate and systematic measurements, and do not depreciate the vector addition of bond moments as a general tool in structural studies, *e.g.* in stereochemistry. This conclusion can be supported by the following statistical considerations: If the mean deviation (s) found in this paper is say 0.4, it is comparable to the experimental error in routine work. In order to compare the precision of the bond moment scheme to other empirical relationships in other fields, this value is to be related to the standard deviation (s_0) of all possible dipole moment values from their mean³⁵. The latter value is difficult to estimate due to the unsymmetrical statistical distribution³⁶. If we adopt the values $s_0 = 3$, the ratio $s/s_0 = 0.13$ means an empirical relationship of somewhat less predictive power than *e.g.* the Hammett equation or additivity of molar refraction. Due to the unsymmetric distribution, however, the predictive power strongly increases with the actual values of the dipole moment³⁶.

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