

The Dipole Moments of Substituted Adamantanes and the Correlation of the Dipole Moments of Aliphatic Compounds with Substituent Constants

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Dipole moments are reported for a representative series of monosubstituted adamantanes. An analysis of the results together with a measurement of the electronic polarisation of adamantanes suggest that the atomic polarisations are small. A method is reported to allow correlation of the dipole moments of series of aliphatic compounds with substituent inductive effects and is illustrated with methyl, t-butyl, cyclohexyl, cyclopentyl, cyclopropyl, and adamantyl derivatives.

MUCH interest continues to be shown^{1,2} in the chemistry of adamantane and its derivatives. Until recently, however, dipole moment values were available for only

¹ R. C. Fort and P. von R. Schleyer, *Chem. Rev.*, 1964, **64**, 277.

two of the monosubstituted compounds. The values obtained¹ for 1-bromo- and 1-chloro-adamantane were calculated using various methods but in each case were

² V. V. Sevost'yanova, M. M. Krayushkin, and A. G. Yurchenko, *Russian Chem. Rev.*, 1970, **39**, 817.

higher than the values for other alicyclic and aliphatic halides. It was suggested^{1,3} that this arose because of an unusually high atomic polarisation of unknown origin. More recently, values have been reported⁴ for the dipole moments of a limited series of adamantanes and it was suggested that the higher values obtained compared with those from analogous t-butyl compounds might indicate the greater inductive effect of the adamantyl group. Analysis of their results led the authors to suggest that they provided some evidence for a concentration of positive charge close to the adamantane nucleus.⁵

These results lead us to report our own values for a more extensive series of adamantanes. At the same time, we have looked at the correlation of such results against substituent constants and report successful correlations for both adamantanes and other aliphatic series.

EXPERIMENTAL

Adamantanes.—1-Bromoadamantane (Koch-Light), adamantane-1-carboxylic acid (Koch-Light), and 1-aminoadamantane (Aldrich; as hydrochloride) were commercial samples. 1-Hydroxy-, m.p. 284–285° (lit.,⁶ 283–285°), 1-chloro-, m.p. 162° (lit.,⁷ 165°), 1-fluoro-,⁸ m.p. 246–252° (lit.,⁹ 240–250°), 1-acetamido-, m.p. 185–187° (lit.,¹⁰ 189°), 1-nitro-,¹⁰ m.p. 160° (lit.,¹¹ 159°), 1-methoxy-,⁹ b.p. 156–160° at 25 mmHg, 1-phenyl-, m.p. 80–82° (lit.,⁷ 82°), 1-methoxycarbonyl-, m.p. 34–36° (lit.,¹² 38–39°), 1-hydroxymethyl-, m.p. 111–114° (lit.,⁷ 115°), 1-bromomethyl-,¹³ m.p. 41–43° (lit.,¹⁴ 41–43°), and 1-methyladamantane, m.p. 99–101° (lit.,¹³ 103°) were prepared by literature methods.

1-Cyanoadamantane.—1-Acetamidoadamantane (9.9 g) and thionyl chloride (100 ml) were refluxed (2 h) and the mixture was then evaporated to dryness *in vacuo*. The residual solid was washed with sodium hydroxide (100 ml; 10%) and crystallisation of the residue from ethanol gave the product (7.4 g, 82%) m.p. 192–193° (lit.,⁹ 193–194°).

1-Dimethylaminoadamantane.—1-Aminoadamantane (10 g), formic acid (20 ml; 90%), and formalin (50 ml; 38%) were heated (30 h, steam-bath). The mixture was then evaporated to dryness *in vacuo*. The residue was dissolved in chloroform (200 ml), washed with saturated sodium bicarbonate solution (2 × 50 ml), and dried (MgSO₄). The oily residue from evaporation of the solvent was converted to the perchlorate salt (7.4 g, 69%), m.p. 191–

193° (from water) (lit.,¹⁵ 180–184°). The free base, b.p. 197–200° at 50 mmHg, was liberated as required.

Dipole Moments.—The dipole moments for most of the substituted adamantanes were calculated by the method of Guggenheim (method A).^{16,17} The dielectric constants were measured at 20° by the heterodyne beat method using a DFL-1 cell in a DMO1 dipolemeter operating at 2 MHz. The dielectric constant was taken as the mean of five determinations and these were made on a series of at least five concentrations in the range 0.001–0.01M in carbon tetrachloride. The procedure was repeated two to four times per compound. The refractive indices were measured by an Abbé refractometer and taken as the mean of five determinations.

This method was used for adamantyl derivatives of dipole moment greater than 1 D and the dipole moments of chloro-, bromo-, and bromomethyl-adamantane obtained agreed with previously reported values^{3,4} for these compounds.

Dipole moments of the least polar adamantyl derivatives were obtained by the method of Halverstadt and Kumler (method B).¹⁸ The dielectric measurements were made¹⁹ using a modified Sayce-Briscoe cell and a Wayne Kerr type B631 transformer arm bridge. The specific volume measurements were made with a Paar digital densimeter.

TABLE I

Dipole moment measurements at 20° for adamantyl-Y compounds (method A, heterodyne beat; method B, transformer ratio arm)

Y	$\frac{d\epsilon}{dw}$	$\frac{dV}{dw}$	$\frac{dn^2}{dw}$	μ/D	Method
H	0.237	-0.275			B
Me	0.206	-0.233		0.13	B
Ph	0.532	-0.359		0.75	B
NMe ₂	1.664		0.330	1.10	A
OMe	2.959		0.219	1.52	A
	1.271	-0.336		1.43	B
CO ₂ Me	3.450		0.207	1.79	A
CH ₂ Br	3.676		0.310	1.97 ^a	A
F	4.898		0.160	2.11	A
Cl	6.932		0.233	2.39 ^b	A
Br	6.110		0.348	2.50 ^c	A
	2.890	-0.582		2.60	B
NO ₂	16.250		0.290	3.82	A
CN	19.187		0.249	3.92	A

^a 2.10 D ref. 4. ^b 2.32 D ref. 4; 2.53 D ref. 3. ^c 2.49 D ref. 4; 2.59 D ref. 3.

The dipole moments of methoxy- and bromo-adamantane were also determined by this method and comparison of figures from the two methods shows reasonable agreement.

Values of $d\epsilon/dw$, dV/dw , dn^2/dw , and μ are shown in Table I. One typical determination is shown for the

³ W. E. Vaughan, W. P. Purcell, and C. P. Smyth, *J. Amer. Chem. Soc.*, 1961, **83**, 571.

⁴ I. B. Mazleika, I. S. Yankovskaya, and Y. Y. Polis, *Zhur. obshchei Khim.*, 1971, **41**, 1633.

⁵ P. von R. Schleyer, R. C. Fort, W. E. Watts, M. B. Comisarow, and G. A. Olah, *J. Amer. Chem. Soc.*, 1964, **86**, 4195.

⁶ H. W. Geluk and J. L. M. Schlatmann, *Tetrahedron*, 1968, **24**, 5361.

⁷ H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, 1959, **92**, 1629.

⁸ R. C. Fort and P. von R. Schleyer, *J. Org. Chem.*, 1965, **30**, 789.

⁹ P. H. Owens, G. J. Gleicher, and L. M. Smith, *J. Amer. Chem. Soc.*, 1968, **90**, 4122.

¹⁰ H. Stetter, J. Mayer, M. Schwarz, and K. Wulff, *Chem. Ber.*, 1960, **93**, 226.

¹¹ G. W. Smith and H. D. Williams, *J. Org. Chem.*, 1961, **26**, 2207.

¹² H. Koch and W. Haaf, *Org. Synth.*, 1964, **44**, 2.

¹³ F. N. Stepanov and V. F. Baklan, *J. Gen. Chem. (U.S.S.R.)*, 1964, **34**, 580.

¹⁴ J. E. Norlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, J. J. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, 1966, **88**, 4475.

¹⁵ M. Paulshock and J. C. Watts, U.S.P. 3,310,469/1967 (*Chem. Abs.*, 1967, **67**, 11275c).

¹⁶ E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.

¹⁷ F. Oehme and H. Hirth, 'Determination of the Molecular Dipole Moment,' Karl Scientific Instrument Corporation, El Cajon, California.

¹⁸ I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

¹⁹ R. A. Y. Jones, A. R. Katritzky, P. G. Lehman, K. A. F. Record, and B. B. Shapiro, *J. Chem. Soc. (B)*, 1971, 1302.

heterodyne beat method for each compound. Average dipole moment values for the adamantyl compounds are shown in Table 2 together with values from the literature for methyl, t-butyl, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl compounds.

DISCUSSION

Adamantyl Compounds.—It is clear from the values listed in Table 2 that dipole moments of the adamantyl compounds are generally somewhat greater than those in the other series. It had earlier been suggested¹

Correlation with Substituent Constants.—There have been many investigations^{20,24,25} into the relation between dipole moments and substituent constants for both aliphatic and aromatic compounds. In simplest terms this can be represented by equation (1), where μ_{RY} is

$$\mu_{RY} - \mu_{RH} = \rho\sigma \quad (1)$$

the dipole moment of compound RY, μ_{RH} refers to the parent hydrocarbon, σ_Y represents the electronic effect of substituent Y, and ρ is the slope of the correlation line. In the aliphatic compounds under consideration here,

TABLE 2
Dipole moments (μ/D) of some aliphatic derivatives, RY

	R = Me		R = t-Bu	R = Cyclo-hexyl ^{e,f}	R = Cyclo-pentyl ^{e,g}	R = Cyclo-butyl ^e	R = Cyclo-propyl ^{e,h}	R = Ad ^{4,j}
	Gas ^a	Soln. ^b						
CN	3.94	3.47	3.7 ^a					3.89
NO ₂	3.50	3.13	3.48 ^a	3.6				3.82
Cl	1.87	1.86	2.14 ^c	2.18	2.08		1.76	2.39
Br	1.80	1.84	2.21 ^c	2.31	2.20	2.09	1.69	2.51
F	1.81	1.71	2.05 ^{a(g)}	1.94	1.86			2.11
CH ₂ Br	2.01	1.89 ^a						1.97
CO ₂ Me	1.67	1.74		1.4	1.63	1.96		1.79
OMe	1.29	1.25	1.23 ^d	1.35				1.52
NMe ₂	0.64	0.86						1.10
Ph	0.37	0.40 ^a	0.5 ^a				0.49	0.75

^a C. P. Smyth, 'Dielectric Behaviour and Structure,' McGraw-Hill, New York, 1955. ^b C. W. N. Cumper, *Tetrahedron*, 1969, **25**, 3131. ^c Ref. 22. ^d H. Lumbroso and G. Dumas, *Bull. Soc. chim. France*, 1955, 651. ^e Ref. 25. ^f CF₃ = 2.4. ^g I = 2.06 D. ^h COMe = 2.84 D. ⁱ This work. ^j Me = 0.13 D.

that the greater dipole moment of adamantyl bromide and chloride compared with the analogous t-butyl halides arose from a relatively high atomic polarisation term in the adamantanes. This seems unlikely since the adamantane skeleton does not have any particularly polar bonds and the bending force constants are not unusually low.²⁰

We carefully measured the polarisation of adamantane itself and the value of 42.8 obtained is in close agreement with the value of 41.4 for the electronic polarisation estimated from tables²¹ of bond polarisations. Further, the dipole moments of the substituted adamantanes plot very well against those of the corresponding methyl compounds. It therefore seems that the somewhat higher dipole moments found for adamantanes compared to other tertiary alkyl series arises from an intrinsically easier polarisation. This is in accord with the observation²² that in a series of alkyl halides, the dipole moment increases with increasing size of the alkyl group and the increase is more marked with branched chain isomers. We have recently measured²³ the effect of the adamantyl group as a *para*-substituent in benzoic acid dissociation; the σ_p value of an adamantyl substituent is -0.24 compared to -0.20 for t-butyl and -0.17 for methyl. This evidence supports the idea of greater polarisability of the adamantyl group.

²⁰ L. E. Sutton in 'Determination of Organic Structures by Physical Methods,' eds. E. A. Braude and F. C. Nachod, Academic Press, New York, 1955.

²¹ R. J. W. Le Fevre and K. D. Steel, *Chem. and Ind.*, 1961, 670.

²² J. W. Smith, 'Electric Dipole Moments,' Butterworths, London, 1955.

²³ T. J. Broxton, G. Capper, L. W. Deady, A. Lenko, and R. D. Topsom, *J.C.S. Perkin II*, 1972, 1237.

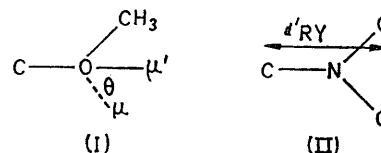
μ_{RH} may be regarded as zero and substituent resonance effects will not operate. Equation (1) may be simplified to equation (2), where σ_I represents the inductive

$$\mu_{RY} = \rho\sigma_I \quad (2)$$

effect of the substituent Y and is known²⁶ from reactivities of aliphatic compounds. It has been found²⁷ that better correlations are obtained when a distance factor is introduced into the calculations. We have, therefore, additionally modified equation (2) to equation (3) for the purpose of our correlations of monosub-

$$\mu_{RY}/d'_{RY} = \rho\sigma_I \quad (3)$$

stituted hydrocarbons, where $\mu'_{RY} (= \mu_{RY} \cos \theta)$ in the dipole moment resolved in the direction of the bond between the substituted carbon atom and the atom of the substituent attached to it (I) while d'_{RY} is the distance of charge separation in this direction. The



distance d'_{RY} was taken to be that between the substituted carbon atom and the most electronegative

²⁴ C. N. Rao, W. H. Wahl, and E. J. Williams, *Canad. J. Chem.*, 1957, **35**, 1575; M. Charton, *J. Org. Chem.*, 1965, **30**, 552; R. D. Kross and V. A. Fassel, *J. Amer. Chem. Soc.*, 1956, **78**, 4225; A. N. Sharpe and S. Walker, *J. Chem. Soc.*, 1961, 4522.

²⁵ M. Charton, *J. Chem. Soc.*, 1964, 1205.

²⁶ R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343.

²⁷ O. Exner, *Coll. Czech. Chem. Comm.*, 1960, **25**, 642.

atom of the substituent measured along the stated axis, as illustrated (II) for the nitro-group. The values of the constants used are given in Table 3.

TABLE 3

Bond moment angle and charge separation of aliphatic derivatives, RY

Y	θ°	$d'_{RY}/\text{\AA}^a$
CN	0	2.62
NO ₂	0	2.02
Cl	0	1.78
Br	0	1.94
F	0	1.38
CH ₂ Br	70	2.20
CO ₂ Me	43	2.14
OMe	55	1.43
NMe ₂	70	1.47
CF ₃	0	2.01
COMe	60	2.14
I	0	2.14

^a Derived from bond lengths in 'International Tables for X-Ray Crystallography,' eds. C. H. Macgillivray and G. D. Rieck, Kynoch Press, Birmingham, vol. III, 1962.

Table 4 shows the derived values of the effective charge, μ'_{RY}/d'_{RY} , used in the correlations (alkyl and phenyl derivatives were excluded from the correlations since the dipole moments are very low and the most

the substituent dipole, obtained by vector addition of bond moments in this direction. The statistical correlation of A with σ_I for sixteen substituents was only fair.

Inspection of any of the dipole moment series indicates that the halogen-containing compounds cause the greatest deviations from a plot of dipole moment with σ_I . Incorporation of the distance factor eliminates these deviations and the results in Table 5 show that now superior correlations are obtained in all cases. For example, correlation of the dipole moments of the same series of substituted methane (gas) and cyclopentane compounds with σ_I gives r (correlation coefficient) = 0.840 [s (standard deviation) = 0.68] and $r = 0.888$ ($s = 0.55$) respectively compared with values 0.983 and 0.988 in Table 5.

Correlation of the cyclobutane results was omitted since there were results for only three substituents apart from hydrogen. Charton previously found²⁵ that dipole moments of cyclopropyl derivatives were best correlated with the σ_p parameter, indicating the special nature of the three-membered ring. From Table 5, the correlation of the effective charge for cyclopropyl compounds with σ_I , based on fewer points, is as good as the correlation for cyclohexyl compounds.

TABLE 4

Effective charges, μ'_{RY}/d'_{RY} , used in correlations

Y	MeY		t-BuY	Cyclo-PrY ^a	Cyclo-PenY ^b	Cyclo-HexY ^c	AdY	σ_I^d
CN	1.52	1.32	1.40	1.43	1.42		1.48	0.56
NO ₂	1.71	1.55	1.72			1.78	1.89	0.63
Cl	1.05	1.04	1.22	0.99	1.17	1.22	1.34	0.47
Br	0.93	0.95	1.13	0.87	1.11	1.19	1.29	0.45
F	1.34	1.24	1.49		1.35	1.41	1.54	0.52
CH ₂ Br	0.31	0.29					0.31	0.17
CO ₂ Me	0.59	0.59			0.56	0.48	0.61	0.30
OMe	0.52	0.50	0.49			0.54	0.60	0.25
NMe ₂	0.14	0.20					0.25	0.10

^a COMe = 0.67 D, $\sigma_I = 0.28$. ^b I = 0.96 D, $\sigma_I = 0.38$. ^c CF₃ = 1.19 D, $\sigma_I = 0.41$. ^d C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.

TABLE 5

Correlation of effective charges of some aliphatic series, RY, with σ_I using equation (3) (see text)

	MeY (gas)	MeY (soln.)	t-BuY	Cyclo-HexY	Cyclo-PenY	Cyclo-PrY	AdY
ρ	2.74	2.56	2.77	2.94	2.61	2.31	3.03
r	0.983	0.992	0.989	0.977	0.988	0.976	0.987
s	0.11	0.07	0.10	0.13	0.09	0.13	0.11
Number of points	10	10	7	8	7	5	10
Intercept at $\sigma_I = 0$	-0.13	-0.08	-0.08	-0.14	-0.05	-0.12	-0.11

electronegative atom is not obvious). These values are only approximate measures of charge separation but should be related to the effect of the substituent at a distant centre as assessed by σ_I . A related attempt at including a distance factor in dipole moment calculations has been reported recently. Sekigawa derived²⁸ a function $A = \mu/l$, where l is the distance between the carbon atom to which the substituent is bonded and the centre of mass of the charge, and μ is

²⁸ K. Sekigawa, *Tetrahedron*, 1972, **28**, 505.

²⁹ C. G. Swain and E. C. Lupton, *J. Amer. Chem. Soc.*, 1968, **90**, 4328.

These correlations of effective charges would thus seem to provide a satisfactory method for estimating or interpreting the dipole moments of aliphatic compounds. Correlations using equation (3) but with the \mathcal{F} parameter of Swain and Lupton²⁹ instead of σ_I , were always inferior to those reported in Table 5.

From these results, it would be expected that effective charges in aliphatic compounds could be correlated with any other property which was related to the inductive effect of the substituent. This is so and, for example, correlation of the effective charge of seven adamantane derivatives with the dissociation constant of substituted

bicyclo-octylcarboxylic acids³⁰ (insufficient data on adamantane acids is available for a meaningful correlation) gave $r = 0.980$ ($s = 0.07$), while the effective charge of eight substituted methanes correlates reasonably ($r = 0.969$, $s = 0.14$) with the pK_a of the analogous substituted acetic acids.³¹

The effective charge can also be related to the electronegativity of the substituent. For example, the effective charges for substituted methanes in solution (Table 4) correlate well ($r = 0.981$, $s = 0.10$) with theoretically calculated group electronegativities.³²

³⁰ H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, 1964, **86**, 5188.

This correlation between experimental results and independently derived electronegativity values further supports the choice of the effective charge as the correct quantity for interpreting substituent effects on molecular dipole moments.

We thank R. P. Duke and R. Scattergood for making the transformer ratio arm measurements.

[2/1489 Received, 26th June, 1972]

³¹ A. Albert and E. P. Serjeant, 'Ionization Constants of Acids and Bases,' Methuen, London, 1962.

³² J. E. Huheey, *J. Phys. Chem.*, 1965, **69**, 3284; 1966, **70**, 2086; *J. Org. Chem.*, 1966, **31**, 2365.
