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ELECTRIC BOND AND GROUP DIPOLE MOMENTS

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Abstract—Three concepts of bond moments are discussed to demonstrate that theoretical values, those determined from spectral intensities, and those from the analysis of experimental dipole moments cannot be combined into a satisfactory single scale of bond and group moments. A scale is given, based upon measured dipole moments, with special emphasis on the group moments of organic substituents and the moments associated with C—C bonds.

THE concept of an electric dipole moment associated with a chemical bond has existed since 1923 when Thomson[1] suggested that the dipole moment of a molecule was the vector sum of its component bond moments. Bonding electrons are not distributed symmetrically about the atomic nuclei so that a bond possesses an electric moment. The main factors contributing to this moment are:[2, 3]

(a) the asymmetric charge distribution arising from the different electronegativities of bonded atoms,

(b) the homopolar dipole caused by the different sizes of the bonding atomic orbitals,

(c) the atomic dipole from utilizing hybridized atomic orbitals. Since it is impossible to form a single hybrid this may give rise to,

(d) the lone-pair moment from non-bonding electrons in hybridized atomic orbitals.

The intrinsic bond moment. Factors (a), (b), and (c) above result in the centroid of negative charge of the valence electrons being displaced from the centroid of the positive nuclear charges. This gives rise to an intrinsic bond moment. It cannot be determined experimentally and requires detailed wave mechanical calculations to furnish acceptable values (c.f. Refs. 4, 5). The molecular dipole moment of a polyatomic molecule is the vector sum of these bond moments, together with contributions from any lone-pair electrons.

The dynamic bond moment. Experimental values for bond moments in polyatomic molecules can be obtained from the intensities of IR absorption lines[5, 6] and from IR dispersion measurements.[7] The intensity, however, depends upon how the dipole moment changes during a normal vibration. The electron distribution also alters during a vibration and with it the bond lengths, bond angles, and atom hybridization. The electrons are not necessarily even symmetrical about the internuclear axis during all stages of the vibration so that there can be a considerable transverse moment in addition to the longitudinal one along the bond.[8] These changes in electron distribution manifest themselves in a dynamic bond moment which is not vectorially additive and which depends upon the vibrational mode considered and method of analysis.[5, 6] The contribution, if any, made by the atomic dipoles is uncertain.

The static bond moment. The third method of assigning bond moments is an empirical one of breaking down measured dipole moments into component moments. Complications can arise from induced, mesomeric, and interaction moments. With some inorganic molecules it is possible to express their measured dipole moments in terms of a single bond moment (e.g. H_2O, NH_3), but its value includes a substantial contribution from the lone-pair electrons. More frequently dipole moments can only be expressed in terms of several bond moments in which case an arbitrary origin of zero bond moment is required. This is always the situation with organic molecules. Normally a value is assigned to the C—H bond and moments on this scale will be called static bond moments.

Intrinsic, dynamic, and static bond moments each have a different basis and caution must be exercised when comparing them.* Intrinsic and static moments are vectorially additive (subject to corrections for inductive and mesomeric effects) but this is not so for dynamic moments. The numerical relationship between the first and third scales depends upon the origin chosen for the static scale and the method of dealing with atomic dipoles. These will be discussed with particular reference to organic molecules.

HYBRIDIZATION AND STATIC BOND MOMENTS

In molecules the atomic dipole moments virtually cancel out and Hamilton[10] suggested that they are best omitted. This is desirable as it reduces both the lone-pair moments and the static moments of bonds between differently hybridized C atoms.

The concept of static bond moments presupposes that they are independent of the situation of the bond in the molecule. Force constants, bond energies, and bond lengths of atoms joined to carbon, however, depend upon its hybridization.[11] Bond moments are similarly affected. The more *s* character in a carbon orbital the greater is its electronegativity and atomic dipole, and the smaller is its radius;[3, 11, 12] each factor contributing to the intrinsic moment is altered. Coulson initially suggested[3] that the intrinsic C—H moment changes by 0·05 D over the range sp^1 to sp^3 hybridization but this conclusion would be affected by the altered electronegativity of the C atom.[12]

The assignment of different values to static C—H bond moments would only be desirable if they are *more sensitive to hybridization changes* than are the moments of other C—X bonds. The change, with hybridization, in the homopolar dipole and that arising from the altered electronegativity of a C atom may not be markedly dependent upon the nature of X. Consequently, little advantage ensues from postulating different static C—H moments; in this respect a scale of static bond moments differs from other scales.

Experimental results confirm the desirability of a constant C—H bond moment.

(1) Unless the C—H moment is constant bonds between differently hybridized C atoms would have large static bond moments.[13]

(2) The mesomeric moment, introduced by Sutton,[14] correlates well with the directing character of substituents in aromatic and heterocyclic molecules. It is based upon a constant C—H bond moment.

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* The N—H bond moments in the ammonia molecule, for example, have been given as, intrinsic[9] −1·96 D, dynamic[9] *ca.* 0·7 D, static 1·03 D.

(3) Two suggested sets of C—H bond moments are shown in Table 1; those of Smith fit the empirical relationship,

$$\mu(\overset{-}{\mathrm{C}}\text{—}\overset{+}{\mathrm{H}}) = 1{\cdot}72 - 0{\cdot}67\,\lambda^2$$

where λ is the hybridization parameter of the carbon orbital ($\psi = \psi_s + \lambda\psi_p$).

If the hybridized orbitals of pyridine are mutually orthogonal, and point along the bond directions, their hybridization parameters may be evaluated[12] from the bond angles.* The above equation gives the bond moments $\mu(\overset{-}{\mathrm{C}}_2\text{—}\overset{+}{\mathrm{H}})$ 0·02 D, $\mu(\overset{-}{\mathrm{C}}_3\text{—}\overset{+}{\mathrm{H}})$ 0·40 D, ($\overline{\mathrm{C}}_4$—H) 0·51 D. Two points follow.

(a) The resultant dipole moment of the C—H bonds in pyridine would be 0·95 D (0·87 D using Petro's values) which is 43% of the total dipole moment (2·21 D[18]) and is surely too great. The lone-pair moment of the N atom and the polarity of the C—N bonds[19] must make the main contributions to its dipole moment; the C—H moment, and that from the π-electron distribution,[20] being secondary factors. A constant C—H moment of 0·4 D however gives a resultant C—H moment of 0·34 D for pyridine. Similar situations exist in other heterocyclic molecules.

TABLE 1. C—H BOND MOMENTS

Hybridization of carbon atom	λ	$\overset{-}{\mathrm{C}}\text{—}\overset{+}{\mathrm{H}}$ bond moment (D)	
		Smith[15]	Petro[13]
sp^3	3	−0·3	0·31
sp^2	2	0·4	0·65
sp^1	1	1·0	1·05

(b) The group moments of many substituents in pyridine and quinoline,[18, 21] measured relative to that of the substituted C—H bond, are much as anticipated. If the C—H moments varied the group moments of all substituents in the 2 position would have to be altered by 0·5 D when compared with positions 3 and 4.

SCALE OF STATIC BOND MOMENTS

The simplest scale of static bond moments would seem to be one in which the C—H bond moment is independent of the hybridization of the C atom; small moments then have to be assigned to bonds between differently hybridized C atoms. Cahill and Mueller[22] calculate that the $\overset{+}{\mathrm{C}}(sp^3) - \overset{-}{\mathrm{C}}(sp^2)$ bond has a moment of 0·14 D and the C—H bond moments with sp^3 and sp^2 C atoms only differ by 0·06 D. Other calculations[4] indicate larger moments between differently hybridized C atoms.

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* The approximation in assuming the atomic and not the molecular orbitals are orthogonal cannot be serious in view of the agreement between the molecular geometry predicted on this basis[16] and the experimental results.[17]

The magnitude of the C—H bond moment has been reviewed.[15, 23, 24] Its value is unknown but all indications are that the intrinsic moment increases with the *s* character of the hybridized orbital. For a scale of static bond moments the precise value for the C—H bond is unimportant and there seems no point in taking it to be other than the origin of the scale, i.e. μ (C—H) = O.

Hydrocarbons are virtually non-polar unless unsaturation is present when they have small dipole moments.[25] These could arise from induced moments, from hyperconjugation although this phenomena has been discredited for molecules in their ground states,[11] and from the presence of bent bonds. The major factor, however, appears to be the polarity of bonds between differently hybridized C atoms.

TABLE 2. C—C BOND MOMENTS

Hybridization $\overset{+}{C}$—$\overset{-}{C}$	Bond moment (D)	
$C(sp^3)$—$C(sp^2)$	0·30	These values are increased by about 0·10 D if a CH_3 group is attached to the $C(sp^3)$ atom and by about 0·15 D for longer hydrocarbon chains.
$C(sp^3)$, $C(sp^3)$ > $C(sp^2)$	0·50	
$C(sp^3)$—$C(sp^1)$	0·70	
$C(sp^2)$—$C(sp^1)$	0·40	

The bond moments suggested in Tables 2–4 for the commoner bonds are "average values", consistent with the dipole moments[25] of many molecules. They only refer to the bond angles[26] and other component moments quoted in the Tables and they are listed for experimental results for gases and also for solution in non-polar solvents.

TABLE 3. H—X BOND MOMENTS

Compound		Dipole moment gas	Dipole moment solution	Bond moment gas	Bond moment solution	
($\overset{+}{H}$	$\overset{-}{C}$)			(0	0)	
H	F	1·82	(1·98)	1·82	1·98	
H	Cl	1·08	1·27	1·08	1·27	
H	Br	0·82	1·02	0·82	1·02	
H	I	0·44	(0·58)	0·44	0·58	
H_3	N	1·47	1·42	1·30	1·28	with ∠HNH = 106·8°
H_3	P	0·58	—	0·36	—	with ∠HPH = 93·5°
H_2	O	1·85	(1·77)	1·51	1·45	with ∠HOH = 104·5°
H_2	S	0·97	0·9	0·70	0·65	with ∠HSH = 92·1°

Table 4. R—X Group moments

Compound	Dipole moment		Group moment or dipole angle			
	gas	solution		gas	solution	
Me F	1·85	(1·71)				
R F	1·96					
Ph F	1·60	1·47				
Me Cl	1·87	1·86				
R Cl	2·06	1·97				
Ph Cl	1·69	1·59				
Me Br	1·81	(1·84)				
R Br	2·18	1·97				
Ph Br	1·70	1·56				
Me I	1·62	(1·46)	The C—X group moment equals the experimental dipole moment in these molecules since the resultant moment lies along the C—X bond direction.			
R I	2·04	1·87				
Ph I	1·70	1·30				
H CN	2·97	2·60				
Me CN	3·97	3·47				
R CN	4·04	3·60				
Ph CN	4·18	3·97				
Me $\mathrm{NO_2}$	3·46	3·13				
R $\mathrm{NO_2}$	3·63	3·32				
Ph $\mathrm{NO_2}$	4·22	3·99				
Me ONO		2·3				
R ONO	2·40	2·29		gas	solution	
H $\mathrm{ONO_2}$	2·16		—$\mathrm{ONO_2}$	1·54		with ∠HON = 90°
Me $\mathrm{ONO_2}$	3·12	(2·88)	—$\mathrm{ONO_2}$	2·44	2·19	with ∠CON = 105°
R $\mathrm{ONO_2}$		2·99	—$\mathrm{ONO_2}$		2·30	with ∠CON = 105°
Me OH	1·70	1·70	C—O	1·42	1·39	with ∠COH = 109°
R OH	1·68	1·71	C—O	1·38	1·41	with ∠COH = 109°
Ph OH	1·45	1·57	Ph—O	0·75	1·24	with ∠COH = 109°
Me SH	1·52		C—S	1·43		with ∠CSH = 96·5°
R SH	1·58	1·50	C—S	1·50	1·43	with ∠CSH = 96·5°
Ph SH		1·20	Ph—S		1·09	with ∠CSH = 96·5°
$\mathrm{Me_2O}$	1·30	(1·25)	C—O	1·15	1·11	with ∠COC = 111·5°
$\mathrm{R_2O}$	1·18	1·20	C—O	1·04	1·06	with ∠COC = 111·5°
$\mathrm{Ph_2O}$	1·3	1·18	Ph—O	1·1	1·04	with ∠COC = 111·5°
$\mathrm{Me_2S}$	1·50	1·45	C—S	1·15	1·12	with ∠CSC = 99°
$\mathrm{R_2S}$	1·54	1·60	C—S	1·29	1·35	with ∠CSC = 107
$\mathrm{Ph_2S}$		1·55	Ph—S		1·30	with ∠CSC = 107°
$\mathrm{Me_2SO}$	3·96	3·89	S=O	3·04	2·92	with ∠CSC = 97° and ∠CSO = 107°
$\mathrm{R_2SO}$		4·00	S=O		2·90	
$\mathrm{Ph_2SO}$		4·07	S=O		3·03	
$\mathrm{Me_2SO_2}$	4·49	4·26	S=O	3·26	2·92	with ∠CSC = 103° and ∠OSO = 124°
$\mathrm{R_2SO_2}$		4·53	S=O		3·00	
$\mathrm{Ph_2SO_2}$		5·05	S=O		3·65	
$\mathrm{Me_3N}$	0·61	0·86	C—N	0·59	0·83	with ∠CNC = 108·7°
$\mathrm{R_3N}$	0·66	0·77	C—N	0·64	0·74	with ∠CNC = 108·7°
$\mathrm{Ph_3N}$		0·60	Ph—N		0·99	with ∠CNC = 116°

TABLE 4—(*continued*)

Compound	Dipole moment		Group moment or dipole angle			
	gas	solution		gas	solution	
Me_2NH	1·03	(1·18)	H—N	1·23	1·38	with ∠CNC = 108°
R_2NH	0·92	1·05	H—N	1·08	1·23	with ∠CNC = 108°
Ph_2NH		1·08				
$MeNH_2$	1·31	(1·47)				
RNH_2	1·20	1·37				
$PhNH_2$	1·53	1·56	Moment at 48·5° to C—N bond[31]			
Me_3NO		5·02	N → O		4·16	
Me_3P	1·19		C—P	0·83		with ∠CPC = 99·1°
R_3P		1·48	C—P		1·03	with ∠CPC = 99·1°
Ph_3P		1·49	Ph—P		1·04	with ∠CPC = 99·1°
Me_2PH	1·23		C—P	0·97		with ∠CPC=∠CPH = 99°
$MePH_2$	1·10		C—P	1·11		moment at 27° to C—P bond
RPH_2	1·17		C—P	1·19		moment at 25° to C—P bond
R_3PO		4·36	P═O		2·88	
Ph_3PO		4·44	P═O		2·95	
MeCHO	2·69	2·51	C═O	2·51	2·33	with ∠CCO = 123·9°
RCHO	2·74	2·58	C═O	2·50	2·34	with ∠CCO = 123·9°
PhCHO		2·98				
H_2CO	2·33		C═O	2·33		
Me_2CO	2·88	2·83	C═O	2·38	2·33	with ∠CCC = 116·2°
R_2CO		2·73			2·23	with ∠CCC = 116·2°
Ph_2CO		2·98				
HCO_2H	1·41	(1·5)	Acting approximately in the C═O direction			
$MeCO_2H$	1·74	1·76				
RCO_2H	1·76	1·77				
$PhCO_2H$		1·8				
HCO_2Me	1·77					
$MeCO_2Me$	1·72	1·74				
RCO_2Me	1·78	1·75				

Values in brackets are either the result from a single determination or where literature values are not consistent.

They may be employed to predict dipole moments and in discussions of molecular conformations, but it must be remembered that some allowance ought to be made for:

(a) induced dipole moments (an approximate allowance can be made by the method of Hampson and Weissberger[15, 27]),

(b) mesomeric moments arising from electron delocalisation within the molecule. Conjugation effects also mean that the dipole moments of parent heterocyclic molecules like furan, thiophen and pyridine, cannot be adequately predicted in terms of component bond moments.

(c) the consequences of free or restricted rotation of component dipoles within the molecule. The effect of free rotation can be calculated[28] but it is not possible for restricted rotation unless an appropriate potential function is available.[15, 29]

(d) H-bonding and other specific interactions. Corrections to the calculated dipole moments from (a) and (b) above are best made by utilizing experimental data for the dipole moments of molecules in which these effects are likely to be similar.

The bond and group moments in Tables 2–4 differ from other published scales[24, 30] by placing greater emphasis upon group moments and by including moments for bonds between differently hybridized C atoms. It recognises that unsaturated hydrocarbons may be polar and that, for example, part of the difference between the dipole moments of formaldehyde and acetaldehyde and between formic and acetic acids is due to the different moments of $H—C(sp^2)$, 0·0 D, and $CH_3—C(sp^2)$, 0·30 D. The bond values include contributions from any lone-pair electrons (e.g. the C—S bond) and the moments quoted for coordinate bonds are really the change in moment when an acceptor atom is attached to a lone-pair· (e.g. the $S \rightarrow O$ bond.)

The greater C—O bond moment of alcohols compared to ethers may be due to a small change in the bond angles and to a change in the effective electronegativity of the oxygen atom. The Ph—O bond moment in Ph_2O is close to that in the corresponding aliphatic compounds because any mesomeric effect is repressed sterically; this is not so when only one phenyl ring is present as in phenol. The above effects are also observed in analagous sulphur and other compounds.

The bond moments computed from the dipole moments of amines are sensitive to the values accepted for the bond angles and to the extent of conjugation between the lone-pair of the nitrogen atom and any appropriate substituents.[31]

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