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Commentationes

Theoretical Calculation of Electric Dipole Moments for Conjugated Systems

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A detailed survey has been made of the potentialities of the VESCF molecular orbital procedure for computing electric dipole moments of conjugated molecules. Forty-one molecules, ranging from non-alternant hydrocarbons to a wide variety of heterocycles and benzene derivatives have been studied. The agreement between theory and experiment is always within 0.4 D and notably better than has been achieved by any alternative theoretical procedure so far. Some assessment is made of the relative merits of alternative techniques for dealing with neutral-atom penetration integrals and with two-electron coulomb integrals. Comments are made on the contributions of σ-bond polarities and of hydrogen atom hybridization moments.

The possibility that the present procedure for treating heterocyclic oxygen is less satisfactory than for nitrogen is indicated, the molecules showing greatest deviations from experiment being oxygen heterocycles.

The present study points up the fact that for some of the key molecules studied the experimental values are of uncertain reliability or, occasionally, not yet available.

Im Rahmen der VESCF-Methode sind die Dipolmomente von 41 Molekülen mit konjugierten Systemen berechnet worden, beginnend mit nicht alternierenden Kohlenwasserstoffen bis zu einer Reihe von Heterocyclen und Benzolderivaten. Theorie und Experiment stimmen in den meisten Fällen bis auf 0.4 D — und damit wesentlich besser als bei den meisten bisherigen Verfahren — überein. Einige Bemerkungen in bezug auf die Vorteile einzelner Methoden, Durchdringungs- und Coulombintegrale zu behandeln, auf den Beitrag der σ-Elektronen und der Wasserstoffhybridisierungsmomente werden zur Ergänzung gemacht.

Die angewandte Methode scheint zur Behandlung von Heterosauerstoff weniger geeignet als für Stickstoff zu sein, da Moleküle mit Sauerstoff die größten Abweichungen vom Experiment zeigen. Andererseits zeigt sich, daß die experimentellen Werte für einige wichtige Moleküle zweifelhaft sind.

Etude détaillée des possibilités de la méthode des orbitales moléculaires SCF à électronégativité variable pour le calcul des moments dipolaires électriques des molécules conjuguées. L'étude a porté sur quarante et une molécules s'étendant d'hydrocarbures non alternants jusqu'à une large classe de dérivés benzéniques et d'hétérocycles. L'accord entre la théorie et l'expérience est presque toujours à moins de 0,4 D, étant notablement meilleur que celui obtenu jusqu'alors par une autre technique. On établit en partie les mérites relatifs des différentes techniques d'utilisation des intégrales de pénétration et des intégrales coulombiennes. On fait des commentaires sur les contributions des polarités des liaisons σ et des moments d'hybridation de l'atome d'hydrogène.

On mentionne la possibilité pour le présent procédé de traiter l'oxygène hétérocyclique d'une manière moins satisfaisante que l'azote, les hétérocycles oxygénés étant les molécules présentant le plus grand désaccord avec l'expérience.

Cette étude souligne le fait que pour certaines molécules clés les données expérimentales sont peu certaines sinon inexistantes.

1. Introduction

One of the long-standing problems in theoretical chemistry is the prediction of electric dipole moments. When experimental values for a considerable number of molecules had been collected it was found that a table of empirical "bond moments" could be established from which the moments of saturated molecules could be estimated with reasonable accuracy by vector addition. Various minor complications were uncovered; in particular the results were not so satisfactory for conjugated systems, the defect being attributed to π-electron delocalization effects [52].

Dipole moments have been calculated in conjunction with ab initio quantum mechanical treatments for a number of simple molecules, the best wave functions being chosen by the criterion of minimum energy. The prediction of dipole moments appears to be a sensitive test of the reliability of molecular wave functions because even those functions that are regarded as relatively accurate still may give unsatisfactory values for this property. Consequently the calculation of dipole moments is regarded [22, 23] as a difficult problem in molecular quantum mechanics.

It is only recently that ab initio calculations have been extended to a sufficient number of terms to yield reasonably satisfactory dipole moments even for the first row hydrides as shown in Tab. 1. These treatments involve expansion in terms of many basis functions centred on one atom [57] or on all atoms [59]. We cannot hope at present to apply such exhaustive techniques to even the smallest of conjugated molecules. The performance of ab initio calculations with a minimal basis set restricted to inner and valence shell atomic orbitals, a method which might now be practicable for larger systems, as shown in Tab. 1 is less satisfactory for dipole moments of the simple hydrides [46, 29, 28, 45].

An analysis of the most complete calculation yet performed on HF shows that the dipole moment arises mainly from the lone pair orbitals on the fluorine atom, not from the HF bond moment [59]. In the simple method used in this paper to assign σ-electron contributions in heteroaromatic molecules the only net contributions to the dipole moment are associated with lone pairs of electrons. For comparison the results of applying this method to the first row hydrides are included in Tab. 1. They are obtained by superimposing the density distributions for neutral atoms, with orthogonal hybrids of Slater type orbitals defined by the internuclear lines. These estimates compare favourably with those obtained by ab initio calculation using a restricted basis set, and the value for HF corresponds closely to the

Table 1. *Dipole Moments Calculated for First Row Hydrides by ab initio Methods*

Orbital Type	Method	Basis Set	HF	H_2O	NH_3
Slater type	SCF	Minimal	0.85 [46]	1.51 [29]	1.96 [28]
Hartree Fock	CI	Minimal	1.83 [46]		1.82 [45]
Gaussian	SCF	Complete	2.35 [36]	1.99 [58]	
One-centred	SCF	Extended	2.10 [57]	2.09 [57]	1.51 [57]
Optimized	SCF	Extended	1.83 [59]		
Observed [56]			1.82 D [4]	1.84 D	1.47 D
Directed Slater type hybrids			1.41	1.58	1.75

Table 2. *Dipole Moments Computed from Charge Distributions in Nonalternant Hydrocarbons, Obtained by Various Methods*

	obs.	Hückel	ST.SCF	CI	OP.SCF	OP + VE.SCF	VE.SCF	
Fulvene[a]	1.1 D [*56*]	4.73 [*78*]	1.14 [*7*]		0.96 [*43*]	0.7 [*44*]	BJ 1.21,	BJ* 0.73 [*12*]
Heptafulvene[a]	3.07 D (est) [*89*]		0.34 [*39*]		0.23 [*40*]		BJ 0.89,	BJ* 0.79 [*12*]
Azulene[a]	0.80 D [*87*]	6.54 [*11, 64*]	1.71 [*39*][c]	1.93 [*64*]	2.52 [*44*]	2.06 [*44*]	BP 1.87 [*18*],	BP* 1.33 [*12*]
Acenaphthylene[b]		3.01 [*71*]						BJ* 0.60 [*12*]
Fluoranthene[b]	0	1.82 [*71*]						BJ* 0.78 [*12*]

The key to the quantum mechanical procedure is given with Tab. 4, * indicating that non-neighbour core resonance integrals were included. Charge distributions are referred to a single geometrical structure in each case obtained

[a] By the method described in Appendix 3.

[b] By fusing ethylene ($r = 1.36$ Å) and benzene ($r = 1.40$ Å), by single bonds ($r = 1.48$ Å) onto naphthalene (all $r = 1.40$ Å, all internal angles 120°) and therefore differ slightly from values quoted in the references.

[c] See also Ref. [*9*].

Table 3. *Dipole Moments Estimated by the Method of* Orgel, Cottrell, Dick *and* Sutton [*61*]

Molecule	Dipole Moment (D)	
	obs [*56*]	calc
Benzoic acid	2.12	4.35 [*34*]
Pyridine	2.25	2.1 [*25*]
Pyridine N-oxide	4.24	6.9 [*25*]
Benzonitrile	4.14	7.7 [*25*]
Benzonitrile N-oxide	4.00	8.9 [*25*]
Isoxazole	3.07[a]	2.7 [*25*]
Indoxazene	3.06	3.1 [*25*]
Anthranil	3.09	3.6 [*25*]

[a] Ref. [*54*].

lone pair moment of 1.580 obtained by Nesbet [*59*]. A recent empirical study of methylamines also shows that dipole moments in saturated molecules containing first row atoms may be attributed almost completely to the eccentricity of non-bonded electron distributions [*88*].

Thus the detailed analysis of the polarity of σ-bonded systems from first principles is not yet feasible. Semi-empirical techniques beginning from a knowledge of atomic properties and introducing reasonable approximations to overcome the problems of the massive σ-orbital overlap are now being developed [*69*]. Other investigations are demonstrating the possibility of using empirical properties of simple systems to define the most satisfactory orbital representation of a type which remains comprehensible in qualitative terms [*2, 3, 4*]. None of these are yet capable of extension to a conjugated hetero-system but as will be seen below many of the problems may be circumvented for a molecule containing π-electrons without serious loss of validity.

Less ambitious quantum-mechanical methods have been used for larger polyatomic molecules containing conjugated systems, attention being focussed on the π-electrons. The Hückel MO method, which has been most widely applied to large conjugated systems, noticeably overemphasizes the polarity of molecules. In systems containing hetero-atoms this can be masked by the problem of selecting suitable values for the heteroparameters, but the overemphasis is evident in calculations on nonalternant hydrocarbons, as exemplified in Tab. 2. Some *ad hoc* improvement proved possible for heterocycles through empirical adjustment of heteroparameters [*61*]. However more recent applications of this technique have not always been so satisfactory (see Tab. 3).

The more objective SCF molecular orbital method yields improved results, as evidenced by the data in Tab. 2, but there is some evidence [*16, 18*] that the purely theoretical treatment is apt to over-estimate polarities because it does not fully allow for electron repulsions. SCF and configuration interaction procedures have now been applied to a variety of conjugated heteromolecules. A survey of dipole moments estimated from such treatments applied to systems containing oxygen and nitrogen atoms is given in Tab. 4. Among these the VESCF method [*14, 16, 17, 19, 20*] shows encouraging results for predicted dipole moments and so we have now investigated its potentialities for predicting dipole moments of moderately

Table 4. *Objective Calculations of Dipole Moments for π-electron Systems Containing Oxygen or Nitrogen as Heteroatoms. Estimates of π-, σ- and resultant moments are given in sequence. Alphabetical symbols indicate orbital type, method of variation and extent of basis set. Integral prescriptions are indicated in parentheses*

Carbon monoxide: obs. 0.118 D				
DE.SCF + CI.	—	—	0.13	[*51*]
HF.SCF.	—	—	0.36	[*60*]
ICC.	−1.77	2.13	0.37	[*37*]
ST.SCF.VS.	0.42	−1.43	−1.00	[*37*]
ST.SCF.VS.	—	—	0.73	[*74*]
HF.SCF.	—	—	−0.59	[*74*]
Hydrogen cyanide: obs. 2.99 D				
ST.SCF + CI.VS.	—	—	2.66	[*38*]
Formaldehyde: obs. 2.34 D				
ST.SCF.AE.	—	—	1.1	[*32*]
PP.SCF.	0.9	—	—	[*83*]
PP.SCF.	2.3	—	—	[*49*]
ST.SCF + CI.	0.5	∼1.8	∼2.3	[*82*]
ST.SCF.AE.	—	—	−0.62	[*33*]
OP.SCF.	1.68	0	0	(*p*)
	1.32	1.52[b]	2.84 (sp^2)	[*41*]
VE.SCF.	0.57	1.83[c]	2.40	(CP, *sp*)
	0.26	1.52[c]	1.98	(CP, sp^2) [*14*]
Methyleneimine: obs. 1.53 D (CH_2NCH_3) [*80*]				
PP.SCF.	0.39	1.77	1.99	[*21*]
VE.SCF.	0.49	1.77	2.03	[*21*]
Furan: obs. 0.66 D				
PP.CI.	−1.84	1.30[a]	−0.54	[*79*]
PP.SCF.	−0.95	—	—	[*85*]
PH.SCF.	−1.82	—	—	[*70*]
OP.VE.SCF.	−0.89	1.63[b]	0.74	[*72*]
Pyrrole: obs. 1.84 D				
ST.SCF.	−0.71	—	—	[*16*]
PP.SCF.	−1.53	—	—	[*85*]
PH.SCF.	−2.53	—	—	[*70*]
OP.VE.SCF.	−1.8	0	−1.8	[*42*]
VE.SCF.	−1.77	0	−1.77	(AP)
	−2.12	0	−2.12	(BP) [*16*]
VE.SCF.	−1.84	0	−1.84	(BJ) [*24*]
Pyridine: obs. 2.25 D				
ST.SCF.CI.	0.36	1.97[c]	2.33	[*15*]
OP.VE.SCF.	0.30	1.85[b]	2.15	(BJ)
	0.22	1.85[b]	2.07	(CJ) [*73*]
VE.SCF.	0.52	2.03[c]	2.55	(BP)
	0.55	2.03[c]	2.58	(BJ) [*17*]

Table 4. (Continued)

Aniline: obs. 1.49 D				
ST.SCF.	0.72	—	—	[*31*]
PP.SCF.	0.78	—	—	[*31*]
PH.SCF.	1.13	—	—	[*70*]
VE.SCF.	1.87	—	—	[*10*]
Phenol: obs. 1.40 D				
PH.SCF.	0.45	—	—	[*70*]
Pyrazole: obs. 1.58 D				
VE.SCF.	1.67	2.10[c]	2.28	(AP)
	1.94	2.11[c]	2.73	(BP) [*20*]
Imidazole: obs. 3.87 D				
VE.SCF.	1.184	1.98[c]	3.75	(AP)
	2.61	1.99[c]	4.53	(BP) [*19*]
o-Benzoquinone: obs. 5.1 D				
OP.VE.SCF.	2.17	2.68	4.85	[*8*]

Orbital Type:

DE	Double exponential atomic orbital functions.
HF	Hartree Foch atomic orbitals for constituent atoms.
ICC	Intra-atomic correlation correction.
ST	Slater type atomic orbitals.
PP	Parr-Pariser atoms-in-molecules procedure.
OP	PP procedure with orthogonalized atomic orbitals.
VE	PP procedure with variation of electronegativity terms.
PH	Perturbed hydrocarbon SCF orbitals.

Variation Method:

SCF	Self consistent field molecular orbital method.
CI	Antisymmetrized molecular orbital configuration interaction method.

Extent of Basis Set:

VS	Valence shell electrons considered.
AE	All electrons included in the variation treatment.

Integral prescriptions:

CP	See Appendix 1.
AP	
BJ	
CJ	

Assignment of σ-contributions:

[a] Calculated as in this paper but with $\mu(C^{-}\text{-}H^{+}) = 0.199$ D.

[b] Calculated as in this paper but using orthogonalized $2s$ orbitals in the nonbonded hybrids.

[c] Estimated from empirical bond moments (Ref. [*61*]).

large molecules by studying a wide range of compounds. The results of this study are reported here.

The variable-electronegativity self-consistent field method as developed in previous papers is described in detail in Appendix 1. It differs from the conventional SCF method in that the orbital exponent Z_μ of each atomic orbital χ_μ is varied according to the net charge borne by the atom; consequently several quantities appearing in the SCF treatment vary with the net charges at the different atomic positions.

Detailed treatment is confined to the π-electrons, these being assumed to move in the potential field of a purely covalent molecular core. Thus in order to assess core charges, or the final net charge at each atom, one electron of each pair forming a σ-bond is assigned to each of the orbitals that overlap to form the σ-bond. Hence each core charge, obtained by taking the nuclear charge and subtracting from it the total number of electrons in other than π orbitals on the nucleus, always comes out to be integral.

If we accept the implications of the atoms-in-molecules method, that the atomic electron distributions should be regarded as superimposed to form the σ-bonded framework, then the dipole moment comes from two sources; the unequal distributions of π-electrons around the conjugated system and a σ-electron hybridization contribution from lone pairs, if present. For a hybrid orbital of the form

$$\chi_n = \chi_{2s} + \lambda \chi_{2p} \tag{1}$$

the hybridization moment, computed using Slater functions, is

$$\mu_{at} = 14{\cdot}68\, \lambda / \boldsymbol{Z}(1 + \lambda^2)\ \mathrm{D}\,. \tag{2}$$

This relation corresponds to the moment of one non-bonding electron about the nucleus, the other being balanced by the bonded electrons*. Hybridization moments calculated in this way would be only slightly different if hydrogen-like or orthogonalized Slater 2*s* atomic orbital functions (as in Ref. [*72*]) were assumed. Hameka et al. [*35*] employ an almost equivalent prescription ignoring all the contributions of bonding electrons in the conjugated framework and restricting the analysis to lone pairs and hybrids involved in bonding to hydrogen. This technique leads to somewhat lower estimates for the σ-moment in hetero-aromatic systems, but is exactly equivalent when applied to simple hydrides.

We have evaluated hybridization parameters, λ, from the geometry of the molecules by assuming that the bonding hybrids have their maxima along the bonding directions and that lone-pair hybrids bisect bond angles externally.

The reliability of such estimates, as demonstrated in Tab. 1, is limited. They are relatively insensitive to internal angle, in the range 105° to 180°, and also to the net charge. Thus for simplicity values for sp^2 hybrids on neutral atoms have been taken throughout, *viz.*

$$\mu_{\mathrm{N}} = 1{\cdot}77\ \mathrm{D}\,,$$

$$\mu_{\mathrm{O}} = 1{\cdot}52\ \mathrm{D}\,.$$

The possibility of an additional hybridization contribution from hydrogen atomic orbitals because these may include a small amount of 2*p* character instead of being purely 1*s* is considered in Section 4.

The VESCF calculations have followed other molecular calculations of this kind in assuming zero differential overlap and so the evaluation of π-electron

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* It is straightforward to show that the resultant mean position of equal numbers of electrons in three co-planar orthogonal hybrids composed of *ns* and *np* orbitals coincides with the nucleus.

densities and their conversion to a dipole moment is based on the assumption of orthogonal atomic orbitals. Where precise experimental data on molecular geometry was not available it was estimated from data for related molecules [*86*] for computation of quantum mechanical integrals and the dipole moment. Structures assumed are given in Appendix 2.

Polarization of Bonds

Since we have previously found the VESCF calculations to be surprisingly successful in predicting dipole moments one is tempted to conclude that our assumptions, indicated in the preceding Section, are valid, in particular that there is no appreciable polarization of σ-bonds in these conjugated systems. However, it is possible that the calculations are insensitive to this assumption. Light is thrown on this possibility by some unpublished data made available to us by Dr. M. L. Heffernan on pyrrole and pyridine. VESCF calculations were performed on the assumption that CN σ-bonds are polarized by transfer of electrons from a bonding hybrid on nitrogen to one on carbon. For pyridine 5% polarization of these bonds was assumed so that the core charges for the carbons at the 2- and 6-positions are $+1.05$ and the core charge on nitrogen is $+0.9$. This produces an increased σ-electron contribution to the total moment of about 0.1 D and the new core field produces a new set of π-electron densities leading to a calculated π-electron contribution, lower than that for an unpolarized core by about 0.1 D. Thus the computed effect of substantial polarization of the σ-core is a slight increase in the total dipole moment (for details see Tab. 5).

For pyrrole, when the CN σ-bonds are assumed to be 10% polarized this corresponds to a σ contribution of about 0.3 D opposing the π-electron contribution while the change in core field leads to an increase in the π-electron moment by about 0.1 D. The overall effect is a slight reduction in the total moment (see Tab. 6 for details).

The numerical results of these calculations should be accepted with caution but the qualitative implication is significant — that a substantial amount of

Table 5. *Effect of σ-Polarization on the Calculated Dipole Moment in Pyridine*[a]

	I[b]	II[c]
P_1	1.106	1.072
P_2	0.952	0.972
P_3	1.004	0.999
P_4	0.981	0.986
μ_π	0.519 D	0.409 D
μ_σ	0	0.134 D
μ_N	1.844 D	1.855 D
μ	2.363 D	2.398 D

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[a] The method **BJ** was used for evaluating integrals.

[b] Unpolarized σ-core assumed.

[c] Core assumed to contain 5% polarized CN σ-bonds.

Table 6. *Effect of σ-Polarization on the Calculated Dipole Moment of Pyrrole*[a]

	I[b]	II[c]
P_1	1.700	1.662
P_2	1.076	1.098
P_3	1.074	1.071
μ_π	-2.081 D	-2.195 D
μ_σ	0	0.349 D
μ	-2.081 D	-1.846 D

P_ν is the π-electron density on the νth atom

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[a] The method **BP** was used for evaluating integrals.

[b] Unpolarized σ-core assumed.

[c] Core assumed to contain 10% polarized CN σ-bonds.

Table 7. *Total Dipole Moments Derived from the Charge Distributions Illustrated in Fig. 1*

	Molecule	Dipole Moment (D)				
		Calculated by Method:				
		BJ	**CJ**	**BP**	**CP**	Observed
1	Furan	0.19	0.09			0.66 M
2	Pyrrole	−1.79	−1.88			1.84 G
3	Benzofuran	0.52	0.15			0.79 CS_2 (i)
4	Indole	1.76	1.87			2.13 b
5	Isoxazole	2.32				3.07 M (ii)
6	Pyrazole	2.28				2.21 M (iii)
7	Phenol	1.34				1.40 g
8	Aniline	1.42				1.49 g
9	Oxazole	2.01				1.50 M (ii)
10	Imadazole	3.82				3.87 B
11	"Isonitrous acid"	3.38				3.46 (CH_3NO_2)
12	Nitrobenzene	3.65				4.28 G
13	Furan 2-aldehyde	3.19				3.63 b
14	Pyrrole 2-aldehyde	1.52				1.88 b
15	Formaldehyde	2.60				2.34 M
16	Benzaldehyde	2.87				2.80 b
17	Furan 2-carboxylic acid	2.28				1.38 b
18	Pyrrole 2-carboxylic acid	0.57				—
19	Formic acid	1.75				1.35 M
20	Benzoic acid	1.72				2.12 B
21	Furan			0.02	−0.12	0.66 M
22	Pyrrole			−2.06	−2.15	1.84 G
23	Benzofuran			0.44	0.17	0.79 CS_2
24	Pyrrole N-phenyl	1.08				1.32 b
25	Pyridine	2.31	2.12			2.25 G
26	Pyridazine	4.05	3.29			3.97 d
27	Pyrimidine	2.32	1.91			2.0 b
28	Pyrazine	0	0			0
29	Quinoline	2.33	1.90			2.31 G
30	Cinnoline	4.09	3.54			4.14 b
31	Quinazoline	2.55	2.40			2.2 b (2-Me)
32	Quinoxaline	0.05	0.62			0.3 b (2,3-diMe)
33	Isoquinoline	2.41	2.13			2.75 G
34	Phthalazine	4.40	3.80			—
35	Pteridine	2.52	—			2.7 (iv)
36	Pyridine N-oxide	3.80	—			4.24 b

Methods of Experimental Determination

M	Stark effect on microwave spectrum.
G	Dielectric constant determination in vapour phase.
g	Vapour phase study at a single temperature.
B	Dielectric constants of benzene solutions with temperature variation.
b	Dielectric constants of benzene solutions at a single temperature.
CS_2	Dielectric constants of carbon disulphide solutions.
d	Dielectric constants of dioxan solutions.
(i)	Ref. [*81*];
(ii)	Ref. [*54*];
(iii)	Ref. [*48*];
(iv)	Ref. [*1*].

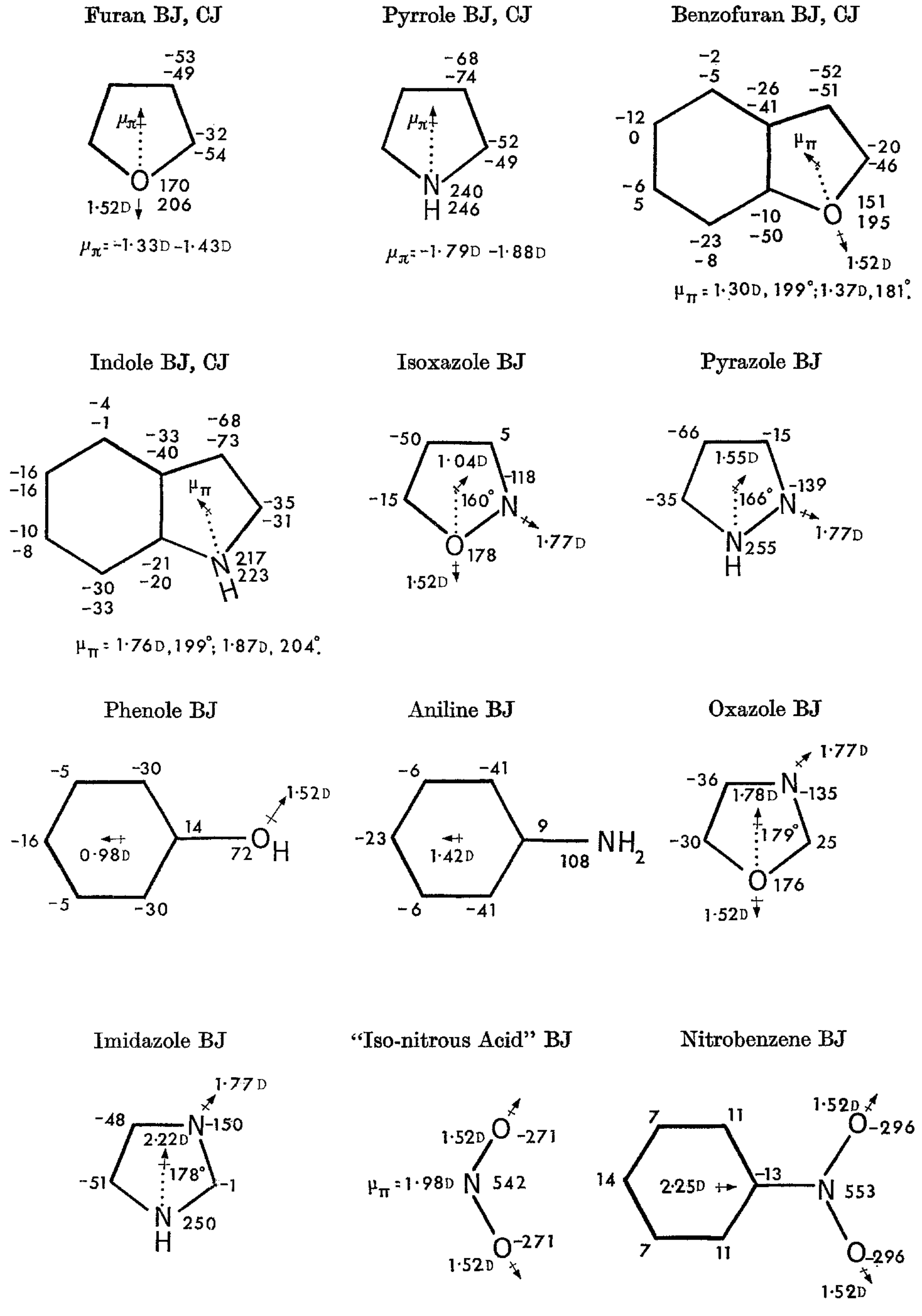
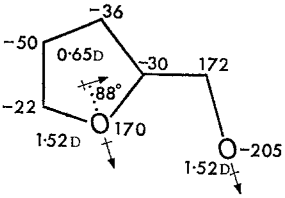
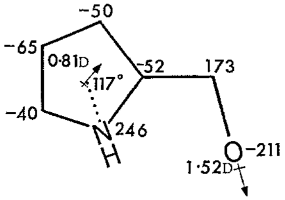


Fig. 1. Molecular Diagrams Showing Net Charges in Milliprotonic Units, π-moments and Atomic Contributions to Dipole Moments

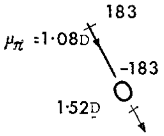
Furan-2-aldehyde BJ



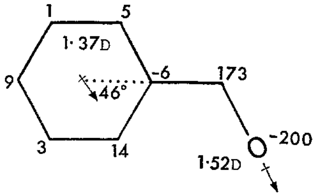
Pyrrole-2-aldehyde BJ



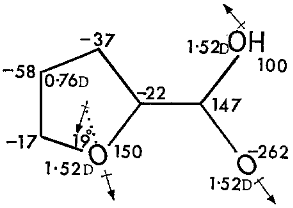
Formaldehyde BJ



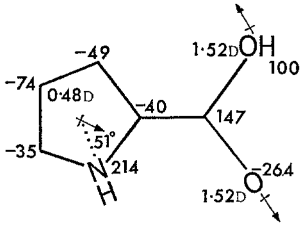
Benzaldehyde BJ



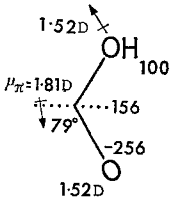
2-Furoic-acid BJ



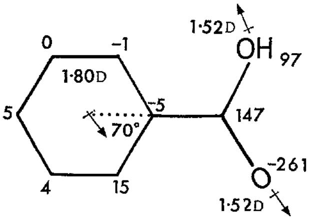
Pyrrole-2-carboxylic acid BJ



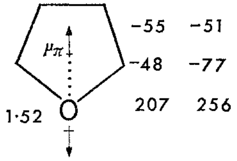
Formic acid BJ



Benzoic acid BJ

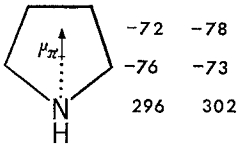


Furan BP CP



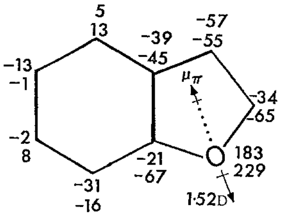
μ_π = −1·50D, −1·64D.

Pyrrole BP CP



μ_π = −2·06D, −2·15D.

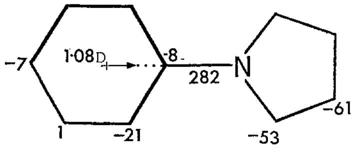
Benzofuran BP, CP



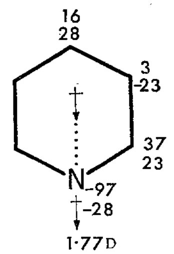
μ_π = 1·46, 193°; 1·36D, 172°

Fig. 1 (Continued)

Pyrrole N-phenyl BJ

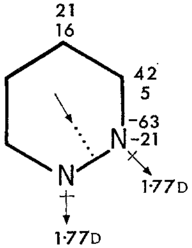


Pyridine BJ, CJ



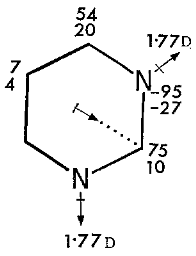
μ_π = 0·54D, 0·35D.

Pyridazine BJ, CJ



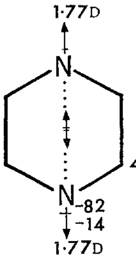
μ_π = ·98D, 0·22D.

Pyrimidine BJ, CJ

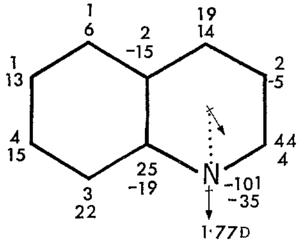


μ_π = 0·54D; 0·14D.

Pyrazine BJ, CJ

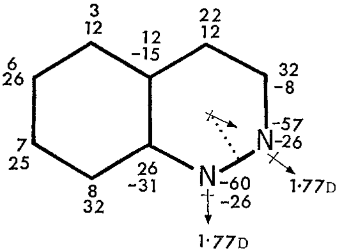


Quinoline BJ, CJ



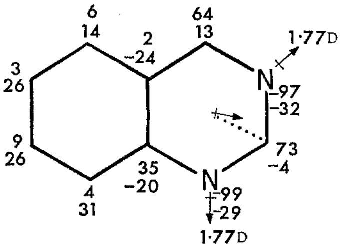
μ_π = 0·56D, 2°; 0·32D, 72°.

Cinnoline BJ, CJ



μ_π = 1·05D, 13°; 0·68D, 50°.

Quinazoline BJ, CJ

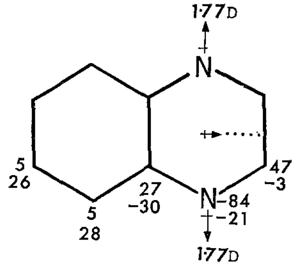


μ_π = 0·78D, -1°; 0·68D, 28°.

Fig. 1 (Continued)

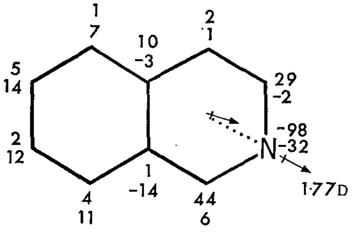
redistribution of π-electrons occurs, in a direction tending to nullify σ-electron polarization in the conjugated framework. Calculated total dipole moments are thus relatively insensitive to the assumptions made about the σ-electron polarization so that it seems acceptable to use the most convenient assumption about σ-polarization in performing the VESCF calculations. Undoubtedly this is to assume that the core is unpolarized.

Quinoxaline BJ, CJ



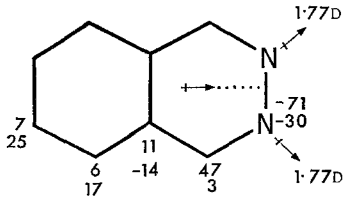
μ_π= 0·05D,0·62D

Isoquinoline BJ, CJ



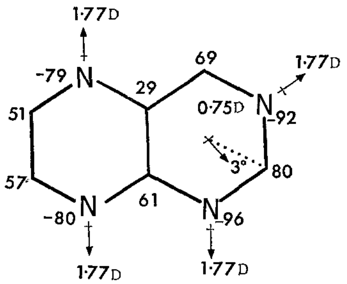
μ_π= 0·66D, 16°; 0·38D, 24°.

Phthalazine BJ, CJ



μ_π= 1·32D; 0·73D.

Pteridine BJ



Pyridine-N-oxide BJ

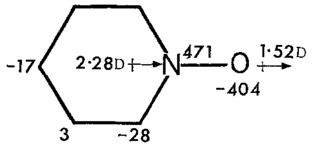


Fig. 1 (Continued)

Hydrogen Hybridization Moment

In previous VESCF studies [*14*] a hybridization moment of 0.2 D, deduced from Dickenson's calculations [*27*] on H_2^+, was used when computing the total moment of conjugated molecules. It was felt that the nature of the hybrid used by H for bonding to other atoms might well vary appreciably with the nature of the bond. As a preliminary, various wavefunctions for H_2 and some for H_2^+ were studied. A wide variety of hybridization moments emerged (and a numerical error was found in the previous value deduced from Dickenson's wavefunction). In view of this sensitivity of the moment to the type of wavefunction it does not seem profitable to seek theoretically the most suitable value for a CH bond. An empirical study showed that the agreement between calculated and observed moments was not statistically improved by incorporating a non zero CH moment and so we have finally assumed the CH bond moment to be zero.

Results and Discussion

Net charges, π-moments and atomic contributions are presented diagrammatically in Fig. 1. Directions of π-moments are given relative to an indicated axis bisecting one of the bond angles. The calculated resultant dipole moments are compared with observed values in Tab. 7. The extent of the correlation between theory and experiment for the thirty three molecules of various kinds listed can best be judged from the graph in Fig. 2. Nearly all points fall within 0.4 D of the observed moment. An experimental error of this magnitude may be expected in many instances, particularly where measurements were made on solutions at a single temperature.

We have no reason to regard the procedure used here for estimating atomic and σ-bond moments as being accurate to better than 0.3 Debye units (see Tab. 1) and considering this limitation the VESCF method is remarkably successful in the prediction of dipole moments. The molecules studied differ widely in types of charge distribution from pyrrole and its N-phenyl derivative in which the asymmetry is associated with the π-electrons to the 1:2 diazines in which large dipole moments arise largely from eccentricity of electron distributions around nitrogen atoms, and from furans with small resultant moments due to opposing atomic and π-type contributions to pyridine N-oxide and nitrobenzene which have large values because these contributions are reinforcing.

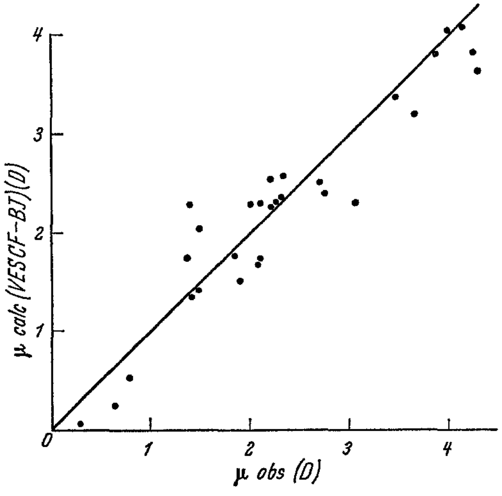


Fig. 2. Resultant Dipole Moments Calculated by the VESCF-BJ Method versus Observed Values

In the formic acid molecule the VESCF-BJ calculations lead to the prediction that the resultant dipole moment is directed at an angle of 81.9° to the H–C bond extended into the quadrant occupied by the carbonyl oxygen. The results of microwave determination of the molecular structure [*50*] and components of the dipole moment [*30*] may be combined to obtain possible directions for the moment but Stark effect studies on a single isotopic species do not give the senses of the individual components. If the VESCF results are used to assign the quadrant into which the resultant is directed, the observed moment is found to be at 78.5° to the H–C bond extended, in excellent agreement with the direction predicted theoretically. In the light of this the present technique might be useful in preliminary assessment of microwave spectra in predicting relative intensities of different transitions os asymmetric tops.

The present technique also could sometimes be useful in helping to select the conformation of some conjugated systems like formic acid and benzoic acid. The alternative conformations (I) and (II) lead to notably different calculated moments:

	μ_{calc}(D) (I)	(II)	μ_{obs}(D)
formic acid	1.75	2.59	1.35
benzoic acid	1.72	2.86	2.12

The conformation of formic acid is known to be (I) [*50*], and this could also be deduced from the above data. It is suspected that the conformation of benzoic acid is also (I), in line with the above data. This technique for deducing conformations may be particularly useful for molecules that are too large to be studied by microwave spectroscopy.

Aniline has been treated as a planar molecule in the current calculations and the derived moment is found to correspond closely to that observed by vapour dielectric measurements, but doubts have previously been expressed concerning the assignment of terms because of evidence that the C–NH atoms are not coplanar [*10*]. It has recently been shown [*53*] that the plane of HNH lies at an angle of 39.35° to the plane of C_6H_5N, with $< HNH = 113.9°$. This geometry corresponds to a bond angle, $<$ CNH, of 115.0° and for orthogonal directed hybrids the "non-bonded" orbital available for interaction with the π-system is an sp 7.5 hybrid directed at 75.3° to the C–N bond extended and given by

$$\chi_n = 0.3433\,(2s_N) + 0.2384\,(2p\sigma_N) + 0.9080\,(2p\pi_N)\,.$$

This implies that 91% of the π-type conjugation may be retained but introduces an atomic hybridization moment with components of 1.17 D perpendicular to the ring and 0.31 D parallel to the ring, but opposed to the π-moment, for each electron in excess of one occupying χ_n. It would be appropriate to reduce one-electron integrals between χ_n and $\chi_C = 2p\pi_C$ in the π-electron VESCF calculation by a factor of 0.908 and to adjust the ionization potential function to the new valence state for nitrogen. Both of these alterations should lead to a reduced π-moment. As a simple means of comparison we have taken the charge distribution given in Fig. 1 and introduced the hybridization moment for a charge of

+0.108 e on nitrogen. This leads to a resultant of 1.48 D directed at 45° to the plane of the ring. More rigorous calculations are thus likely to be insensitive to the assumption of the non-planar structure.

The present results indicate that the resultant dipole moment in furan is directed outward through the oxygen atom. This conclusion is consistent with the findings of Pujol and Julg [*72*] and with their argument that the π-moment in furan would have to exceed that in pyrrole for the moment to be reversed; a requirement which is unlikely to be satisfied because of the greater electronegativity of oxygen. Nevertheless it appears that the π-moments obtained here for furan are too large, most probably because the resonance integral between carbon and oxygen has been given by analogy, the same value as for C–N in pyrrole but is likely to be smaller in magnitude. The lesser extent of transfer of electrons to the benzene ring in benzofuran compared with indole is consistent with lower reactivity of dibenzofuran to electrophils when compared with carbazole [*26*, *13*].

For three systems the disparity between calculated and experimental dipole moments exceeds 0.5 Debye units. For nitrobenzene the result is quite good considering the large magnitude of the observed moment, and a more suitable choice of β_{CN} may reduce the anomaly. With furan 2-carboxylic acids we cannot decide whether the error lies in the experimental data or in the planar conformation which we have chosen on the basis of minimum electrostatic repulsions. For isoxazole the experimental value seems beyond question. On the theoretical side there is a possibility that our estimate of the geometry could be sufficiently in error to lead to a noticeable error in the calculated value of μ. This should shortly be resolved when the microwave studies currently in hand [*54*] are extended sufficiently to provide a complete framework geometry of the molecule. The completion of microwave studies of the geometry of pyrazole and of isoxazole are similarly awaited with interest.

Comparing methods of calculation we find that the Parr-Pariser formula (method P) for electronic repulsions leads to larger π-moments and poorer performance in predicting resultants. Inclusion of neutral atom penetration integrals (method C) yields larger π-moments in the furans and smaller values in the monocyclic azines. The most significant terms in the penetration potentials arise from the "dipolar part" of the electron distribution in non-bonded hybrids and appear to demand transfer of electrons from the benzene ring into the heterocyclic ring in the bicyclic azines. The π-moment being only a small part of the resultant in these systems comparison with experiment does not provide a means of judging the relative importance of penetration-dipole potentials.

In previous VESCF studies the relative merit of neglecting neutral-atom penetration integrals and of computing them theoretically using Slater-type orbitals has been considered without reaching any decisive conclusion. Tab. 7 includes dipole moments computed via these alternative procedures. In a substantial majority of cases the result obtained by neglecting penetrations is superior to that obtained by including penetrations. If this conclusion can be further substantiated it is of particular significance for the theoretical treatment of heterocyclic systems at this level of sophistication because for some types of system the auxiliary coulomb effects can be traced to neutral-atom penetration effects [*13*].

We might finally draw attention to the VESCF results presented in Tab. 2 for some nonalternant hydrocarbons. From these it seems likely that the experimental values for fluoranthene and especially heptafulvene are open to question. Accurate experimental values for all the hydrocarbons listed in Tab. 2 would be very valuable for testing the present theoretical technique and future refinements of it because the complex problem of a correct allowance for the electronic effects of heteroatoms does not of course arise.

Appendix 1

Formulation of the VESCF atoms-in-molecules method as applied to planar conjugated heteromolecules:

For a system of n coplanar conjugated atoms with m π-electrons the π-type LCAOMOs will be given by

$$\phi_i = \sum_{\mu} C_{i\mu}\chi_{\mu},\ i = 1, n;\ \mu = 1, n\ .$$

With formal neglect of overlap

$$\text{i.e. } S_{\mu\nu} = \delta_{\mu\nu}$$

the π-electron densities are given by

$$P_{\mu\nu} = \sum_{i} \nu_i C_{i\mu} C_{i\nu}$$

with ν_i equal to the orbital occupation number. The secular matrix equation

$$[F_{\mu\nu} - S_{\mu\nu}\varepsilon_i]\, C_{i\nu} = 0$$

for π-type MOs with the assumption of zero-differential-overlap is then specified by

$$\begin{aligned} F_{\mu\mu} &= (\mu \mid T + V_{\mu} \mid \mu) + \sum_{\varrho \neq \mu} (\mu \mid V_{\varrho} \mid \mu) + \tfrac{1}{2} P_{\mu\mu}(\mu\mu \mid \mu\mu) + \sum_{\varrho \neq \mu} P_{\varrho\varrho}(\mu\mu \mid \varrho\varrho) \\ &= -I_{\mu} - \sum_{\varrho \neq \mu} \{X_{\varrho}\gamma_{\varrho\mu} - (\varrho : \mu\mu)\} + \tfrac{1}{2} P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\varrho \neq \mu} P_{\varrho\varrho}\gamma_{\mu\varrho} \end{aligned}$$

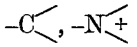
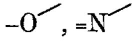
terms in ϱ being summed over all atoms in the molecule,

$$F_{\mu\nu} = (\mu \mid T + V_{\mu} + V_{\nu} \mid \nu) + \sum_{\varrho \neq \mu,\nu} (\mu \mid V_{\varrho} \mid \nu) - \tfrac{1}{2} P_{\mu\nu}(\mu\mu \mid \nu\nu) = \beta_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}\gamma_{\mu\nu}\ .$$

The net charge of an atom, $Q_{\mu} = X_{\mu} - P_{\mu\mu}$ may be used in conjunction with Slater's rules for first row atoms to derive the orbital exponent

$$Z_{\mu} = 0.65\,(G_{\mu} + 1) + 0.65\, Q_{\mu},\ G_{\mu} = \text{group number}\ .$$

Core coulomb integrals: The terms $(\mu \mid T + V_{\mu} \mid \mu) = -I_{\mu}$ may be obtained from the observed valence state ionization potentials [14] of constituent atoms

	$I = sp^3,\ V_4 \rightarrow sp^2,\ V_3$
	$I = s^{1+x}\, p^{4-x},\ V_3 \rightarrow s^{1+x}\, p^{3-x},\ V_2$
=O	$I = s^{1+x}\, p^{5-x},\ V_2 \rightarrow s^{1+x}\, p^{4-x},\ V_1$

where $x = 1/(1 + \lambda^2)$, and, given a single non-bonded hybrid

$$\chi_n = 2s + \lambda\, 2p_{\sigma}$$

in the plane of σ-bonding, orthogonal to the bonded hybrids and directed to bisect the bond angle θ externally,

$$\lambda = [-\cos\theta/\cos^2\tfrac{1}{2}\theta]^{\frac{1}{2}} .$$

The value of λ must be arbitrarily selected for carbonyl oxygen.
We assume that

$$\boldsymbol{I}_\mu(x) = [1 - x]\,\boldsymbol{I}_\mu(x = 0) + x\boldsymbol{I}_\mu(x = 1)$$

and that the variation with charge may be derived from

$$\boldsymbol{I}_\mu(\boldsymbol{Q}_\mu) = \frac{\boldsymbol{G}_\mu}{\boldsymbol{G}_\mu + \boldsymbol{Q}_\mu}\boldsymbol{I}_\mu(\boldsymbol{G} = \boldsymbol{G}_\mu + \boldsymbol{Q}_\mu)$$

with quadratic interpolation for non-integral values of $\boldsymbol{Q}_\mu$

$$\boldsymbol{I}_\mu(\boldsymbol{Q}_\mu) = \boldsymbol{a}\boldsymbol{Z}_\mu^2 + \boldsymbol{b}\boldsymbol{Z}_\mu + \boldsymbol{c}\ \text{e.v.}$$

Atom	Core charge	x	a	b	c
C	1	—	0.3605	9.092	−21.818
N	2	—	0.4510	11.362	−27.267
N	1	0	0.4955	9.604	−30.338
N	1	1	0.3795	11.296	−36.154
O	2	0	0.5945	11.525	−36.407
O	2	1	0.4555	13.555	−43.382
O	1	0	0.6455	9.842	−40.353
O	1	1	0.6620	9.992	−41.884

Quadratic coefficients which may be used in application to conjugated carbon, nitrogen and oxygen atoms are listed above.

This variation of valence state ionization potential with net charge is the most essential feature of the VESCF method.

Monocentric repulsion integrals: $(\mu\mu \mid \mu\mu) = \gamma_{\mu\mu}$ may be obtained by comparison of valence state ionization potentials $\boldsymbol{I}_\mu$ and affinities for a second π-type electron $\boldsymbol{A}_\mu$ in the appropriate valence state.

$$\gamma_{\mu\mu} = \boldsymbol{I}_\mu - \boldsymbol{A}_\mu\ [66] .$$

The empirical relation [*62*]

$$\gamma_{\mu\mu} = 3.294\ \boldsymbol{Z},\ \text{eV}$$

has been derived this way.

Core attraction integrals, $(\mu \mid \boldsymbol{V}_\varrho \mid \mu)$, and penetration integrals $(\varrho : \mu\mu)$: Potentials corresponding to net attraction may arise because the density distribution of a π-electron on one atom lies within some part of the electron density of a nearby neutral atom. These cannot be readily estimated from empirical properties of the constituent atoms and several alternative techniques for assigning values to such terms have been used in semi-empirical SCF methods.

Method ***A***: Taking $(\mu \mid \boldsymbol{V}_\varrho \mid \mu) = (\mu \mid \boldsymbol{V}_\varrho^{\neq} \mid \mu) - \gamma_{\mu\nu}$, where $\boldsymbol{V}_\varrho^{\neq}$ represents the potential field of the atomic σ-core plus one π-electron, the first term is evaluated theoretically using Slater atomic orbital functions and the second by one of the methods indicated below.

Method $\boldsymbol{B}$: All such penetration terms are neglected on the assumptions that they are somewhat smaller than indicated by method $\boldsymbol{C}$ and that their sums at each of the atoms will be approximately equal.

Method $\boldsymbol{C}$: Taking $(\mu \mid V_\varrho \mid \mu) = \boldsymbol{X}_\varrho \gamma_{\mu\varrho} + (\varrho : \mu\mu)$ the penetration integrals may be estimated by employing Slater type atomic orbital density distributions.

Method $\boldsymbol{A}$ appears to overestimate core attractions as well as penetration potentials and has not been used in the current work. Where method $\boldsymbol{C}$ has been applied we have taken neutral atom effective nuclear charges to define the orbital functions and have assumed sp^2 hybridization throughout.

Two-centre repulsion integrals: $(\mu\mu \mid \nu\nu) = \gamma_{\mu\nu}$ may also be estimated in several ways.

Method $\boldsymbol{T}$ *[76]*: Theoretical evaluation using Slater type atomic orbital functions.

Method $\boldsymbol{P}$ *[66, 67]*: Interpolation up to 3.7 Å using

$$\gamma_{\mu\nu} = ar^2 + br + \tfrac{1}{2}(\gamma_{\mu\mu} + \gamma_{\mu\nu})$$

from

$$\gamma_{\mu\nu} = 7.70 \left\{ [1 + (\tfrac{1}{2}(\boldsymbol{R}_\mu - \boldsymbol{R}_\nu)/r)^2]^{-\frac{1}{2}} + [1 + (\tfrac{1}{2}\, \boldsymbol{R}_\mu \boldsymbol{R}_\nu / r)^2]^{-\frac{1}{2}} \right\} / r \text{ eV}$$

at 2.8 and 3.7 Å; $\boldsymbol{R}_\mu = 4.597/\boldsymbol{Z}_\mu$ Å. Beyond 3.7 Å method $\boldsymbol{R}$ is used.

Method $\boldsymbol{J}$ *[54]*: Interpolation by means of the relation

$$\gamma_{\mu\nu} = 14.40\, [r + 28.80/(\gamma_{\mu\mu} + \gamma_{\nu\nu})]^{-1} \text{ eV} .$$

Method $\boldsymbol{R}$ *[68]*: Use of the point-charge electrostatic relation

$$\gamma_{\mu\nu} = 14.40/r \text{ eV} .$$

Results of studies of the Parr-Pariser-Pople SCF type indicate that methods $\boldsymbol{T}$ and $\boldsymbol{R}$ overestimate the effective repulsion potentials.

The semiempirical interpolation methods $\boldsymbol{P}$ and $\boldsymbol{J}$ are more satisfactory alternatives. Both have been applied in this work, the latter being simpler and possibly more successful. Values were calculated for neutral atoms and not varied during the self consistent field calculations.

Core resonance integrals, $\beta_{\mu\nu}$: The relation *[66, 67]*

$$\beta_{\mathrm{CC}} = -6442 \exp\left(-5.6864\, \boldsymbol{r}_{\mathrm{CC}}\right) \text{ eV}$$

obtained by PARR and PARISER for neighbouring carbon atoms (zero for non-neighbours) in calculation of electronic transitions for hydrocarbons has been used here*. Values of $\beta_{\mu\nu}$ between carbon and heteroatoms, consistent with the VESCF formalism,

β_{CO}(formaldehyde) $= -2.69$ eV *[14]*
β_{CN}(pyrrole) $= -2.30$ eV *[16]*
β_{CN}(pyridine) $= -2.47$ eV *[17]*

have been obtained in a corresponding manner.

---

* Since this work was initiated a corrected function $\beta_{\mathrm{CC}} = -2517.5 \exp\left(-5.007\, \boldsymbol{r}_{\mathrm{CC}}\right)$ eV has been supplied by the original authors *[65]*. For the bond distances considered here this relation does not lead to appreciably different values.

Since these values are not very different from each other we have used them for similar bond types in the present studies relating to dipole moments, viz.

$\beta_{\mu\nu} = -2.30$ eV for CN in pyrroles, aniline and nitro benzene,
for CO in furans, phenol and carboxylic acids (COH),
NN in pyrazole,
and for NO in isoxazole and also in pyridine N-oxide;
$\beta_{\mu\nu} = -2.69$ eV for CO in aldehydes and carboxylic acids (CO),
and
$\beta_{\mu\nu} = -2.311$ eV for CC in benzene rings, CN in azines,
and for NN in pyridazine, cinnoline and phthalazine.

The exponential relation above is used for carbon-carbon bond lengths differing from 1.395 Å and all non neighbour core resonance integrals were neglected.

Appendix 2

Assumed Structures of Heterocycles.

Geometrical structures used in this work for estimation of quantum mechanical integrals and dipole moments of heteroaromatic systems: All molecules are assumed to be planar for the purpose of the calculations and conformations are indicated in Fig. 1. The key to the numbers is given in Tab. 7. Chosen structures are based on data listed in Ref. [*86*]. Non-neighbour distances were obtained by geometrical construction. Benzene — $r_{CC} = 1.395$ Å; $< CCC = 120°$.

1. $\boldsymbol{r}_{CO} = 1.363$ Å; $\boldsymbol{r}_{CC} = 1.362,\ 1.442$ Å; $< COC = 107°$; $< OCC = 109°$; $< CCC = 107°$ [*6*];

2. $\boldsymbol{r}_{CN} = 1.387$ Å; $\boldsymbol{r}_{CC} = 1.367,\ 1.428$ Å; $< CNC = 107°$; $< NCC = 109°$; $< CCC = 107°$ [*5*];

3. From 1 with three sides of benzene symmetrically attached, $\boldsymbol{r}_{CC} = 1.395$ Å;
4. From 2 as 3 from 1;
5. 9 Identical with 1;
6. 10 Identical with 2;
7. C_6H_5 as in benzene, $\boldsymbol{r}_{CO} = 1.37$ Å, $< CCO = 120°$;
8. C_6H_5 as in benzene, $\boldsymbol{r}_{CN} = 1.37$ Å;
11. $\boldsymbol{r}_{NO} = 1.22$ Å, $< ONO = 125°$, from nitromethane;
12. C_6H_5 as in benzene, NO_2 as in 11, $\boldsymbol{r}_{CN} = 1.367$ Å;
13. C_4H_3O as in 1, CO as in 15, $< CCC = 125\frac{1}{2}°$, $< CCO = 119°$;
14. From 2, 15 as 13 from 1, 15;
15. $\boldsymbol{r}_{CO} = 1.22$ Å;
16. C_6H_5 as in benzene, CO as in 15, $\boldsymbol{r}_{CC} = 1.47$ Å, $< CCO = 119°$ $< CCC = 120°$;
17. X-ray crystallographic structure as given in Ref. [*86*];
18. From 17 correcting for differences between 2 and 1;
19. $\boldsymbol{r}_{CO} = 1.16$ Å, $\boldsymbol{r}_{COH} = 1.26$ Å, $< OCO = 124°$, $< COH = 120°$;
20. From benzene and 19, $\boldsymbol{r}_{CC} = 1.47$ Å, $< CCC = 120°$, $< CCO = 117°$;
21.—23. See 1—3;
24. From benzene and 2, $\boldsymbol{r}_{CN} = 1.387$ Å;
25.—35. All bonds 1.395 Å, all angles 120°;
36. From 25, $\boldsymbol{r}_{NO} = 1.36$ Å.

Appendix 3

Optimisation of Bond Angles in Planar Systems.

Comparison of dipole moments, particularly in the non-alternant hydrocarbons, calculated by various authors is difficult if the molecular structure has not been completely determined, and different geometrical assumptions were made. Generally bond lengths may be estimated to fair accuracy but the bond angles have often been chosen in a more or less arbitrary fashion.

Here we describe an objective method for making a realistic choice of angles by minimizing for planar systems the sum of squares of deviations of all angles from 120°. The terms may be weighted according to the bending force constants, but in the present application to non-alternant hydrocarbons, equal weights have been taken for distortions of all angles.

The trigonometric conditions for ring closure at any atom μ in a ring of $\boldsymbol{n}$ atoms with internal angles θ_μ and a given set of bond lengths $\boldsymbol{r}_{\nu,\nu-1}$ are

$$\boldsymbol{y}_\mu = \sum_{\nu=1}^{\mu-1} \boldsymbol{r}_{\nu,\nu-1} \sin\left[(1-\nu)\,\pi - \theta_1' + \sum_{\eta=1}^{\nu-1} \theta_\eta\right]$$
$$= -\boldsymbol{r}_{1,n} \sin\theta_1', - \sum_{\nu=\mu+1}^{n} \boldsymbol{r}_{\nu,\nu-1} \sin\left[(1-n-\nu)\,\pi + \sum_{\eta=\nu}^{n} \theta_\eta + \theta_1'\right]$$

where θ_1' is the angle of the vector $\tilde{\boldsymbol{r}}_{1,n}$ to chosen $\boldsymbol{x}$ axis and $\boldsymbol{y}_\mu$ is the ordinate of atom μ.

In any ring of n atoms the sum of internal angles is $(\boldsymbol{n} - 2)\pi$ radians and generally the individual deviation $\delta\theta_\mu$ from the mean angle $\bar{\theta}$ will be less than 2°. The substitution

$$\cos\theta_\mu = \cos(\bar{\theta} + \delta\theta_\mu) = \cos\bar{\theta} - \delta\theta_\mu \sin\theta$$

and

$$\sin\theta_\mu = \sin(\bar{\theta} + \delta\theta_\mu) = \sin\bar{\theta} + \delta\theta_\mu \cos\theta$$

with angles expressed in radians are thus satisfactory approximations.

With an appropriate choice of bond lengths it is then possible to express $\delta\theta$ for all angles in terms of $\delta\theta$ for a number of angles equal to the number of degrees of freedom, $\boldsymbol{f} = \boldsymbol{n} - 3 - \boldsymbol{m}$, where $\boldsymbol{m}$ is the number of axes of symmetry that may be drawn to pass between atomic positions, using the ring closure conditions.

The sum of squares of deviations

$$\sum_{\text{all angles}} \left[\delta\theta + \left(\frac{2\pi}{3} - \bar{\theta}\right)\right]^2$$

may then be minimized with respect to all degrees of freedom. Since the highest term in $\delta\theta_\mu$ is $(\delta\theta_\mu)^2$ the partial derivative of this sum is linear in $\delta\theta_\mu$ and a set of simultaneous equations is obtained which may be readily solved.

If the approximations $\sin\delta\theta = \delta\theta$ and $\cos\delta\theta = 1$ prove to be of insufficient accuracy the solution on this basis may be used as the starting point for a second cycle, referring the deviations to the approximate values of θ. With the exception of fused ring systems, if all angular distortions are given equal weight the problem reduces to evaluation of the least squares of deviations from the mean internal angle in each ring since

$$\sum_{\mu=1}^{n} \delta\theta_\mu = 0\,.$$

In this scheme exocyclic bonds bisect the internal angles externally.

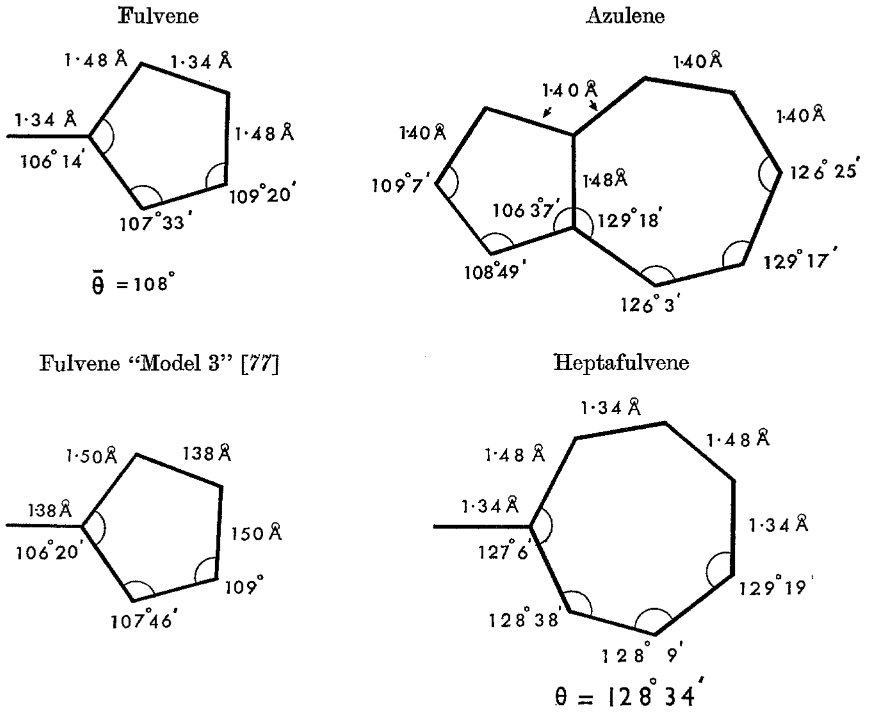


Fig. 3. Optimized Skeletal Structures for Non-alternant Hydrocarbons and an Electron Diffraction Model for Fulvene

Structures obtained in this way for fulvene and heptafulvene assuming bond distances of 1.48 Å for formal single bonds and 1.34 Å for formal double bonds are shown in Fig. 3. The estimate derived for fulvene corresponds very well with one of the alternative structures (model 3) offered by Rouault [77] on the basis of election diffraction measurements. The structure shown for azulene was obtained using annular bond lengths of 1.40 Å and 1.48 Å for the transannular $C_9 - C_{10}$ distance as determined by X-ray diffraction [75]. These are used as an objective basis for calculation of comparative dipole moments from various charge distributions as listed in Tab. 2.

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