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CALCULATION OF DIPOLE MOMENTS OF HETEROATOM MOLECULES

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The calculation of the dipole moments of heteroatom-containing molecules has not met with frequent success. In particular, the estimation of the σ bond contribution to the total dipole moment has been difficult. This has been commonly treated by using standard bond moments and summing them vectorially (1). As a first approximation the σ and π moments are regarded as being independent, hence a calculated total dipole moment is a vectorial sum of the two (2).

We have calculated the μ_σ and μ_π using semi-empirical molecular orbital methods and have obtained calculated dipole moments in good agreement with experimental values. The μ_π were calculated from charge densities obtained by the use of the Huckel LCAO-MO ω-Technique. The heteroatom parameters used were those of Streitwieser (3), with only two modifications. We found it necessary to employ a slightly higher h value for the pyridine nitrogen which gave a better dipole moment agreement. For the same reason we employed a slightly higher value for the h of chlorine. The values used are listed in Table I.

TABLE I

Values of h and k Parameters Used

Atom	h_x	k_{cx}
$\dot{N}$	0.8	1.0
$\ddot{N}$	1.7	0.7
$\dot{O}$	1.3	0.8
$\ddot{O}$	2.7	0.6
Cl	2.8	0.5
CH_3	3.0	0.7

The μ_σ values were calculated from the charge densities of the σ skeleton atoms using the method of Del Re (4). The procedure is an adaptation of the LCAO-MO method, treating all σ bonds as localized orbitals, $\Psi_{AB} = C_A\chi_A + C_B\chi_B$ to which an inductive effect is introduced from neighboring atoms. Appropriate values of the Coulomb and resonance integrals are written in terms of a standard α and β. The secular equations in matrix form are then

$$\begin{vmatrix} \alpha + \delta_A\beta - E & \epsilon_{AB}\beta \\ \epsilon_{AB}\beta & \alpha + \delta_B\beta - E \end{vmatrix} = 0$$

The resonance integral modifying parameter ϵ_{AB} is assumed to be independent of surroundings, while the Coulomb integral modifying terms δ_A and δ_B are assumed to be influenced by atoms bound directly to atoms A or B. This influence is accounted for by the use of an auxiliary inductive parameter γ_{AB}, which is characteristic of the inductive effect of all neighboring atoms, B. The corrected expression for δ_A becomes

$$\delta_A = \delta_A^{o} + \sum_{\text{B adj to A}} \gamma_{A(B)}\,\delta_B$$

The charge density on atom A due to neighboring atom B is then calculated from the corrected δ_A and δ_B values and the ϵ_{AB} parameter

$$q_A^{(B)} = \frac{\dfrac{\delta_B - \delta_A}{2\,\epsilon_{AB}}}{\sqrt{1 + \left(\dfrac{\delta_B - \delta_A}{2\,\epsilon_{AB}}\right)^2}}$$

The total charge density on atom A then becomes

$$Q_A = \sum_{\text{all } B} q_A^{(B)}$$

The values of the parameters δ^o, γ_{AB} and ϵ_{AB} were derived by Del Re from dipole moment values and electronegativities (4). They were used in our calculations and are listed in Table II.

TABLE II

Values of Parameters Used in the σ Bond Treatment

	C(H)	C(C)	C(N)	C(O)	N(H)	O(H)	C(Cl)
ϵ_{AB}	1.00	1.00	1.00	0.95	0.45	0.45	0.65
$\gamma_{A(B)}$	0.3	0.1	0.1	0.1	0.3	0.3	0.2
$\gamma_{B(A)}$	0.4	0.1	0.1	0.1	0.4	0.4	0.4
δ_A^o	0.07	0.07	0.07	0.07	0.24	0.40	0.07
δ_B^o	0.00	0.07	0.24	0.40	0.00	0.00	0.35

The charge densities and calculated and experimental dipole moments are listed in Table III and refer to the structures and atom positions drawn in Figure 1. The total dipole moment, μ_T was obtained by vectorial addition of μ_σ and μ_π. The agreement in all cases was about 95% of the experimental value.

TABLE III

Charge Densities and Dipole Moments

Compound	Atom	Charge Densities		Calculated μ			Experimental μ	
		q_σ	q_π	μ_σ	μ_π	μ_T	μ	Ref.
Formaldehyde	1	-.134	-.288	0.50	1.62	2.12	2.17	(5)
	2	+.046	+.288					
	3	+.044						
Furan	1	-.310	+.080	1.46	0.71	0.75	0.72	(6)
	2	+.100						
	3	+.038	-.009					
	4	-.011						
	5	+.028	-.032					
Pyridine	1	-.142	-.182	0.74	1.21	1.95	2.15	(7)
	2	+.027	+.057					
	3	+.036						
	4	-.025	+.015					
	5	+.032						
	6	-.029	+.039					
	7	+.031						
Pyrrole	1	+.197		0.08	1.52	1.44	1.54	(8)
	2	-.371	+.169					
	3	+.039	-.026					
	4	+.038						
	5	-.022	-.059					
	6	+.032						

TABLE III (Continued)

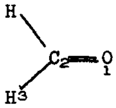
		Charge Densities		Calculated μ			Experimental μ	
Compound	Atom	q_σ	q_π	μ_σ	μ_π	μ_T	μ	Ref.
Toluene	1	+.038						
	2	-.125	+.026	0.05	0.46	0.41	0.39	(9)
	3	+.011	+.016					
	4	-.031	-.014					
	5	+.031						
	6	-.031	-.002					
	7	+.031						
	8	+.031	-.010					
	9	+.031						
Chlorobenzene	1	-.185	+.015	2.02	0.28	1.74	1.58	(10)
	2	+.119	+.008					
	3	-.008	-.007					
	4	+.033						
	5	-.031	-.001					
	6	+.042						
	7	-.036	-.006					
	8	+.030						

TABLE III (Continued)

		Charge Densities		Calculated μ			Experimental μ	
Compound	Atom	q_σ	q_π	μ_σ	μ_π	μ_T	μ	Ref.
Phenol	1	+.299		1.80	0.39	1.58	1.60	(11)
	2	-.471	+.022					
	3	+.140	+.012					
	4	-.018	-.011					
	5	+.032						
	6	-.029	-.002					
	7	+.031						
	8	-.031	-.009					
	9	+.031						
Aniline	1	+.216		1.32	0.73	1.54	1.53	(12)
	2	-.535	+.052					
	3	+.085	+.017					
	4	-.024	-.021					
	5	+.032						
	6	-.032	-.004					
	7	+.031						
	8	-.031	-.017					
	9	+.031						

FIGURE 1

Structures Calculated with Numbering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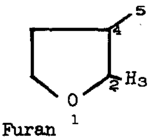
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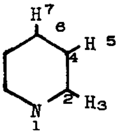
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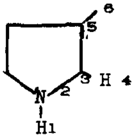
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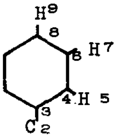
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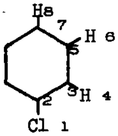
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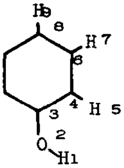
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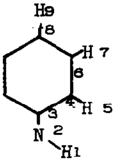
Aniline

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