

increase with pressure so that, if rates permit, ECL will be formed with increasing abundance.

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D. V. REES
D. C. BASSETT

J. J. Thomson Physical Laboratory,
University of Reading.

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Charge Distributions of Conjugated Molecules

POINT charges located at the atom centres of conjugated molecules can be calculated using the Del Re procedure for σ electrons, the Hückel procedure for π electrons and the principle of σ - π additivity. Such point charges, calculated by this and other procedures, have been used in biophysical problems¹⁻⁴. Can the very simple Del Re-Hückel procedure give reasonable values for the charges? This report provides a partial answer by comparing observed dipole moments with those calculated from Del Re-Hückel charges obtained with established sets of the necessary parameters^{5,6}.

The most appropriate comparison is with vapour phase dipole moments of molecules of known vapour phase structure. In five of the twenty-two compounds found to satisfy these criteria the components of the dipole moment along the principal molecular axes were available and were used as an added test of the computed charges. The comparisons are presented in Table 1 and the parameters used are given in Table 2. The bromine σ parameters are new and were determined by fitting the dipole moments of CH_2Br and CHBr_3 (refs. 7 and 8). We observed (Table 1) improvement in the calculated moments of carbonyl-

Table 1. COMPARISON OF CALCULATED AND OBSERVED DIPOLE MOMENTS

Compound	Calculated (D)		Observed μ
	μ_σ	μ_π	
Chlorobenzene ^{7,8}	1.94	0.29	1.65
<i>o</i> -Dichlorobenzene ^{7,8}	3.33	0.49	2.84
<i>m</i> -Dichlorobenzene ^{7,8}	1.93	0.28	1.65
Chloroethylene ⁹	1.82	0.30	1.53
μ_A^0	1.74	0.29	1.45
μ_B^0	0.55	0.07	< 1.00
<i>Cis</i> -dichloroethylene ^{7,8}	2.95	0.22	2.73
Fluorobenzene ^{7,8}	1.88	0.51	1.37
<i>m</i> -Difluorobenzene ^{7,8}	1.88	0.51	1.37
Fluoroethylene ^{7,10}	1.85	0.55	1.48
$\mu_A^{7,10}$	1.65	0.54	1.12
$\mu_B^{7,10}$	0.83	0.13	0.97
1,1-Difluoroethylene ^{7,8}	2.07	1.04	1.03
<i>Cis</i> -difluoroethylene ^{7,8}	3.07	0.20	2.78
<i>p</i> -Bromofluorobenzene ^{7,8}	0.02	0.29	0.27
Bromobenzene ^{7,8}	1.85	0.22	1.63
Bromoethylene ^{7,8}	1.78	0.23	1.59
Toluene ^{7,8}	0.05	0.82	0.77
Pyridine ^{7,8}	0.71	1.12	1.83
Pyrrole ^{7,8}	0.11	2.42	2.58
Furan ^{7,8}	1.45	1.04	0.49
Formaldehyde ^{7,8}	1.06	2.60 (1.41)	3.66 (2.47)
Acetone ^{7,8}	1.09	4.10 (2.26)	5.19 (3.35)
Acetaldehyde ¹¹	1.07	3.50 (1.89)	4.56 (2.95)
μ_A^{11}	0.90	3.20 (1.71)	4.10 (2.61)
μ_B^{11}	0.58	1.42 (0.79)	2.00 (1.37)
<i>l</i> -Acrolein ¹²	1.09	4.70 (2.18)	5.78 (3.28)
μ_A^{12}	1.01	4.57 (2.09)	5.58 (3.10)
μ_B^{12}	0.40	1.11 (0.64)	1.52 (1.04)
Formic acid ^{13,14}	0.52	3.76 (2.04)	3.26 (1.54)
$\mu_A^{13,14}$	0.42	3.50 (1.89)	3.08 (1.47)
$\mu_B^{13,14}$	0.30	1.38 (0.77)	1.08 (0.47)

Table 2. PARAMETER VALUES FOR σ AND π CALCULATIONS

Bond	σ^*									
	C-H	C-C	C-N	C-O	N-H	O-H	C-F	C-Cl	C-Br	
$\epsilon_{\sigma y}$	1.00	1.00	1.00	0.95	0.45	0.45	0.85	0.65	0.60	
γ_{-y}	0.30	0.10	0.10	0.10	0.30	0.30	0.10	0.20	0.20	
γ_{y-x}	0.40	0.10	0.10	0.10	0.40	0.40	0.10	0.40	0.40	
δ_{σ}^{\pm}	0.07	0.07	0.07	0.07	0.24	0.40	0.07	0.07	0.07	
δ_{σ}^{\pm}	0.00	0.07	0.24	0.40	0.00	0.00	0.57	0.35	0.30	

Bond	π									
	C-C	C-N	C-O	C-O	C-CH ₃	C-F	C-Cl	C-Br		
k_y	1.0†									
h_y	1.1‡	0.80	1.00	0.80	1.00	0.70	0.70	0.40	0.30	
	0.9§				(2.00)					
	0.00	1.50	0.50	2.00	1.00	2.00	3.00	2.00	1.50	

* Charges computed using the formula for bond charges as in ref. 15.

† For bond length of about 1.40 Å.

‡ For bond length of about 1.34 Å.

§ For bond length of about 1.47 Å.

containing compounds (values in brackets in Table 1) when the value of $k_{C=O}$ was changed from 1.0⁶ to 2.0, another generally used value¹⁶⁻¹⁹.

This communication extends recent evaluations^{20,21} of the Del Re-Hückel type calculations of charge distributions to include dipole moment components and previously unexamined heteroatoms, as well as a larger numerical sample. The agreement between computed and observed moments emphasizes that this simplistic procedure gives reasonable values for the point charges.

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H. A. NASH
S. R. GROSSMAN
D. F. BRADLEY

Laboratory of Neurochemistry,
National Institute of Mental Health,
Bethesda, Maryland.

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Benzo[*a*]pyrene, Phenols and other Products from Pyrolysis of the Cigarette Additive, (*d,l*)-Menthol

THIS communication surveys the chief products from the thermal degradation of (*d,l*)-menthol and discusses some qualitative and quantitative differences in product composition at two selected temperatures. The thermal decomposition of menthol—a naturally occurring alcohol