ON THE CRITERIA FOR PI-ELECTRON DELOCALIZATION

IN SOME CYCLIC CONJUGATED SYSTEMS

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Discussions of "aromaticity" of cyclic conjugated

molecules have invoked a variety of criteria for the

estimation of the extent of π-electron delocalization.

Two especially widely used properties are the permanent

molecular dipole moment[2] and the proton magnetic resonance

(NMR) chemical shift of hydrogens adjacent to the π-

electron system.[3-6]   In the language of resonance theory

the dipole moment is a measure of the contribution to

the resonance hybrid of structures with charge separation;

molecules that are not formal zwitterions must undergo

some electron delocalization in order for such structures

to contribute. The NMR chemical shifts of ring and side-

chain protons depend in part on ring currents, which in turn

are also associated with π-bond delocalization. We wish to

point out that, regardless of the general validity or

inadequacy of these criteria of "aromaticity," the two kinds

of experimental observation measure fundamentally different
properties, and attempts to predict charge distributions
or dipole moments from NMR chemical shifts (or <u>vice</u> <u>versa</u>)
can lead to inconsistencies. The properties of the
anhydrobases 1-methyl-2-cyclopentadienylidene-1,2-dihydro-
pyridine (I)[7] and 1-benzyl-4-cyclopentadienylidene-1,2-
dihydropyridine (II)[8,9] which are isoelectronic with the
hydrocarbon sesquifulvalene (III), exemplify these
discrepancies. We report here a molecular orbital method
by which the charge distributions may be calculated and
compare the results to the observed dipole moments and to
the conclusions from NMR data.
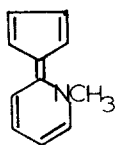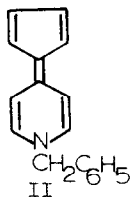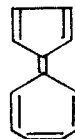
I   II   III

Simple Hückel theory[10] predicts substantial charge
separation in all three systems, I, II, and III, but as
is usually the case in attempts to predict quantitatively
the dipole moments of non-alternant hydrocarbons,[2] the
calculated values are too high (<u>e.g.</u>, II, calcd. $\mu = 17.6\underline{D}$,
observed, $\mu \sim 9 \underline{D}$). Even the ω -technique, in which the

Hückel charge densities are re-inserted as modifying terms
in the diagonal matrix elements of the secular determinant,
and re-cycling of the energy calculation is continued to
self-consistency of the charge distribution, is ineffective
in reducing the calculated dipole moments of I and II to
satisfactory values.

Significantly, much better agreement is achieved by
modifying the ω-technique to take bond alternation
explicitly into account. This is done in calculation "A"
by choosing all initial resonance integrals β_0 as equal and
then evaluating the off-diagonal elements of the secular
determinant in the Nth cycle as

$$\beta_{rs} = \beta_0 \exp (0.517\ p_{ij} - 0.344)$$

where p_{ij} is the bond order between atoms r and s in
the (N-1)th cycle.[11b] The modifying terms vanish
($\beta_{rs} = \beta_0$) when p_{ij} has the benzene π-bond order 0.667.
In calculation "B", the initial resonance integrals are
varied as $\beta_{rs} = k\beta_0$, with k having the value 1.06 for
all formal C=C bonds, 0.90 for all formal C-C bonds, 0.75
for all formal C-N and C-O bonds, and 1.00 for all formal
C=O bonds and pyridine ring bonds, these values being
retained throughout. In both calculations, the Coulomb
integral for the Nth cycle is taken as[2,11a] $\alpha_i = \alpha_x$
+ 1.4 $(n-q_i)\beta_0$, where α_x is the initial coulomb integral
($\alpha_O = \alpha_C + \beta$; $\alpha_N = \alpha_C + 1.5\beta$); q_i is the computed
charge density at atom i for the (N-1)th cycle, and n is
the number of core charges contributed by atom i (n = 1 for

carbon and oxygen and 2 for nitrogen). In most cases, the
charge distributions converge to three-place self-
consistency in about seven to ten cycles in both calculations.
Convergence is expedited by using for the Nth cycle the
q_i value obtained by averaging the values from the $(N-1)$th
and $(N-2)$th cycle. The dipole moments calculated from the
final charge distributions and reasonable molecular
geometries for compounds I, II, and a group of related
heterocyclic substances are recorded in Table I, where
comparisons with available measured dipole moments are
also given. The agreement is satisfactory and may be taken
as suggestive of pronounced bond alternation. Although it
is difficult to give an accurate estimate of the magnitude
of the sigma moment that would be expected for these
compounds,[12] it seems likely that in each case it would be
substantially smaller than the π-moment (probably not
greater than 1-2D) and would oppose it.

The observed large dipole moments (Table I) thus
imply substantial π-electron delocalization, despite
the bond alternation suggested by the calculations. In
resonance terminology, zwitterionic structures Ia and IIa
contribute about 25-30% to the resonance hybrids.[13,14]
This conclusion is contrary to that deduced from studies
of the NMR spectra of II ($CH_2C_6H_5 =$ n-butyl), I, and IV,
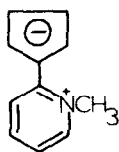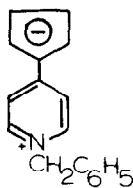
Ia   IIa

TABLE I

Calculated and Observed Dipole Moments

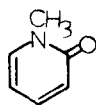| Compound	μ, Debyes			
	calcd. "A"	calcd. "B"	obs.	Ref. to μ_{obs}.
I	9.8	7.9	5.1	13
II	12.9	10.5	9.7;8.9	16a, 13
V	12.6	13.6	13.5	8b, 16b
VI	--	4.5	4.5	17
VII	4.0	4.0	4.15	18
VIII	6.7	6.4	6.9	18
IX	--	4.32;5.26[a]	4.18	19
X	--	5.6	--	
XI	--	4.9	--	

[a] Did not converge after 24 cycles of iteration. Values shown are average of those of 8th and 9th cycles, which approached more closely than any other vicinal pair.
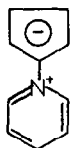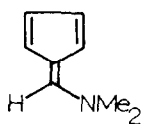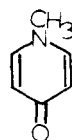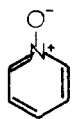

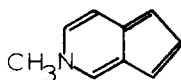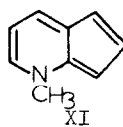V   VI   VII   VIII

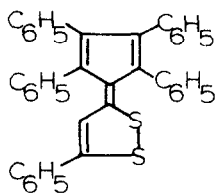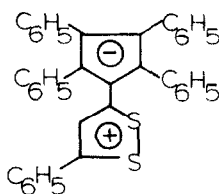IX   X   XI

where the proton chemical shifts are interpreted[4,6,20]   as
indicating that the homopolar structures are adequate
representations of these molecules and that there is
relatively little electron delocalization and charge
separation such as would result from important contributions
of the heteropolar structures Ia, IIa, and IVa.   But

IV   IVa

compound II, for example, has one of the highest dipole
moments ($\mu \sim 9\underline{D}$) recorded for a substance that is not a
formal zwitterion (compare, for example, p-nitrodimethyl-
aniline, $\mu = 6.87\underline{D}$[15]).   In these circumstances, it is
difficult to support the view that the contribution of
the dipolar structure IIa can be neglected.   It remains
to be seen whether a correlation sufficiently precise to
allow the prediction of dipole moments from NMR data will
be discovered.[21]

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(14) These are minimum figures, since the π-moment is
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(20) The NMR data[4,5] are not necessarily incompatible
      with the dipole moments. In fact, some of them seem
      in our opinion to be interpretable on the assumed basis[3]
      in terms of fractional contributions of dipolar structures
      that are in rough accord with those calculated from the
      dipole moments. Without urging the latter interpretation,
      we merely question the conclusion[4,6] that the dipolar
      structures are "unimportant".

(21) For previous contributions to the problem of relationships
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