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GRAPH-THEORETICAL RESONANCE ENERGIES OF BENZENE AND HETEROBENZENES FROM PHOTOELECTRON SPECTRA[1]

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Summary. Experimental values of π ionization potentials, non-subjective linear regression techniques, and graph theory are used to calculate resonance energies with the results, C_6H_6, 0.821 eV; C_6H_5N, 0.618 eV; C_6H_5P, 0.661 eV; C_6H_5As, 0.545 eV; C_6H_5Sb, 0.607 eV.

Group V heterobenzenes are judged to be aromatic[2] on the basis of NMR ^1H and ^{13}C chemical shifts [3-5], planarity , lack of bond alternation, and benzenoid bond lengths.[6-10] Photoelectron (PE) spectra for the heavier heterobenzenes can be correlated with the spectra of pyridine and benzene.[11-13] No quantitative estimates of resonance energies are available, due to the dearth of thermodynamic data and suitable resonance-free model compounds.

Resonance energies listed in Table I are obtained using graph theory[1,14,15] and PE experimental vertical π ionization potentials (IP's)[11-13], derived according to the following procedure:

(1) Linear correlations of the heterobenzene IP's with ionization energies of the free heteroatoms[2,11,16] suggest that an HMO approach will model experimental results. Coulomb integrals, $\alpha(C)$, $\alpha(C\text{ adj. }X)$, $\alpha(X)$, and resonance integrals, $\beta(CC)$, $\beta(CX)$, comprise a set of parameters[17] consistent with the PE/IP data.

(2) Non-subjective methods based on a linear regression analysis and first-order perturbation theory[18,19] are used to obtain the parameters of the HMO structural model. The set of IP data leads to a unique and non-adjustable set of parameters. They are listed in Table II and give calculated IP's that are identical with the experimental values.

(3) The characteristic polynomial for a π system is

$$P(\lambda)^M = \det|H - \lambda I| = \sum_{j=o}^{n} a_j \lambda^{n-j}$$

where H is the parameterized Hückel matrix, and I is a unit matrix. Graph theory relates the coefficients a_j to structural molecular graph components[15,20-24]. The characteristic polynomial for a hypothetical resonance-free reference system $P(\lambda)^R$ is obtained by deletion of coefficients corresponding to cyclic components.

(4) Roots of $P(\lambda)^M$ and $P(\lambda)^R$ correspond to energy levels. The resonance energy for a particular system is

$$RE = \sum_{i=1}^{n} g_i (\lambda_i^M - \lambda_i^R)$$

where g_i is 0, 1, or 2, depending on the number of π electrons.

This abstract definition of resonance energy relies on the viewpoint ascribing aromaticity to cyclic delocalization.[25,26] Graph-theoretical resonance energies precisely parallel those obtained by other theoretical methods,[1,14,15,27-29] and this fact could constitute a justification for this approach. A useful advantage is that experimental data used to determine the parameters of the electronic model completely establish the π energies of both parent and reference molecular systems. One cannot make post-facto adjustments of the parameters to fit preconceived ideas. Objections to using IP data to examine aromaticity questions[30] may be mitigated by these procedures.

Table I. Ionization Potentials and Resonance Energies for Heterobenzenes

Compound	IP's and assigned[a] irreducible representations (eV's)			Resonance Energies (eV's)	% RE Benzene
C_6H_6	9.24(E_{1g})		12.25(A_{2u})	0.821	100
C_6H_5N	9.8 (A_2)	10.5(B_1)	12.6 (B_1)	0.618	75.3
C_6H_5P	9.2 (B_1)	9.8(A_2)	12.1 (B_1)	0.661	80.5
C_6H_5As	8.8.(B_1)	9.6(A_2)	11.8 (B_1)	0.545	66.4
C_6H_5Sb	8.3 (B_1)	9.4(A_2)	11.7 (B_1)	0.607	73.9
C_6H_5Bi	7.9 (B_1)	9.2(A_2)			

[a] References 11, 13 and 16.

Table II. Parameters for Heterobenzene Hückel MO Calculations (Units of -eV's)

Heteroatom	α(X)	α(C adj. X)	β(CX)
N	10.52	7.26	1.70
P	7.79	6.26	1.85
As	7.80	6.91	1.40
Sb	6.79	6.54	1.53
α(C) = 6.23	β(CC) = 3.01		

The calculated benzene resonance energy, 0.821 eV, is in excellent agreement with the value 0.869 eV found in LCAO-MO-SCF calculations[31] parameterized using thermochemical data. This remarkable confluence of results obtained from very different kinds of experimental data and theories argues for the validity of this value. Resonance energies of heterobenzenes are relatively constant, and somewhat diminished from that of benzene. One concludes that the heterobenzenes are aromatic compounds, and that the elements N, P, As, and Sb, can participate in aromatic π structures. These conclusions agree with the qualitative observations previously published.[2]

Frontier orbital coefficients and electronic charges are obtainable using the parameters given in Table II, and are listed in Table III. Part of the enhanced basicity of pyridine as compared to heavier heterobenzenes[32] can be attributed to the large calculated negative charge on nitrogen. From charge distributions, the heavier heterobenzenes are expected to be more similar to benzene than to pyridine, and the limited available experimental

Table III. Charges and Reactivity Indices

Atom Position	Charge	HFMO coeff. B_1 Type Orbital	Free Valence
C_6H_6	0.00		0.399
C_6H_5N			
N	-0.66	0.660	
α	+0.12	-0.003	0.507
β	+0.09	-0.376	0.382
γ	+0.25	-0.512	0.454
C_6H_5As			
P	-0.17	0.687	
α	-0.04	-0.263	0.396
β	+0.09	-0.253	0.390
γ	+0.09	-0.512	0.454
C_6H_5As			
As	-0.31	0.780	
α	+0.04	0.275	0.403
β	+0.06	-0.185	0.380
γ	+0.12	-0.433	0.480
C_6H_5Sb			
Sb	-0.09	0.707	
α	+0.00	0.348	0.382
β	0.03	-0.157	0.380
γ	+0.04	-0.456	0.454

evidence[2] indicates that this conjecture is correct. For heterobenzenes the free valence or the eigenvector coefficient in the highest filled B_1 type molecular orbital has a higher value at the γ position than at α or β positions. Either reactivity index correlates with the result of the few acetylation studies in these systems, in particular with the partial rate factors for the reaction of arsabenzene.[33]

The resonance energy and other characteristics of bismabenzene cannot be calculated using these procedures because all of the π vertical ionization potentials are not assignable in the PE spectrum[12]. This difficulty illustrates the essential experimental basis of the calculations summarized in this communication. More detail, and calculations for several other types of compounds will be forthcoming.

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