

PERTURBATION-GRAPH THEORY III. RESONANCE ENERGIES FROM PHOTOELECTRON SPECTRA

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Abstract - Experimental values of π ionization potentials are used to model π systems in terms of Hückel molecular orbital theory. HMO parameters are calculated using a non-subjective linear regression technique, and calculated negative eigenvalues show a high correlation with the ionization potentials. The results allow the use of graph theory to calculate resonance energies. The types of systems considered included alternant aromatic and non-alternant cross-conjugated molecules, heterobenzenes, and cyclic unsaturated compounds with carbonyl groups. There is good agreement of calculated resonance energies with LCAO-MO-SCF calculations parameterized using thermochemical data. There is also good agreement with classical ideas regarding structure and resonance stabilization.

INTRODUCTION

Experimental and theoretical methods for estimating "resonance energies" and "aromatic character" have been delineated in several review articles (1-5). A commonly accepted and useful viewpoint ascribes aromaticity (or anti-aromaticity) to cyclic delocalization of π electrons (6-9). Resonance energies are taken relative to those for hypothetical structures whose energies are functions of strictly additive bond-energy terms. A graph-theoretical definition of resonance energy (10,11) is analogous in that π energies are compared to those calculated for topologically-equivalent hypothetical reference systems neglecting the contributions of cyclic structural components in a prescribed manner.

The initial paper of this series (12a) used graph theory and perturbation theory to discuss in a general way the effects of heteroatoms on resonance energies in monocyclic systems. Preliminary results for resonance energies of group V heterobenzenes were derived from photoelectron spectroscopy (PES) data and summarized in paper II (12b). The purpose of the present paper is to give the details of how the graph-theoretical definition of resonance energy can be combined with experimental PES results to yield precise and clear-cut estimates of resonance energies. The heterobenzenes will be examined more closely, and the discussion will be expanded to include cross-conjugated unsaturated cyclic hydrocarbon systems and cyclic conjugated carbonyl compounds. The calculated resonance energies are of course defined within a particular electronic structural model that must be parameterized using the experimental data. A non-subjective linear regression technique (13) based on first-order perturbation theory is used to parameterize the π electron model in the examples to be given.

The use of PES data to assign parameters in independent electron model schemes (14-17) assumes that orbital energies are given by the negative PES vertical ionization potentials (IP's). In the structure-representation model (18-22) the IP's correspond to state energies. In either case, the parameters are the diagonal and off-diagonal elements of the effective molecular Hamiltonian matrix, and their values are chosen to give agreement of calculated and experimental ionization energies.

The signs and magnitudes of the matrix elements have been used to quantify qualitative concepts like "through-space" and "through-bond" interactions (23), and many successful applications have been recorded (24,25). However, the use of this approach to examine questions regarding aromaticity has been interdicted (26) because of the highly critical dependence of calculated aromatic character on the choice of the hypothetical reference system parameters. The graph theoretical method that will be outlined mitigates this objection by requiring that the same experimental data be used to parameterize both the parent system and the reference system, and by not allowing post-facto adjustments of parameters to fit preconceived ideas.

PROCEDURES

For detailed descriptions of the theory and methods used the reader is referred to the original papers to be cited. Only an outline of the approach will be presented. The primary data used are vertical IP's measured by PES for a family of structurally related compounds. Simple Hückel-type molecular orbital (HMO) models with a small number of parameters are consistent with the quantity and quality of the available data. In the Hückel treatment the parameters are Coulomb integrals α_{rr} , and exchange integrals β_{rs} defined only for nearest neighbors interactions. For a chosen set of parameters the calculated energies are obtained (27)

as shown in eq. (1),

$$E_j = \sum_r (c_{rj})^2 \alpha_{rr} + 2 \sum_{r<s} c_{rj} c_{sj} \beta_{rs} \quad (1)$$

where c_{rj} and c_{sj} are eigencefficients corresponding to E_j . The calculated energies will differ from a set of observed energies $E_j^x = -IP^x$ by

$$R_j = E_j^x - E_j \quad (2)$$

An iterative procedure for optimizing the parameters has been derived by using Newton's method for roots to minimize the residuals, eq. (2). The parameters of the i th iteration determine the coefficients of the $(i+1)$ th equation. Each equation is a linear equation in the unknown parameters, one equation for each experimental IP, and the full set of linear equations is solved by linear regression procedures. The process converges rapidly to final Coulomb and exchange intergral parameters that minimize the sum of the squares of the differences between calculated and experimental energy level values.

The resonance energy for a particular system is then obtained as follows: The characteristic polynomial for a π system M is

$$P(\lambda)^M = \det|H - \lambda I| = \sum_{j=0}^n a_j \lambda^{n-j} \quad (3)$$

where H is the parameterized Hückel secular matrix, and I is a unit matrix. Graph theory relates the coefficients a_j to structural features of the molecular graph (28-32). Each a_j is a function of the numbers of bonds, cyclic components, and vertices of the graph, with each function weighted properly according to the values of Coulomb and exchange parameters. The characteristic polynomial for the resonance-free reference system $P(\lambda)^R$ is obtained by deletion of the cyclic component contributions to the a_j coefficients.

The roots of $P(\lambda)^M$ and $P(\lambda)^R$, and the corresponding π energies, can be found by algebraic methods. They can also be obtained using the standard available molecular orbital computer programs, since our previous work (12a) demonstrates how one can obtain an acyclic molecular graph (reference graph; see appendix) which has a characteristic polynomial identical to that of the hypothetical reference structure.

After the energy levels for the parent system and the reference system have been found, the resonance energy is

$$RE = \sum_{i=1}^n g_i (\lambda_i^M - \lambda_i^R) \quad (4)$$

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

Justification for this rather abstract definition lie in the precise parallels of calculated resonance energies with those obtained by other theoretical methods for benzenoid and nonbenzenoid molecules, radicals, and ions (10-12,33-35). For the present purpose, a unique advantage is that no arbitrary choices of parameters are necessary to define the energy of the resonance-free reference system. The hypothetical reference structure parameters are functionally dependent upon those determined for the parent system. The choosing of an orbital model, and the fitting of the experimental data to the model, completely fixes the π energies of both parent and reference molecular systems.

HYDROCARBON π SYSTEMS

PES data and calculated energy levels are listed in Table I for several cyclic and acyclic olefinic and aromatic molecules. All of the listed experimental IP's are used to derive the parameters of Hückel-type molecular orbital treatments, and the results are summarized in Table II. The correlative ability of the second parameterization is fairly adequate, as demonstrated by the calculated energy levels in Table I.

These parameters can be used in the graph-theoretical approach to calculate resonance energies as outlined in the previous section. The reference graphs for the cyclic compounds that yield the same characteristic polynomial as the hypothetical resonance free reference system are listed in the appendix. Resonance energies of acyclic compounds are, of course, zero under the graph-theoretical definition. Resonance energies for the cyclic compounds in Table I and several structurally related compounds are presented in Table III.

The results given in Table I, II, and III are remarkable in that there is substantial agreement with the results of most earlier theoretical treatments, and with estimates of resonance energy or aromatic character based on other, very different, experimental criteria (1-4). With regard to the parameterization, it has previously been demonstrated that

TABLE I. Ionization Potentials for Hydrocarbon π Systems (eV's)

Compound	Vertical	-Energy	Compound	Vertical	-Energy
	IP's	Levels		IP's	Levels
	(Expt.) ^a	(Calc.) ^b		(Expt.)	(Calc.)
Ethylene	10.51	10.50	Heptafulvene	7.69	7.42
Butadiene	9.03	9.03		10.22	10.03
	11.46	11.55		11.24	10.74
Hexatriene	8.32	8.26		---	12.70
	10.27	10.49	Sesquifulvalene	7.40	7.63
	11.90	11.90		7.60	8.25
Benzene	9.24	9.13		9.80	10.03
	9.24	9.13		10.16	10.26
	12.25	12.34		---	11.97
	8.49	8.61		---	13.23
Styrene	9.27	9.13	Bismethylenecyclobutene	8.80	8.46
	10.53	10.70		9.44	9.42
	---	12.79		13.30	13.22
	8.55	8.25	Trimethylenecyclopropane	8.94	9.06
Fulvene	9.54	9.56		---	9.06
	12.80	12.78		---	13.74
	8.09	8.25	p-Quinodimethane ^c	7.87	7.92
6-Vinylfulvene	8.69	8.74		9.70	9.42
	10.80	10.93		---	11.06
	---	12.86		---	12.97

^aValues of vertical IP's were mostly taken from tabulation in references 17, 36, 37, and 38. ^bSix parameter calculation. See Table II. ^cReference 20.

TABLE II. Parameters for Hydrocarbon π System Calculations




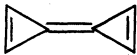

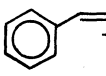

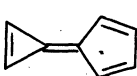

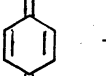

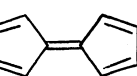

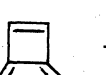

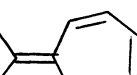
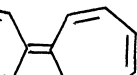
Parameters (eV's)	IP Correlations ^a		
	Ave. Dev.	Std. Dev.	Corr. Coeff.
Two Parameter Model:			
$\alpha = 6.76$	$\beta = 2.80$	± 0.303	± 0.403
Six Parameter Model:			
$\alpha(=CH_2) = 6.99$	$\beta(C=C) = 3.51$	± 0.133	± 0.222
$\alpha(=CH-) = 5.91$	$\beta(C-C) = 2.93$		0.999
$\alpha(=C) = 6.06$	$\beta(\text{Arom.}) = 3.22$		

^aBased on data from Table I.

one must distinguish Coulomb integrals for different types of sp^2 hybridized carbon atoms (36), and must make corrections for first order bond fixation (37), in order to obtain a good correlation of IP data for compounds of the types listed in Table I. In the present work the use of different parameters for different types of CC bonds is tantamount to the introduction of first order bond fixation (37). The great improvement of the correlation of PES data over that obtained from the simple Hückel MO model is demonstrated by the statistical results in Table II. It is perhaps surprising that this large variety of compound types can be successfully treated by a single set of parameters.

The calculated resonance energy obtained for benzene (0.88 eV) is practically identical to that found in LCAO-MO-SCF-PPP calculations (0.87 eV) which are parameterized using

TABLE III. Resonance Energies for π Hydrocarbons (eV's)^a

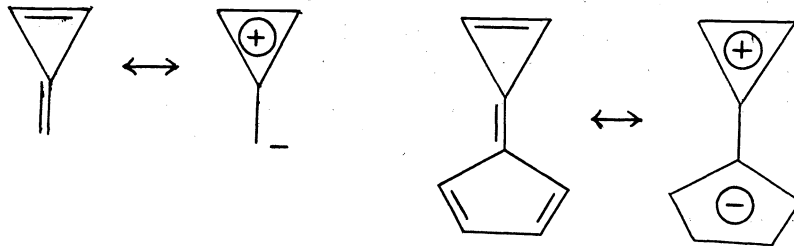
	(+0.50)		+0.88		+0.13		(-0.90)
	-0.26		+0.81		(-0.13)		(+0.94)
	-0.08		+0.10		(-0.02)		(-0.53)
	+0.19		-0.33		(+0.01)		+0.50
							(-0.26)

^aResonance energies in parentheses are for compounds where no PES data were available. Predicted IP's can be obtained from the author.

experimental thermodynamic data (39). The agreement is also reasonable with the value 0.54 eV found in structure-resonance theory calculations for aromatic hydrocarbon heats of formation (40-42). The discrepancy may be due to omission of data for olefinic systems in the structure-resonance theory calculations. The fact that these very different approximations, based variously on ground state thermodynamic properties or on PES data, yield the same order of resonance energy for benzene could be coincidental. However, we feel that the confluence of these results argues for the correctness of this resonance energy value. Limits of accuracy are difficult to assess, but an error estimate of ± 0.15 eV is compatible with the quality of the available experimental data.

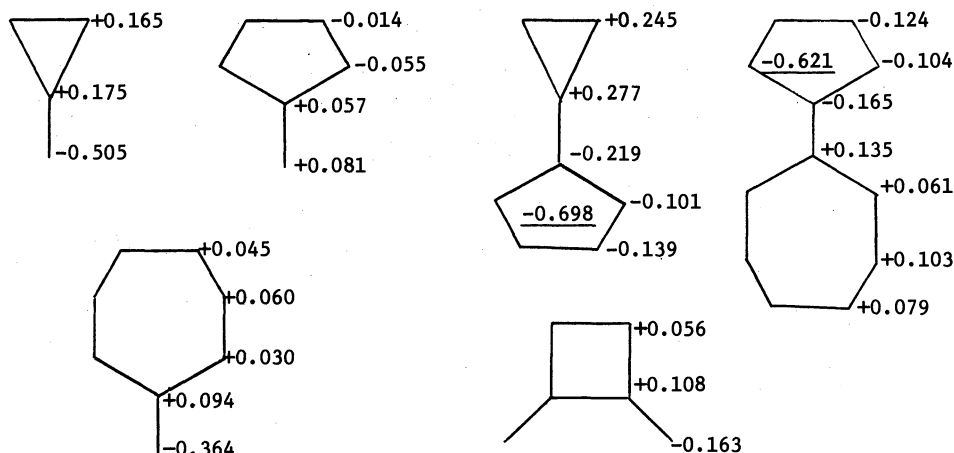
The calculated resonance energies of the remaining compounds in Table III are generally in accord with experimental properties of known compounds, and with other calculations detailed in several review articles (43-47). Therefore only a selection of the more significant results will be discussed here. The calculated resonance energy of styrene is almost the same as that of benzene, a result that also follows from LCAO-MO-SCF or structure-resonance theory calculations. This is in agreement with the idea that resonance stabilization only arises from cyclic delocalization (6-9). With the exception of bismethylenecyclobutene and methylenecyclopropene, the remaining monocyclic compounds in Table III have low calculated negative and positive resonance energies, and on this basis should be classified as non-aromatic compounds. They should behave as typical polyenes consistent with their representation by a single valence bond structure containing alternating double and single bonds.

The resonance energies for methylenecyclopropene and the cross-conjugated bicyclic compounds in Table III can be rationalized by invoking the usual effects of resonance with ionic structures as shown in 1. The effect is only stabilizing for structures in which



$4n + 2$ electrons ($n = \text{integer}$) are contained in each odd-membered ring. The effect is rapidly attenuated with increasing size of the molecular π system and the largest compounds listed should be regarded as nonaromatic compounds. The small calculated negative resonance energy for fulvene is a consequence of the destabilization that results from imposing a positive charge on the more electronegative CH_2 group.

The parameterized MO calculations can be used to obtain π charge diagrams, 2, that illustrate these effects. It should be noted that these charge diagrams are experimentally



2

based since they can be related back to the experiment IP's. One notes that a dipolar character as large as 36% (heptafulvene) is still associated with a very small calculated resonance energy (+0.19 eV), which echoes previous objections to using dipole moment data to estimate aromatic character (48,49). In the case of bismethylenecyclobutene, the favorable ionic structure does not outweigh the effect of unfavorable topology, and the compound is calculated to be antiaromatic.

HETEROBENZENES

The series of group V heterobenzenes where carbon is successively replaced with N, P, As, Sb, and Bi has been studied by many different physical techniques (50) including PES (14,51,52). The π IP's corresponding to the π energy levels have been identified and assigned by correlating the spectra with the results of semiempirical (51,53) and *ab initio* calculations (54). The energy and angular dependences of the PES intensities also provide corroboration of the assigned IP's which are listed in Table IV.

TABLE IV. PES Data and Resonance Energies for Benzene and Group V Heterobenzenes

Compound	IP's (eV's) and assigned orbital symmetry			Resonance Energies (eV's)	%RE of Benzene	1,4-Cyclo- addition Index
C_6H_6	9.24(E_{1g})	9.24(E_{1g})	12.25(A_{2u})	0.821	100	0.041
$\text{C}_6\text{H}_5\text{N}$	10.5 (B_1)	9.8 (A_2)	12.6 (B_1)	0.618	75.3	0.031
$\text{C}_6\text{H}_5\text{P}$	9.2 (B_1)	9.8 (A_2)	12.1 (B_1)	0.661	80.5	0.046
$\text{C}_6\text{H}_5\text{As}$	8.8 (B_1)	9.6 (A_2)	11.8 (B_1)	0.545	66.4	0.048
$\text{C}_6\text{H}_5\text{Sb}$	8.3 (B_1)	9.4 (A_2)	11.7 (B_1)	0.607	73.9	0.045
$\text{C}_6\text{H}_5\text{Bi}$	7.9 (B_1)	9.2 (A_2)	----			

^aSee references 63-66.

The simplest appropriate HMO model for these systems would incorporate Coulomb integrals for carbon and heteroatom, $\alpha(\text{C})$ and $\alpha(\text{X})$, and resonance integrals for CC bonds and CX bonds, $\beta(\text{CC})$ and $\beta(\text{CX})$. An examination of the IP data in Table IV reveals that this model is inadequate. This first approximation would predict a single common energy for the A_2 type orbitals whereas the actual IP's vary from 9.8 eV to 9.2 eV. Calculated resonance energies (see Table III) are of the order of this 0.6 eV variation, and it is therefore desirable to

seek an alternative parameterization.

Auxillary inductive parameters for carbon atoms adjacent to heteroatoms have been used in many HMO calculations (55). The addition of a parameter of this type, $\alpha(\text{C adj. X})$, allows one to account for the variations in the A_2 type orbital and remain within the HMO approximation. The iterative procedure described previously gives a set of parameters listed in Table V which gives calculated IP's that are identical to the experimental values. The

TABLE V. Parameters for Heterobenzene HMO Calculations ($-eV$'s)

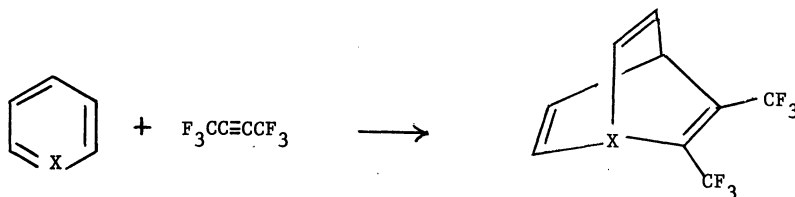
Heteroatom	$\alpha(X)$	$\alpha(\text{C adj. X})$	$\beta(\text{CX})$
N	10.52	7.26	1.70
P	7.79	7.26	1.85
As	7.80	6.91	1.40
Sb	6.79	6.54	1.53
$\alpha(\text{C}) = 6.23$		$\beta(\text{CC}) = 3.01$	

parameters are each uniquely determined since the number of parameters is equal to the number of experimental IP's.

As pointed out earlier, the determined parameters also describe the resonance-free reference systems, and the resonance energies given in Table IV are calculated on that basis. The reference graphs are given in the appendix. The calculated resonance energies for the heterobenzenes are relatively constant, and are somewhat smaller than that of benzene. These values are in quantitative agreement with LCAO-MO-SCF calculations on benzene (39) and pyridine (56), and are in qualitative agreement with the results of Aihara (10), and Hess and Schaad HMO calculations (57). In general, one can conclude that the group V heterobenzenes are aromatic compounds, a conclusion that also follows from determination of other physical, chemical, and spectroscopic properties (50).

In contrast with previous conjectures (57,58), the diminution in resonance energy with substitution is found to be a function of the conjugative properties of the heteroatom rather than primarily related to the heteroatom electronegativity. In fact, there is a good linear relationship, correlation coefficient 0.985, between the heterobond resonance integral and the obtained resonance energy, while the relationship with the heteroatom Coulomb integral is nonsignificant, correlation coefficient -0.388 . These specific results agree precisely with the general conclusions reached earlier using graph-perturbation theory (12a), there being no predicted first-order resonance energy effect of substituent electronegativity in species containing $4n + 2$ ($n = \text{integer}$) π electrons.

Charge diagrams and reactivity indices for the heterobenzenes were calculated using the parameters listed in Table V, and were listed in the preliminary communication on this work (12b). They are in reasonable conformity with experimental chemical properties reviewed recently by Ashe (50). An interesting reaction that has been studied for the entire series including benzene, is the cycloaddition reaction with hexafluoro-2-butyne which yields a bicyclic adduct **3**. (59-61). The order of reactivity is $\text{C}_6\text{H}_5\text{Sb}, \text{C}_6\text{H}_5\text{Bi} > \text{C}_6\text{H}_5\text{As} > \text{C}_6\text{H}_6$ with $\text{C}_6\text{H}_5\text{N}$ giving no cycloaddition product (50). In carbocyclic aromatic systems, the rates



3

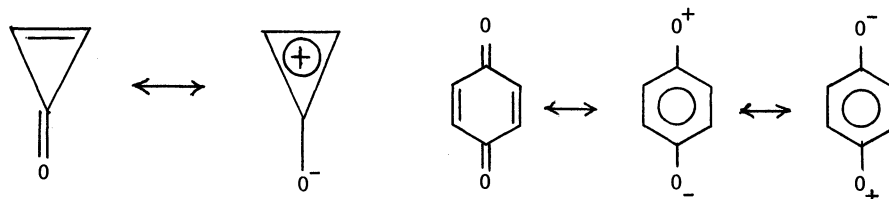
of cycloaddition reactions are precisely related to resonance energy differences between reactants and products (62), but one can see from Table IV that this relationship does not hold in this case. A reactivity index based on frontier molecular orbital theory (63-65) is in better agreement with the chemical reactivity and is listed in the last column of Table IV (66).

The resonance energy and reactivity indices for bismabenzene cannot be calculated using these procedures because all of the vertical π IP's are not assignable, due to overlap of PES bands with bands arising from decomposition products (52). This difficulty emphasizes

the fact that these calculations have an essential experimental basis. Matrix elements of the chosen model Hamiltonian cannot be obtained if the number of available energy level values is less than the number of parameters.

POLYENONES AND QUINONES

Cyclic unsaturated compounds containing carbonyl groups can usually be formulated as resonance hybrids of covalent and ionic structures as shown in 4. An ionic structure is presumed



4

to be stabilized when $4n + 2\pi$ electrons are incorporated within the ring moiety (67). In general, however, the properties of compounds of this type seem to be better represented by the covalent structures of alternate double and single bonds. The degree of aromatic character of such systems is difficult to estimate using the various criteria that have been adopted during the last several years (1-5). An advantage of the method used in this paper is that the resonance energy is obtained from the experimental measurements in a precisely defined manner.

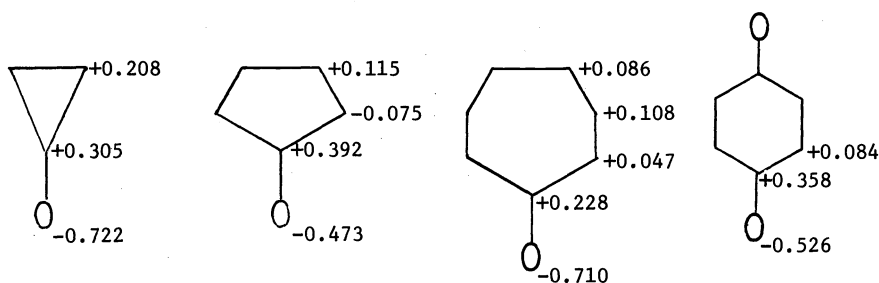
Table VI contains experimental IP's (22,69-78), calculated energy levels, and resonance energies. The calculated parameters that led to the tabulated data are $\alpha(\text{C}) = -7.42$ eV,

TABLE VI. IP's and Resonance Energies of Carbonyl Compounds (eV's)

Compound	Vertical IP's (π) (Expt.)	-Energy Levels (Calc.)	Resonance Energy	Reference for IP's
Formaldehyde	14.40	14.53	0.0	69
Glyoxal (O=CH-CH=O)	14.0 15.4	13.95 15.40	0.0	70,71
Acrolein (O=CH-CH=CH ₂)	10.95 14.90	10.42 14.85	0.0	70,72
Cyclopropenone	11.19 ---	10.91 15.43	1.01	
Cyclopentadienone	9.49 12.0 ---	9.10 11.86 15.25	-1.06	22
Cycloheptatrienone (Tropone)	8.90 10.64 --- ---	9.54 10.81 12.30 15.22	0.47	74,75
1,4-Benzoquinone	10.29 11.16 --- ---	10.14 10.91 14.95 15.43	-0.27	76,77
O-Benzoquinonemethide (C ₆ H ₄) (=CH ₂) (=O)	8.80 10.63 12.02 ---	9.21 10.82 12.28 15.29	+0.20	78

$\alpha(O) = -12.03$ eV, $\beta(CC) = -2.72$ eV, and $\beta(CO) = -4.21$ eV. All available PES data for simple carbonyl π systems without substituents were included in the regression procedure. Missing π IP's have not been assigned in the PES because of overlapping bands. The simplest sensible set of parameters was chosen to model the systems considered, i.e. the parameters $\alpha(C)$, $\alpha(O)$, $\beta(CC)$, and $\beta(CO)$. Additional dissections of the parameters, in particular the assumption of a different parameter for carbonyl carbon atom, did not improve the correlation of data significantly. The correlation coefficient for the IP data is 0.989, average deviation ± 0.23 eV, and standard deviation ± 0.31 eV. The reference system graphs are given in the appendix.

The correlation of the IP data is not as good as for the hydrocarbon data summarized in Tables I and II. This is probably due to the smaller number of IP's for the carbonyl compounds, although a breakdown of the Koopmans theorem assumption for some of the compounds (22) cannot be definitely ruled out. The calculated resonance energies are therefore not as accurately defined as in the former cases. However, assuming that the values of the resonance energies are correct, they turn out to be in striking agreement with the tenets of resonance theory and the $4n + 2$ Hückel rule. Cyclopropenone and tropone ionic structures each contain $4n + 2$ electrons in the cyclic moiety and the compounds are stabilized by resonance, while cyclopentadienone (ionic structure containing 4 electrons) is found to be antiaromatic. The π charge diagrams, 5, indicate the degree of ionic character for these species.



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Qualitatively, the resonance energy results parallel those found in a previous graph theoretical study (79), and those determined in modified HMO calculations based on thermochemical data (80). Both methods also predict an attenuation of the resonance energies with increasing size. Larger cyclic polyenones would therefore be classified as nonaromatic compounds. However, the resonance energy values found in the present work are larger than those from the previous study. This discrepancy can be traced to the value of the parameters obtained in the earlier work, $\alpha(O) = \alpha(C) + 0.22\beta(CC)$ and $\beta(CO) = 0.99\beta(CC)$ (80). The present assignments, $\alpha(O) = \alpha(C) + 1.69\beta(CC)$ and $\beta(CO) = 1.55\beta(CC)$, are in somewhat better agreement with values that have been assumed in many previous HMO calculations (55).

The small negative value of the resonance energy for 1,4-benzoquinone may not be significant, but it is very close to the thermochemically based LCAO-MO-SCF value of -0.17 eV (81). The benzenoid ionic structure shown for benzoquinone in 4 is not supported by these calculations. The system is better considered to be represented by the usual nonionic covalent structure.

The photoelectron spectra of tropone and several benzo derivatives have been determined previously, and the spectra have been correlated by means of simple bond orbital and HMO models (75). It was concluded that "PES data do not yield information concerning the 'aromatic character' of tropones." However, the arguments about aromatic character in that work proceeded from comparisons of the assumed magnitudes of separated inductive and conjugative effects upon calculated orbital energies (74,75,82). It was emphasized that small arbitrary changes in the guessed Hamiltonian matrix elements could have a significant effect upon the assessment of conjugative and inductive effects. The conclusion about deducing aromatic character from the calculated conjugative interactions was therefore well-founded. The graph-theoretical definition of resonance energy by-passes this concern by insuring that the same conjugative and inductive effects that govern the fit of calculated energies to experimental IP's are also present in the resonance-free hypothetical reference structure.

SUMMARY

Measurements of PES, combined with graph-perturbation theory, provide a new method for obtaining quantitative estimates of resonance energies. The resonance energies obtained are structural model and parameter dependent, but the parameters are fixed by the experimental data. One main advantage to this approach is that it has a high and essential experimental content, not unlike the early concept of resonance energy based on experimental thermodynamic measurements (83). Another advantage is that the calculated resonance energies are precisely defined in terms of a resonance-free reference structure for which parameters do not have to be guessed or calculated. In this respect, the graph-theoretical definition of resonance energy is the only available rigorous approach to the concept of aromaticity.

One finds good agreement between PES-graph-perturbation results and the resonance

The reference graphs for homologues of the above structures, and for heteroatom derivatives can be constructed by making the obvious extensions and substitutions. Reference graphs for the last two structures cannot be constructed, so the required reference polynomials were obtained by hand.

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