Table I. Molecular Energies and Mulliken Population Analysis for $CH_2{=}NH$ and Fluorine Derivatives

Molecule					Gross charges					Overlap population			
	R1	R2	R3	Energy	C	N	R1	R2	R3	C=N	N—R1	C—R2	C—R3
2	H	H	H	−92.82303	−0.009	−0.276	0.151	0.060	0.073	1.040	0.622	0.770	0.777
3	F	H	H	−190.26001	−0.034	−0.081	−0.069	0.088	0.096	0.979	0.345	0.781	0.767
4	H	F	H	−190.29267	0.195	−0.308	0.159	−0.133	0.087	1.020	0.622	0.453	0.756
5	H	H	F	−190.28952	0.201	−0.310	0.161	0.070	−0.122	1.009	0.631	0.744	0.465
6	H	F	F	−287.76289	0.399	−0.333	0.170	−0.126	−0.110	0.979	0.631	0.438	0.456
7	F	H	F	−287.71884	0.182	−0.115	−0.061	0.096	−0.102	0.940	0.345	0.743	0.466
8	F	F	H	−287.72019	0.176	−0.114	−0.060	−0.107	0.106	0.940	0.342	0.456	0.760
9	F	F	F	−385.18510	0.389	−0.140	−0.053	−0.102	−0.094	0.896	0.340	0.443	0.457

Table II. STO-3G Optimized Geometries for $CH_2{=}NH$ and Fluorine Derivatives

Molecule				Bond lengths, Å				Bond angles, deg		
	R1	R2	R3	C=N	N—R1	C—R2	C—R3	R1—N—C	R2C—N	R3—C—N
2	H	H	H	1.274	1.049	1.091	1.089	109	125	119
3	F	H	H	1.287	1.377	1.089	1.085	110	124	118
4	H	F	H	1.272	1.048	1.351	1.096	108	125	121
5	H	H	F	1.274	1.045	1.101	1.346	108	127	120
6	H	F	F	1.275	1.045	1.353	1.341	107	126	123
7	F	H	F	1.291	1.378	1.098	1.344	109	125	120
8	F	F	H	1.291	1.379	1.347	1.094	110	124	119
9	F	F	F	1.296	1.381	1.348	1.340	109	126	122

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Ionization Potentials of π Molecular Hydrocarbons[1a]

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Abstract: Adiabatic ionization potentials for cata- and peri-condensed benzenoid hydrocarbons, benzenoid systems with essential single bonds, nonalternant aromatic compounds, and open-chain and cyclic olefins are correlated with an empirical resonance theory that only requires enumeration of structures. For 29 compounds, the average deviation of calculated and experimental ionization potentials is ±0.16 eV and the correlation coefficient is 0.995. For 11 additional large aromatic hydrocarbons, not included in the original correlation, the deviation is ±0.08 eV. Predicted ionization potentials for several interesting nonbenzenoid compounds are listed.

A simple structure-resonance theory with a basis of Kekulé structures has been demonstrated to correlate and predict resonance energies,[2] heats of formation,[3] bond orders and bond lengths,[4] NMR coupling constants,[4] and several types of reactivity[5,6] with high precision. The resonance theory calculations require no more than an enumeration of structures[7] since it has also been shown that an algorithm, logarithm of the Kekulé corrected structure count (CSC),[6,8] gives an excellent approximation to the ground-state eigenvalue of the structure-function Hamiltonian matrix. The structures are enumerated by graph theoretical

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Table I. Structure Counts, Resonance Energies, and Ionization Potentials

Compd	CSC(R)	RE(R), eV	CSC($R\cdot^+$)	RE($R\cdot^+$), eV	IP, eV Calcd.	IP, eV Exptl.[a]
1 Benzene	2	0.821	18	3.018	9.08	9.23
2 Naphthalene	3	1.302	62	4.309	8.27	8.13
3 Anthracene	4	1.643	152	5.245	7.67	7.43
4 Tetracene	5	1.907	310	5.989	7.20	7.01
5 Pentacene	6	2.123	554	6.595	6.81	6.69
6 Phenanthrene	5	1.907	164	5.324	7.86	7.80
7 Triphenylene	9	2.604	396	6.245	7.64	7.86
8 Benzanthracene	7	2.306	350	6.116	7.47	7.45
9 Benzphenanthrene	8	2.464	376	6.190	7.55	7.62
10 Chrysene	8	2.464	378	6.196	7.54	7.61
11 Pyrene	6	2.123	254	5.781	7.62	7.41
12 Coronene	20	3.550	1488	7.627	7.20	7.34
13 Perylene	9	2.604	536	6.561	7.32	7.00
14 Benzo[1,12]perylene	14	3.127	920	7.125	7.28	7.19
15 Benzo[*a*]pyrene	9	2.604	545	6.578	7.30	7.12
16 Ovalene	50	4.636	5890	9.063	6.85	6.86
17 Biphenyl	4	1.643	90	4.698	8.23	8.21
18 Styrene	2	0.821	28	3.479	8.62	8.40
19 1,1-Diphenylethylene	4	1.643	104	4.849	8.07	8.00
20 1,2-Diphenylethylene	4	1.643	122	5.015	7.90	7.75
21 Azulene	2	0.340[b]	62	4.309	7.31	7.42
22 Acenaphthylene	3	1.302	112	4.926	7.65	8.02
23 Fluoranthene	6	2.123	274	5.860	7.54	7.80
24 Fulvene	1	0.0	16	2.895	8.38	8.55
25 Biphenylene	3	1.302	96	4.765	7.81	7.62
26 Ethylene	1	0.0	2	0.724	10.55	10.51
27 Butadiene	1	0.0	6	1.871	9.41	9.11
28 Cyclooctatetraene	1	0.0	32	3.618	7.66	8.00
29 3,4-Dimethylenecyclobutene	1	0.0	10	2.404	8.87	8.80
30 Hexacene	7	2.306	976	7.186	6.40	6.44
31 Benzpentacene	11	2.842	1131	7.340	6.78	6.72
32 Picene	13	3.039	804	6.984	7.33	7.54
33 Dibenzo[*g,p*]chrysene	24	3.766	1764	7.804	7.24	7.18
34 Benzo[*e*]pyrene	11	2.842	598	6.675	7.44	7.43
35 Anthanthrene	10	2.729	764	6.931	7.08	6.92
36 Peropyrene	18	3.425	1738	7.789	6.91	6.77
37 Dibenzo[*e,l*]pyrene	20	3.550	1320	7.502	7.33	7.40
38 Pyreno[4,5-*e*]pyrene	35	4.213	3384	8.484	7.01	6.90
39 9,10-Diphenylanthracene	16	3.286	1352	7.527	7.04	7.10
40 Acepleiadylene	4	1.643	276	5.868	7.05	7.13
41 Cyclobutadiene	0	−0.65[b]	8	2.171	8.46	
42 Benzocyclobutadiene	1	0.0	28	3.479	7.80	
43 Methylenecyclopropene	1	0.0	8	2.171	9.11	
44 Pentalene	0	−0.26[b]	40	3.851	7.17	
45 Cycloocta[*def*]biphenylene	2	0.821	152	5.245	6.85	

[a] Experimental values from ref 10–14. [b] Resonance theory calculations, ref 2b.

methods, and calculated resonance energies are the same as those obtained from highly parameterized SCF-LCAO-MO calculations.[9]

In this paper, the structure-resonance theory will be used to calculate the resonance energies of even-membered radical cations, and the results will be used to correlate ionization potentials.

Procedures and Results

Photoelectron spectroscopy provides experimental vertical and adiabatic ionization potentials (IP) that have been used to confirm results of MO calculations for unsaturated and aromatic hydrocarbons.[10-14] The measured adiabatic values can also be used to test the resonance theory on the following basis. The lowest adiabatic IP is the difference in energy between neutral molecule and radical cation, both in their most stable electronic, vibrational, and rotational state. Assuming there is no gross molecular structural change in the underlying σ framework upon ionization, the ionization energy should be linearly related to the difference in π-resonance stabilization energies of the neutral compound and the cation, eq 1, where A is a constant and all energies are taken with positive sign. The interpretation of A is significant, as will be discussed later.

$$\mathrm{IP} = A + \mathrm{RE(R)} - \mathrm{RE}(\mathrm{R}\cdot^{+}) \qquad (1)$$

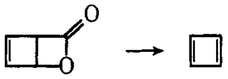
The resonance energies of the neutral systems can be calculated by the algorithm given in eq 2,[8] or by resonance theory[2] or SCF-MO[9] calculations. The resonance energies of cations and anions are similarly related to logarithmic functions of numbers of structures.[6,15] Accordingly, the experimental IP were fitted to eq 1 by regression methods with the results given by eq 3, and tabulated in Table I.

$$\mathrm{RE(R)(eV)} = 1.185 \ln\,[\mathrm{CSC(R)}] \qquad (2)$$

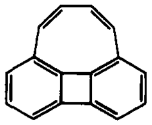
$$\mathrm{IP(eV)} = 11.277 + \mathrm{RE(R)} - 1.044 \ln\,[\mathrm{CSC}(\mathrm{R}\cdot^{+})] \qquad (3)$$

Compounds **1** through **29** in the table were used to establish the linear relationship which gives an average deviation of calculated and experimental IP of ±0.16 eV (correlation coefficient 0.995). The correlated compounds include cata-condensed (compounds **1–10**) and peri-condensed (**11–16**) benzenoid hydrocarbons, benzenoid systems with essential single bonds (**17–20**), nonbenzenoid and nonalternant hydrocarbons (**21–25**), and open-chair or cyclic olefins (**26–29**). Hückel MO calculations cannot correlate IP data for such a wide variety of molecular types. SCF calculations[10–13] and modified Hückel procedures[13c] are as effective as the resonance theory but require the use of digital computers and considerably more time.

IP's of compounds **30–40**, not included in the linear correlation data set, have recently been measured.[12b] Using the parameters given in eq 3, the calculated IP's differ from the experimental values by an average ±0.08 eV. Table I also contains predicted ionization energies for several interesting nonbenzenoid and antiaromatic compounds. The calculated IP for cyclobutadiene is very close to the value of 8.50 eV estimated from the photoelectron spectrum of cyclobutadiene iron tricarbonyl,[16] or 8.20 eV taken from the appearance potential of a mass 52 peak found during flash vacuum pyrolysis of photo-α-pyrone,[17] eq 4. IP's for benzocyclobutadiene, methylenecyclopropene, and pentalene are not available.


(mass 52) (4)

Cycloocta[*def*]biphenylene, **45**, has been synthesized[18] but the IP has not been measured. A value of 7.25 has been estimated for the vertical IP from the frequency of the charge-transfer band with tetracyanoethylene.[19] The resonance energy of **45** from the CSC algorithm, 0.82 eV, is not as high as the calculated SCF value, 1.26 eV,[18b] which would predict an IP of 7.29 eV using eq 3.


45

Discussion

It should be noted that the leading constant in eq 3, 11.28 eV from the least-squares analysis, is very close to the valence state ionization energy, 11.42 eV, of a sp^2 hybridized carbon atom.[20] This fact argues for the essential correctness of the empirical theory and also leads to a very simple interpretation as follows. The adiabatic IP of a π-molecular hydrocarbon is the energy to remove an electron from a carbon 2p orbital plus the resonance energy of the neutral compound minus the resonance energy of the resulting radical cation.

Rigorous quantum-mechanical calculations have recently verified the valence bond concept of resonating structures to describe ground states and lower excited states of π molecular species.[21] The results outlined in the present paper and our previous investigations show that even an empirical valence-bond method can provide a quantitative description of several molecular properties, tantamount to results of SCF-MO procedures.

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