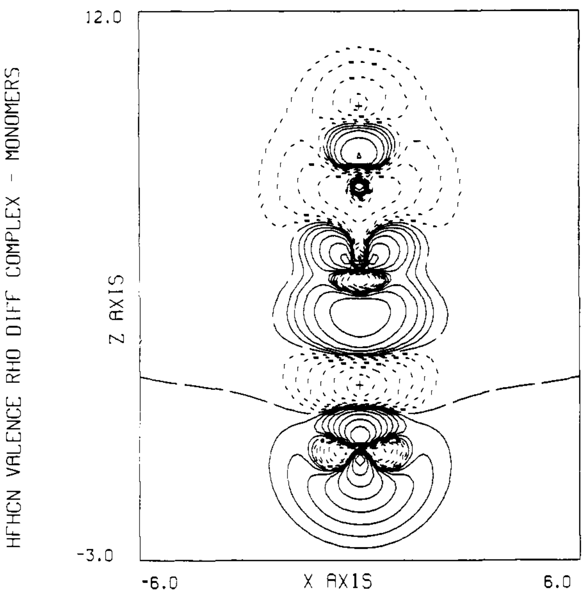

Figure 5. Valence electron density difference plot for the HCN···HF hydrogen-bonded complex. Short dashed lines indicate a depletion of electron density while solid lines indicate an increase of electron density.

much larger. This model, then, also explains the large difference between the binding energies of FHF^- and $FH;CN^-$.

Concluding Remarks

The $FH\cdots CN^-$ and $FH\cdots NC^-$ pair of anionic hydrogen-bonded complexes have been shown to be nearly isoenergetic and the theoretical binding energy is in good agreement with experiment. The $H_2O\cdots CN^-$ and $H_2O\cdots NC^-$ pair of complexes are also very close energetically with the best ab initio binding energy again in good agreement with the experimental value. The equilibrium structures of the isomers, however, do exhibit small differences (e.g., the N···H hydrogen bond is shorter than the C···H hydrogen bond) which lead to slightly different rotational constants. Thus, because the harmonic IR spectra of the two pairs of isomers are so similar, the different rotational constants provide a means by which the isomers may be experimentally distinguished. It is concluded, however, that an accurate theoretical determination of the fundamental frequencies will require a large portion of the potential energy surface to be investigated using a high level of electronic structure theory, such as CCSD coupled with a large one-particle basis set. In addition, a sophisticated solution of the nuclear motion problem capable of treating large anharmonicities will be necessary.

Another significant outcome of this study involves the CCSD investigations of the monomers. This is the first study that has fully optimized molecular structures and evaluated several equilibrium molecular properties at the CCSD level of theory with a large one-particle basis set (i.e., larger than double-ζ plus polarization) for chemical systems exhibiting a range of bonding characteristics. The CCSD equilibrium structures, harmonic frequencies, dipole moments, and IR intensities for HF and H_2O clearly demonstrate that near-quantitative results may be obtained for systems that are well described by a single-determinant reference function. Although the CCSD results for HCN, HNC, and OH^- have slightly larger errors, they are still very good and are superior to the analogous MP2 and CISD quantities.

Acknowledgment. Parts of this study are based upon work supported by the North Atlantic Treaty Organization under a fellowship awarded to T.J.L. for 1987/1988. The work performed for the ELORET Institute was supported by NASA Grant NCC2-552. Professor A. D. Buckingham is thanked for several very interesting and illuminating conversations. Drs. P. R. Taylor, C. W. Bauschlicher, and L. A. Barnes are thanked for reading a draft form of this manuscript and making several helpful suggestions.

New Measures of Aromaticity: Absolute Hardness and Relative Hardness

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Abstract: Building upon the previous Zhou–Parr–Garst argument that *absolute hardness*, or HOMO-LUMO gap, is a good measure of aromaticity, in this paper there is introduced the concept of *relative hardness*. Predictions are made of aromaticity using absolute hardness and relative hardness, and they both are found to give results in agreement with other measures of aromaticity. Values of hardness are reported for 216 cyclic conjugated molecules, and 96 molecules are discussed in detail. A certain *principle of maximum hardness* is proved. Explicit formulas are given for hardness, relative hardness, and topological resonance energy per π electron for annulenes and radialenes. The conclusions are that relative hardness is a particularly good index for identifying aromatic, nonaromatic, and antiaromatic character, and that the hardness concept incorporates all three aspects of aromaticity: high stability, low reactivity, and sustained induced ring current.

I. Introduction

Aromaticity, the property resulting from cyclic conjugation, is an important concept in organic chemistry.[1,2] High stability, low reactivity, and sustained induced ring current imply high aromaticity. Many efforts have been made to quantify aromaticity.[3-10] Most of them are devised to concentrate on one or the other of the above three aspects of the concept.[3-9] Recently, absolute hardness, known to be an index of stability and reactivity, has been shown to be a good measure of aromaticity.[10] Twice the absolute hardness of a species is defined to be the ionization

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potential of the species minus its electron affinity.[11]

Quantitative descriptions of aromaticity usually start from consideration of the thermodynamical stability of aromatic compounds. Signal among them, resonance energy (RE) [or resonance energy per π electron (REPE)] has been extensively employed as a quantitative measure of aromaticity. Resonance energy is defined as the difference between the total π-electron energy of a given conjugated molecule and the total π-electron energy of a corresponding hypothetical reference structure.[2-6] Classically, the reference structure is the same as the original structure except that the double bonds in the reference structure are "isolated".[2] This definition of total RE as a criterion of aromaticity fails in many cases,[1] however. In recent years two general modified RE definitions of aromaticity have been introduced. One definition, by Dewar and de Llano,[3] and Hess and Schaad,[4] is based on the additivity of the bond energies in acyclic polyenes. The total π-electron energy of the reference structure for a given molecule is defined as the sum of the component localized bond energies treated as if they were in *acyclic* polyenes.[3,4] The other definition of aromaticity, due to Aihara,[5] and Gutman, Milun, and Trinajstic,[6] makes use of the graph theory of molecular orbitals. An *acyclic* polynomial, the characteristic polynomial of the reference structure associated with a molecule, can be defined[5,6] (though the corresponding reference structure itself is very difficult to define); hence a total π-electron energy of the reference structure can be obtained. In both procedures, the excess (deficit) of RE for the given molecule is taken to measure aromaticity (antiaromaticity). The predictions by these two definitions of aromaticity agree reasonably well with each other and with chemical facts. Another, less general definition of aromaticity, due to Haddon,[9] makes use of the infinite annulenes and polyacetylenes in defining reference structures.

To characterize the ring current aspect of aromaticity, the minimum bond order in the conjugated molecule of interest has been used by Jug as an index.[8] There are some but few discrepancies between this index and RE indices. For the special case of $4n + 2$ π-electron annulenes, Haddon derived a formula connecting ring currents with REs,[9] the currents being obtained from McWeeny's formulation of the classical London theory.

In an attempt to unify the high stability and low reactivity associated with aromaticity, Haddon and Fukunaga relate the HOMO–LUMO gap with RE for $4n + 2$ annulenes (though they took $I_D - A_A$ as the HOMO–LUMO gap when they discussed the reactivity).[12]

Very recently, Zhou, Parr, and Garst demonstrated that absolute hardness, which is approximately half the HOMO–LUMO gap,[13] correlates with REPE in general.[10] Here we further develop this proposal. We also introduce the concept of *relative hardness*. We compare hardness and relative hardness as measures of aromaticity, and derive and discuss a *principle of maximum hardness*. We give analytical formulas for hardness, relative hardness, and topological resonance energy per π electron (TREPE) for two classes of conjugated molecules.

As our comparison measures of aromaticity, we take the resonance energy per π-electron (REPE) scales of Aihara,[5] Gutman, Milun, and Trinajstić[6] (TREPE) and the scale of Hess and Schaad[4] (REPE(HS)). These differ in the definition of reference structure, as described above.

Figures 1 and 2 contain structures of the compounds studied in this paper.

II. Absolute Hardness and Relative Hardness

The absolute hardness of a chemical species is[11]

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v \tag{1}$$

where E is the electronic energy, N is the number of electrons, and v is the external potential due to the nuclei. Absolute hardness is an important property which measures both the stability and reactivity of a molecule.[14]

A finite approximation to eq 1 is[11]

$$\eta = (I - A)/2 \tag{2}$$

where I and A are the ionization potential and electron affinity, respectively. Note that this formula is independent of any molecular model. In molecular orbital theory, e.g., Hartree–Fock theory or Hückel theory, there results

$$\eta = (\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}})/2 \tag{3}$$

as first emphasized by Pearson.[13] Equation 3 is a good approximation to eq 1. In this paper we take eq 3 as our working definition of hardness.

We now define the *relative hardness* (relative to some hypothetical acyclic reference structure) for a conjugated molecule. To this end, we introduce, by means of a graphical method, following Aihara,[5] and Gutman, Milun, and Trinajstić,[6] a hypothetical acyclic reference structure. Let G be the molecular graph corresponding to a given conjugated molecule. Then the characteristic polynomial for this molecule within Hückel theory is

$$P(G,x) = \sum_{i=1}^{N} a_i(G)x^{N-i} \tag{4}$$

where $a_i(G)$ can be decomposed into two parts graphically:[15] the first part contains the contributions from the cycles in the molecular graph, and the second part comprises all other contributions. We define the hypothetical acyclic reference structure in such a way that its characteristic polynomial has the same form as eq 4:

$$P^{\mathrm{ac}}(G,x) = \sum_{i=1}^{N} a_i^{\mathrm{ac}}(G)x^{N-i} \tag{5}$$

where $a_i^{\mathrm{ac}}(G)$ is the second part of $a_i(G)$, i.e., the one not containing the contributions from the cycles in the molecular graph. $P^{\mathrm{ac}}(G,x)$ can be obtained by standard graphical methods.[6,16c]

All roots of both $P(G,x)$ and $P^{\mathrm{ac}}(G,x)$ are real[16] and can be obtained by using standard subroutines (e.g., the IMSL package). Let $\{x_i\}^N_{i=1}$ and $\{x_i^{\mathrm{ac}}\}^N_{i=1}$ be the roots of $P(G,x)$ and $P^{\mathrm{ac}}(G,x)$, respectively. Then the energies of the Hückel molecular orbitals for the given conjugated molecule and the corresponding hypothetical acyclic reference structure are $\{\epsilon_i = \alpha + x_i\beta\}^N_{i=1}$ and $\{\epsilon_i^{\mathrm{ac}} = \alpha + x_i^{\mathrm{ac}}\beta\}^N_{i=1}$. By eq 3 we then have the absolute hardnesses

$$\eta = \beta(x_{\mathrm{LUMO}} - x_{\mathrm{HOMO}})/2 \tag{6}$$

and

$$\eta_{\mathrm{a}} = \beta(x^{\mathrm{ac}}_{\mathrm{LUMO}} - x^{\mathrm{ac}}_{\mathrm{HOMO}})/2 \tag{7}$$

for the molecule and the corresponding reference structure, respectively. The relative hardness for the molecule is

$$\eta_{\mathrm{r}} = \eta - \eta_{\mathrm{a}} \tag{8}$$

III. Absolute Hardness

Hardness values for benzenoid hydrocarbons, together with their REPE indices, are given in Tables I and II. Figures 3 and 4 are corresponding plots. There is an excellent linear correlation between each of the REPE scales and both the Hückel hardness (Table I, Figure 3) and the experimental hardness (Table II, Figure 4).

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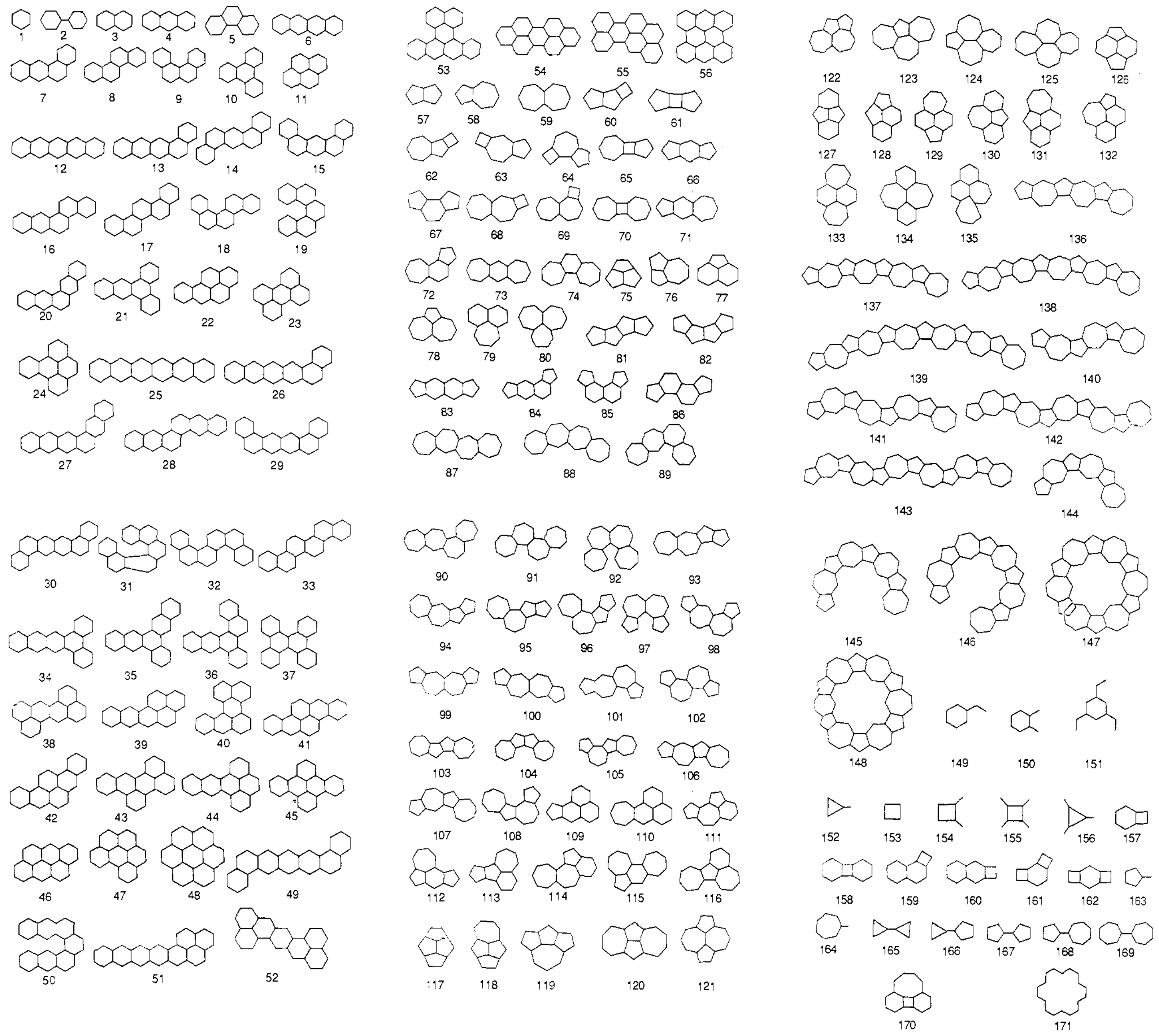

Figure 1. Cyclic conjugated hydrocarbons.

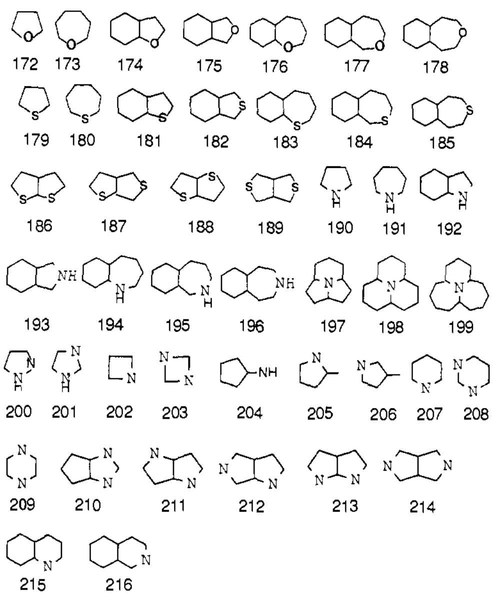

Figure 2. Heterocyclic conjugated hydrocarbons.

For alternant conjugated hydrocarbons, $\eta = -\epsilon_{HOMO}$ by eq 3; hence ϵ_{HOMO} suffices to measure aromaticity.[17,18] To verify that it is η, not ϵ_{HOMO}, that measures aromaticity more generally, we give in Table III the HOMO energies, the hardness values, and

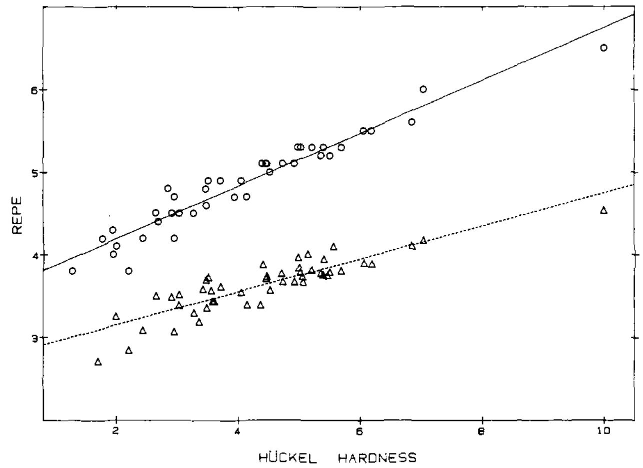

Figure 3. Correlation of REPE with Hückel hardness for benzenoid hydrocarbons: REPEs in units of 0.01β; Hückel hardness in units of -0.1β. Points Δ indicate TREPE; points O indicate REPE(HS).

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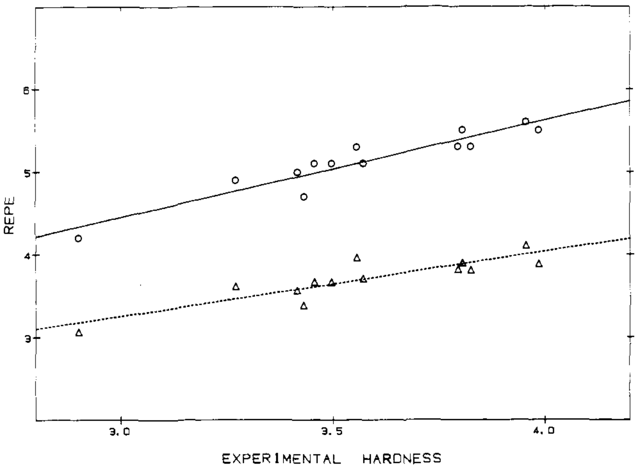

Figure 4. Correlation of REPE with experimental hardness for benzenoid hydrocarbons: REPEs in units of 0.01β; experimental hardness in units of eV. Points Δ indicate TREPE; points O indicate REPE(HS).

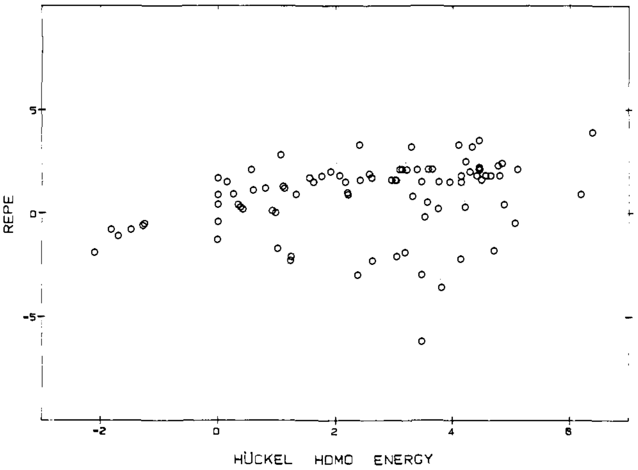

Figure 5. Correlation of REPE(HS) (in 0.01β) with HOMO energy (in -0.1β): nonalternant conjugated hydrocarbons.

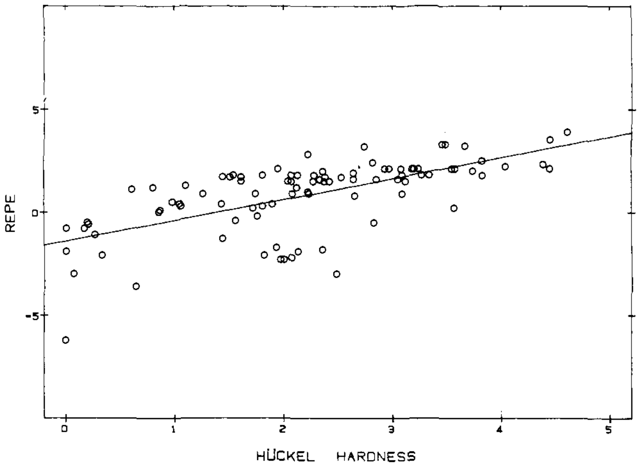

Figure 6. Correlation of REPE(HS) (in 0.01β) with Hückel hardness (in -0.1β): nonalternant conjugated hydrocarbons.

the REPE(HS) indices for 92 nonalternant conjugated hydrocarbons. Figures 5 and 6 are plots of REPE(HS) versus ϵ_{HOMO} and η, respectively. Correlation of REPE with ϵ_{HOMO} fails; with η it succeeds.

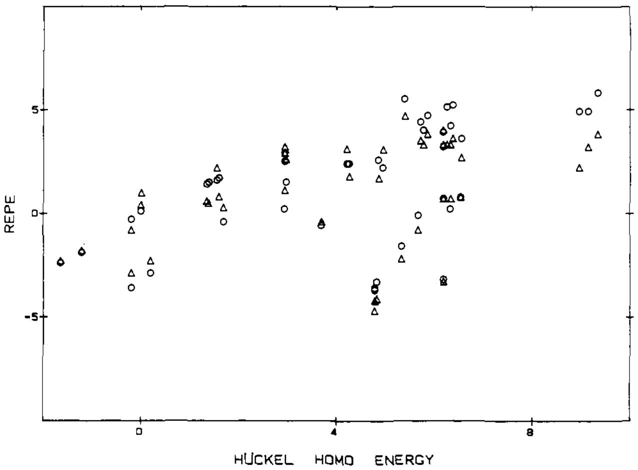

Figure 7. Correlation of REPE (in 0.01β) with HOMO energy (in -0.1β): heteroconjugated hydrocarbons. Points Δ indicate TREPE; points O indicate REPE(HS).

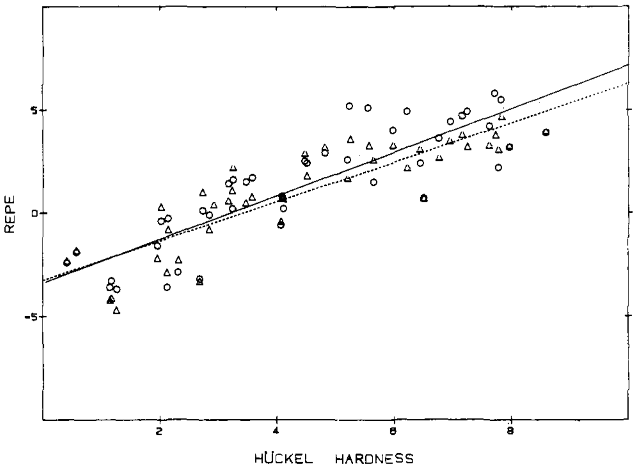

Figure 8. Correlation of REPE (in 0.01β) with Hückel hardness (in -0.1β): heteroconjugated hydrocarbons. Points Δ indicate TREPE; points O indicate REPE(HS).

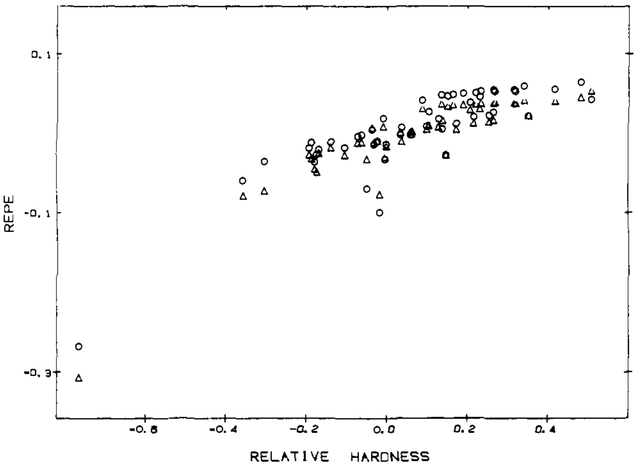

Figure 9. Correlation of REPE (in β) with relative hardness (in $-\beta$): conjugated hydrocarbons. Points Δ indicate TREPE; points O indicate REPE(HS).

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Table I. Hardness Values and REPE Indices for Selected Benzenoid Hydrocarbons

compd	hardness[a]	TREPE[b]	REPE(HS)[c]
1	1.000	0.0454	0.065
2	0.704	0.0418	0.060
3	0.618	0.0389	0.055
4	0.414	0.0339	0.047
5	0.605	0.0390	0.055
6	0.295	0.0307	0.042
7	0.452	0.0357	0.050
8	0.520	0.0382	0.053
9	0.568	0.0381	0.053
10	0.684	0.0411	0.056
11	0.445	0.0371	0.051
12	0.220	0.0285	0.038
13	0.327	0.0330	0.045
14	0.473	0.0367	0.051
15	0.492	0.0367	0.051
16	0.405	0.0355	0.049
17	0.502	0.0379	0.053
18	0.550	0.0379	0.052
19	0.535	0.0378	0.052
20	0.437	0.0339	
21	0.499	0.0384	
22	0.371	0.0362	0.049
23	0.347	0.0370	0.048
24	0.497	0.0396	0.053
25	0.169	0.0272	
26	0.244	0.0309	0.042
27	0.336	0.0319	
28	0.348	0.0336	0.046
29	0.361	0.0344	
30	0.358	0.0344	
31	0.546	0.0375	
32	0.539	0.0376	
33	0.471	0.0377	
34	0.356	0.0357	
35	0.506	0.0367	
36	0.447	0.0374	0.051
37	0.512	0.0401	
38	0.199	0.0325	0.041
39	0.303	0.0339	0.045
40	0.265	0.0350	0.045
41	0.303	0.0352	
42	0.342	0.0359	
43	0.351	0.0373	0.049
44	0.505	0.0374	
45	0.555	0.0410	
46	0.291	0.0348	0.045
47	0.439	0.0388	0.051
48	0.539	0.0395	0.053
49	0.269		0.044
50	0.394		0.047
51	0.194		0.040
52	0.128		0.038
53	0.194		0.043
54	0.285		0.048
55	0.296		0.047
56	0.177		0.042

[a] Hückel hardness (in $-\beta$); values are calculated by using eq 6. [b] REPE values (in β) are from ref 17. [c] REPE values (in β) are from ref 18.

Corresponding results for heteroconjugated hydrocarbons are given in Table IV and Figures 7 and 8. Figures 7 and 8 lead to the same conclusion for heteroconjugated hydrocarbons; it is η that correlates with REPE. In Figures 7 and 8, we exclude two molecules, **202** and **203**, for their anomalous behavior. Parameters for heteroatoms are from ref 21. Most of these results already were given in ref 10.

IV. Relative Hardness

Relative hardness values calculated by means of eq 6–8 for 96 conjugated molecules are given in Tables IV and V. Correlations with REPEs are presented in Figures 9 and 10. We see that relative hardness correlates very well indeed with both REPE indices. η_r can serve as a measure of aromaticity.

Table II. Hardness Values and REPE Indices for Selected Benzenoid Hydrocarbons

compd	hardness[a]	TREPE[b]	REPE(HS)[c]
3	3.985	0.0389	0.055
4	3.430	0.0339	0.047
5	3.805	0.0390	0.055
6	2.900	0.0307	0.042
7	3.415	0.0357	0.050
8	3.795	0.0382	0.053
9	3.825	0.0381	0.053
10	3.955	0.0411	0.056
11	3.570	0.0371	0.051
14	3.455	0.0367	0.051
15	3.495	0.0367	0.051
22	3.270	0.0362	0.049
24	3.555	0.0396	0.053

[a] Experimental hardness (in eV); values are from ref 19. [b] REPE values (in β) are from ref 17. [c] REPE values (in β) are from ref 18.

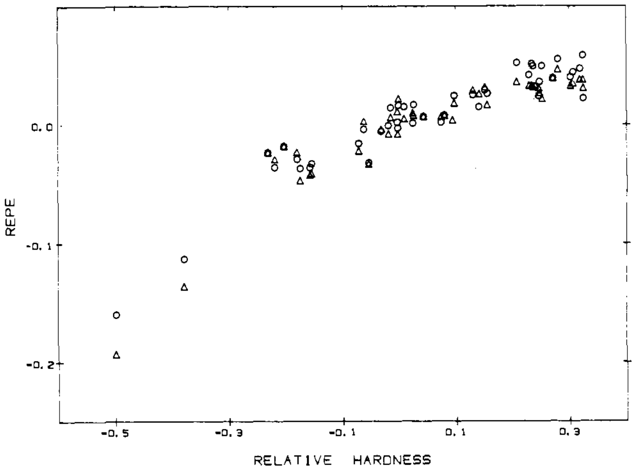

Figure 10. Correlation of REPE(HS) (in β) with relative hardness (in $-\beta$): heteroconjugated hydrocarbons. Points Δ indicate TREPE; points ○ indicate REPE(HS).

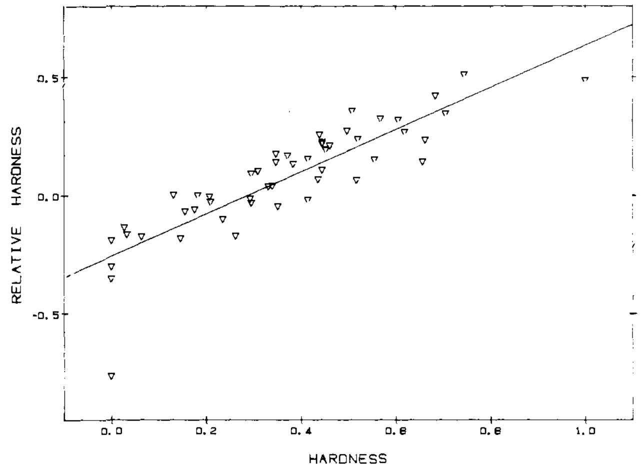

Figure 11. Correlation of relative hardness (in $-\beta$) with hardness (in $-\beta$): conjugated hydrocarbons.

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Table III. HOMO Energy, Hardness, and REPE(HS) Index for Some Nonalternants[a]

compd	ϵ_{HOMO}	hardness	REPE(HS)[b]	compd	ϵ_{HOMO}	hardness	REPE(HS)[b]	compd	ϵ_{HOMO}	hardness	REPE(HS)[b]
57	0.471	0.235	−0.018	**88**	0.034	0.190	0.004	**119**	0.332	0.265	0.008
58	0.477	0.439	0.023	**89**	−0.128	0.021	−0.006	**120**	0.445	0.445	0.021
59	0.000	0.156	−0.004	**90**	0.038	0.181	0.003	**121**	0.445	0.404	0.022
60	0.348	0.248	−0.030	**91**	−0.148	0.001	−0.008	**122**	0.303	0.305	0.016
61	0.414	0.207	−0.022	**92**	0.042	0.172	0.002	**123**	0.133	0.174	0.009
62	0.124	0.200	−0.023	**93**	0.092	0.087	0.001	**124**	0.000	0.105	0.004
63	0.319	0.213	−0.019	**94**	0.220	0.222	0.010	**125**	−0.169	0.027	−0.011
64	0.263	0.197	−0.023	**95**	0.221	0.208	0.009	**126**	0.414	0.207	0.018
65	0.375	0.357	0.002	**96**	0.098	0.086	0.000	**127**	0.456	0.228	0.018
66	0.618	0.309	0.009	**97**	0.456	0.309	0.018	**128**	0.484	0.282	0.024
67	0.305	0.033	−0.021	**98**	0.376	0.237	0.015	**129**	0.445	0.445	0.035
68	0.102	0.193	−0.017	**99**	0.441	0.334	0.018	**130**	0.176	0.154	0.018
69	0.125	0.182	−0.021	**100**	0.346	0.227	0.015	**131**	0.329	0.367	0.032
70	0.000	0.144	−0.013	**101**	0.465	0.327	0.018	**132**	0.411	0.346	0.033
71	0.261	0.238	0.017	**102**	0.395	0.242	0.015	**133**	0.000	0.144	0.017
72	0.422	0.383	0.025	**103**	0.113	0.212	0.012	**134**	0.000	0.151	0.017
73	0.000	0.223	0.009	**104**	0.216	0.312	0.015	**135**	0.057	0.195	0.021
74	−0.181	0.017	−0.008	**105**	0.429	0.374	0.020	**136**	0.162	0.161	0.015
75	0.347	0.000	−0.062	**106**	0.261	0.253	0.017	**137**	0.110	0.110	0.013
76	0.480	0.383	0.018	**107**	0.358	0.358	0.021	**138**	0.080	0.080	0.012
77	0.638	0.461	0.039	**108**	0.295	0.264	0.016	**139**	0.060	0.061	0.011
78	0.241	0.285	0.016	**109**	0.433	0.274	0.032	**140**	0.257	0.264	0.019
79	0.241	0.349	0.033	**110**	0.106	0.222	0.028	**141**	0.206	0.213	0.018
80	−0.209	0.000	−0.019	**111**	0.449	0.233	0.016	**142**	0.175	0.181	0.018
81	0.238	0.007	−0.030	**112**	0.510	0.355	0.021	**143**	0.155	0.161	0.017
82	0.507	0.283	−0.005	**113**	0.446	0.320	0.021	**144**	0.339	0.318	0.021
83	0.414	0.207	0.015	**114**	0.191	0.236	0.020	**145**	0.321	0.308	0.021
84	0.356	0.098	0.005	**115**	0.026	0.126	0.009	**146**	0.313	0.297	0.021
85	0.421	0.106	0.003	**116**	0.015	0.204	0.015	**147**	0.309	0.293	0.021
86	0.488	0.143	0.004	**117**	0.382	0.064	−0.036	**148**	0.365	0.324	0.021
87	−0.125	0.020	−0.005	**118**	0.352	0.176	−0.002				

[a] ϵ_{HOMO} and REPE(HS) are in units of β; hardness is in $-\beta$. ϵ_{HOMO} and hardness values are from standard Hückel calculations. [b] REPE(HS) values are from ref 20.

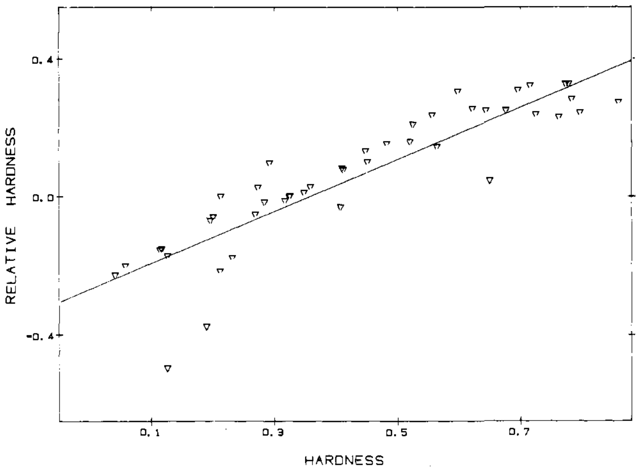

Figure 12. Correlation of relative hardness (in $-\beta$) with hardness (in $-\beta$): heteroconjugated hydrocarbons.

Since both absolute hardness and relative hardness are good measures of aromaticity, they should correlate with each other. Figures 11 and 12 demonstrate that they do. The data in Figures 11 and 12 are from Tables V and IV, respectively.

V. Principle of Maximum Hardness

High aromaticity is generally understood to signify high stability and low reactivity, and so it is not surprising that absolute hardness measures aromaticity, for it has been emphasized from the beginning of the HSAB literature that both high stability and low reactivity are associated with high hardness.[14] Pearson recently has even proposed a maximum hardness principle:[24] "There seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible. A large HOMO-LUMO gap increases stability." Furthermore, there is a basic theorem.[10] Relative to its positive and negative ions, a species is the more stable the larger is its absolute hardness. For a simple proof, note that for the process

$$S^+ + S^- \rightarrow 2S \tag{9}$$

the energy change is

$$A_S - I_S = -2\eta_S \tag{10}$$

Hence, relative to $S^+ + S^-$, S is more stable the greater is η_S; maximum hardness implies maximum stability. The inverse of hardness, softness, has opposite implications.

VI. Aromaticity and Antiaromaticity

Compounds with large η values are expected to have high stability and hence to be aromatic. From Figures 3–8 we can see that the dividing line between aromatic and antiaromatic species is a Hückel hardness of about -0.2β. Those compounds with Hückel hardness around -0.2β (approximately $-0.15\beta \le \eta \le -0.25\beta$) are predicted to be nonaromatic, and those with very small hardness are predicted to be antiaromatic.

For relative hardness, the dividing line between aromatic and antiaromatic is the zero value. Noting that aromaticity is commonly ascribed to cyclic conjugation, we infer in light of the principle of maximum hardness that, for any conjugated molecule, the larger the η_r is, the more aromatic the molecule is. We identify a small range of η_r values near zero, instead of zero itself, as the nonaromatic range. This appropriate range appears to be about $0.08\beta \le \eta_r \le -0.08\beta$. All acyclic polyenes have zero η_r and hence are predicted to be nonaromatic by the η_r criterion.

VII. Discussion of Individual Molecules

Now we discuss the applicability of the η_r measure to the specific molecules in Tables IV and V.

Conjugated Hydrocarbons. As we can see from Table V, compounds **1–11**, **22–24**, **58**, **77**, **120**, **149**, **151**, **158**, **166**, and **168** all have large η_r values and are predicted to be aromatic. Compounds **57**, **67**, **75**, **80**, **117**, **125**, **153**, **157**, **159**, and **162** have large negative η_r values and are predicted to be antiaromatic. The

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(24) Page 565 of ref 14b.

Table IV. HOMO Energy, Hardness, Relative Hardness, and REPE Indices for Some Heteroconjugated Hydrocarbons[a]

compd	ϵ_{HOMO}	η	η_r	TREPE	REPE(HS)	status[b]
172	0.618	0.650	0.043	0.007	0.007	i
173	0.370	0.407	-0.032	-0.004	-0.006	u
174	0.655	0.676	0.248	0.027	0.036	i
175	0.295	0.324	-0.003	0.011	0.002	u
176	0.426	0.451	0.097	0.018	0.024	i
177	0.170	0.201	-0.062	0.003	-0.004	-
178	0.486	0.520	0.156	0.017	0.026	i
179	0.618	0.796	0.240	0.033	0.032	i
180	0.019	0.232	-0.180	-0.023	-0.029	u
181	0.572	0.695	0.307	0.035	0.044	i
182	0.295	0.448	0.130	0.029	0.025	i
183	0.155	0.325	-0.001	0.022	0.016	i
184	-0.122	0.058	-0.203	-0.018	-0.019	-
185	0.160	0.358	0.025	0.008	0.017	u
186	0.495	0.778	0.325	0.031	0.022	i
187	0.298	0.564	0.141	0.026	0.015	i
188	0.422	0.644	0.246	0.031	0.024	i
189	0.000	0.292	0.094	0.004		-
190	0.618	0.859	0.271	0.040	0.039	i
191	-0.021	0.212	-0.219	-0.029	-0.036	u
192	0.586	0.716	0.319	0.038	0.047	i
193	0.295	0.482	0.151	0.032	0.029	i
194	0.135	0.317	-0.015	0.006	0.014	-
195	-0.165	0.041	-0.231	-0.023	-0.024	-
196	0.139	0.347	0.009	0.005	0.015	u
197	0.578	0.598	0.302	0.033	0.040	i
198	0.000	0.273	0.024	0.010	0.001	u
199	-0.019	0.213	-0.002	-0.008	-0.003	-
200	0.539	0.783	0.280	0.047	0.055	i
201	0.633	0.762	0.229	0.033	0.042	i
202	0.252	0.126	-0.498	-0.193	-0.160	-
203	0.380	0.190	-0.378	-0.136	-0.113	-
204	0.618	0.269	-0.054	-0.033	-0.032	-
205	0.653	0.409	0.080	0.008	0.008	-
206	0.633	0.411	0.074	0.007	0.002	-
207	0.935	0.773	0.324	0.038	0.058	i
208	0.915	0.725	0.236	0.032	0.049	i
209	0.897	0.622	0.252	0.022	0.049	i
210	0.478	0.126	-0.174	-0.047	-0.037	-
211	0.482	0.117	-0.154	-0.041	-0.033	-
212	0.532	0.196	-0.071	-0.022	-0.016	-
213	0.478	0.114	-0.157	-0.042	-0.036	-
214	0.568	0.284	-0.019	-0.008	-0.001	-
215	0.638	0.525	0.207	0.036	0.052	i
216	0.626	0.556	0.234	0.033	0.051	i

[a] η and η_r values (in $-\beta$), and ϵ_{HOMO} values (in β) are calculated by using eq 3 to 8. REPE values (in β) are from ref 6 and 21. [b] i, isolated; u, unstable; -, unknown. For preparative work see the references in ref 6.

following compounds have η_r values between 0.080β and -0.080β and are predicted to be nonaromatic: **126**, **150**, **155**, **156**, **160**, **163**, and **164**. Both experimental data and REPEs support all these predictions. However, there are several cases for which predictions by η_r values are inconsistent either with one of the REPE scales or with experimental data. For compounds **59**, **118**, **165**, **167**, **169**, and **170**, the η_r values have correct sign and agree with the experimental data. The magnitudes of the η_r values seem small in comparison with both REPEs. For compounds **66**, **76**, **152**, and **154**, our prediction is aromatic; the experimental situation is that they can exist but are unstable. Compound **171** is predicted to be aromatic by η_r and by REPE(HS) but nonaromatic by TREPE; the experimental fact is that it is stable.

Heteroconjugated Hydrocarbons. From Table II, the following predictions by our η_r index agree with both experimental data and REPE predictions: compounds **174**, **176**, **178**, **179**, **181**, **182**, **186–188**, **190**, **192**, **193**, **200**, **201**, **207–209**, **215**, and **216** are aromatic; compounds **180**, **184**, **191**, **195**, **202**, **203**, **210**, **211**, and **213** are antiaromatic; and compounds **172**, **173**, **177**, **198**, **199**, **205**, **206**, and **214** are nonaromatic. Compounds **185**, **194**, and **196** are predicted to be nonaromatic by both η_r and TREPE, and aromatic by REPE(HS). The experimental data support our prediction. For compound **175** the experimental data agree with the prediction of η_r and REPE(HS) but disagree with the prediction from TREPE. For compounds **204** and **212**, our prediction is nonaromatic, while both REPE scales predict antiaromatic. The experimental situation is unknown. Our scale seems to fail for compound **183**.

Table V. Hardness, Relative Hardness, and REPE Indices for some Cyclic Conjugated Hydrocarbons[a]

compd	η	η_r	TREPE	REPE(HS)	status[b]
1	1.000	0.482	0.046	0.065	i
2	0.705	0.340	0.042	0.060	i
3	0.618	0.264	0.039	0.055	i
4	0.414	0.151	0.034	0.047	i
5	0.605	0.315	0.039	0.055	i
6	0.295	0.088	0.031	0.042	i
7	0.452	0.189	0.036	0.050	i
8	0.520	0.233	0.038	0.053	i
9	0.568	0.319	0.038	0.053	i
10	0.684	0.416	0.041	0.056	i
11	0.445	0.220	0.037	0.051	i
22	0.371	0.164	0.036	0.049	i
23	0.347	0.135	0.037	0.048	i
24	0.497	0.267	0.040	0.053	i
57	0.235	-0.104	-0.027	-0.018	u
58	0.439	0.253	0.015	0.023	i
59	0.156	-0.072	-0.012	-0.004	u
66	0.309	0.099	0.005	0.009	u
67	0.033	-0.168	-0.025	-0.021	-
75	0.000	-0.304	-0.073	-0.036	-
76	0.383	0.128	0.008	0.018	u
77	0.461	0.206	0.030	0.039	i
80	0.000	-0.192	-0.027	-0.019	-
117	0.064	-0.179	-0.045	-0.036	-
118	0.176	-0.062	-0.011	-0.002	-
120	0.445	0.215	0.013	0.021	i
125	0.027	-0.138	-0.018	-0.011	-
126	0.207	-0.009	0.009	0.019	u
149	0.662	0.230	0.031	0.046	i
150	0.295	-0.036	0.007	0.005	u
151	0.618	0.264	0.017	0.027	i
152	0.656	0.138	0.016	0.005	u
153	0.000	-0.765	-0.307	-0.268	u
154	0.555	0.148	-0.027	-0.028	u
155	0.414	-0.023	-0.009	-0.010	u
156	0.516	0.059	0.002	-0.002	u
157	0.262	-0.174	-0.049	-0.027	u
158	0.445	0.104	0.010	0.027	i
159	0.147	-0.186	-0.032	-0.012	-
160	0.339	0.037	-0.010	0.007	u
161	0.351	-0.050	-0.032	-0.070	-
162	0.000	-0.357	-0.079	-0.060	u
163	0.436	0.063	0.003	-0.002	u
164	0.331	0.034	0.001	-0.002	u
165	0.293	-0.018	-0.077	-0.100	-
166	0.745	0.507	0.054	0.043	i
167	0.182	-0.004	-0.030	-0.033	u
168	0.508	0.351	0.023	0.022	i
169	0.131	-0.001	-0.016	-0.014	-
170	0.209	-0.031	-0.011	-0.014	u
171	0.347	0.173	0.005	0.012	i

[a] η and η_r values (in $-\beta$) are calculated by using eq 3 to 8. REPE values (in β) are from ref 4, 6, 18, 20, and 22. [b] i, isolated; u, unstable; -, unknown. For preparative work see ref 23 and the references in ref 6.

VIII. Formulas for η, η_r, and TREPE for Annulenes and Radialenes

For a class of conjugated molecules AP_nB we can obtain the general formulas for $P(G_n,x)$ and $P^{ac}(G_n,x)$ if there is only one line between two adjacent units in the corresponding molecular graph.[25] But $P(G_n,x) = 0$ and $P^{ac}(G_n,x) = 0$ can be solved analytically only in a few cases. In this section we deal with two

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[25] (a) Tang, A. C.; Jiang, Y. S.; Yan, G. S.; Dai, S. S. *Graph Theory of Molecular Orbitals*; Academic Press: Beijing, 1980. (b) Trinajstić, N. *Chemical Graph Theory*; CRC Press: Boca Raton, FL, 1983. (c) Zhou, Z. *Int. J. Quantum Chem.* **1988**, *34*, 325–332 and the references therein.

Table VI. Analytical Formulas of η, η_r, and TREPE for N-Electron n-Annulenes (all in β)

	η	η_r	TREPE
$n = 4m + 2$ $N = 4m + 2$	$-2 \sin (\pi/n)$	$-4 \sin (\pi/4n) \cos (3\pi/4n)$	$8 \sin^2 (\pi/4n)/N \sin (\pi/n)$
$n = 4m$ $N = 4m$	0	$2 \sin (\pi/2n)$	$-\{8 \sin (\pi/4n) \sin (3\pi/4n)\}/N \sin (\pi/n)$
$n = 4m + 1$ $N = 4m + 1$	0	0	$-(2/N) \cos (\pi/2n) \tan (\pi/4n)$
$n = 4m + 1$ $N = 4m + 2$	$-2 \sin (\pi/n) \cos (\pi/2n)$	$-4 \sin (\pi/4n) \cos (\pi/2n) \cos (3\pi/4n)$	$(2/N) \tan (\pi/4n)$
$n = 4m + 3$ $N = 4m + 3$	0	0	$-(2/N) \cos (\pi/2n) \tan (\pi/4n)$
$n = 4m + 3$ $N = 4m + 2$	$-2 \sin (\pi/n) \cos (\pi/2n)$	$-4 \sin (\pi/4n) \cos (\pi/2n) \cos (3\pi/4n)$	$(2/N) \tan (\pi/4n)$

of the simplest of these cases: annulenes and radialenes.

Annulenes. Let G_n be the molecular graph for an n-annulene. Then[25]

$$P(G_n,x) = g_n(x) - g_{n-2}(x) - 2 \qquad (11)$$

and

$$P^{ac}(G_n,x) = g_n(x) - g_{n-2}(x) \qquad (12)$$

where $g_n(x)$ is the Gegenbauer polynomial with superscript 1, or the Chebyshev polynomial in $x/2$ usually labeled as $T_n(x/2)$. Noting that

$$g_n(2 \cos \theta) = \frac{\sin (n + 1)\theta}{\sin \theta} \qquad (13)$$

we get

$$P(G_n,2 \cos \theta) = 2(\cos n\theta - 1) \qquad (14)$$

and

$$P^{ac}(G_n,2 \cos \theta) = 2 \cos n\theta \qquad (15)$$

From eq 14 and 15 we find the roots of $P(G_n,x)$ and $P^{ac}(G_n,x)$

$$x_i = 2 \cos \frac{2i\pi}{n} \qquad i = 0, ..., n - 1 \qquad (16)$$

and

$$x_i^{ac} = 2 \cos \frac{(2i + 1)\pi}{2n} \qquad i = 0, ..., n - 1 \qquad (17)$$

Hence for an N-electron n-annulene[6]

$$\begin{aligned} \text{TREPE} &= (E_\pi - E_\pi^{ac})/N \\ &= \sum_i \lambda_i(\epsilon_i - \epsilon_i^{ac})/N \\ &= \sum_i \beta\lambda_i(x_i - x_i^{ac})/N \end{aligned} \qquad (18)$$

where λ_i is the occupation number of the ith MO.

Using eq 6–8 and 18 we can obtain TREPE, η, and η_r for different n and N. The results are given in Table VI. From Table VI we see that the n-annulenes with $N = 4m + 2$ have TREPE < 0 [$\beta < 0$] and $\eta_r > 0$ and hence are predicted to be aromatic, while n-annulenes with $N = 4m$, TREPE > 0, and $\eta_r < 0$ are predicted to be antiaromatic. This confirms the $4n + 2$ rule. Another interesting point to note is the asymptotic behavior of the formulas in the table

$$\text{TREPE} \rightarrow \begin{cases} (\pi/2n^2)\beta & (N = 4m + 2) \\ -(3\pi/2n^2)\beta & (N = 4m) \end{cases} \quad \text{as } m \rightarrow \infty \qquad (19)$$

$$\eta_r \rightarrow \begin{cases} -(\pi/n)\beta & (N = 4m + 2) \\ (\pi/n)\beta & (N = 4m) \end{cases} \quad \text{as } m \rightarrow \infty \qquad (20)$$

Haddon obtained corresponding results for RE(PE) with his definition of RE.[9]

Radialenes. The characteristic polynomials for n-radialene and the corresponding reference structure can be derived inductively. The results are

$$P(G_n,x) = x^n\left\{g_n\left(\frac{x^2 - 1}{x}\right) - g_{n-2}\left(\frac{x^2 - 1}{x}\right) - 2\right\} \qquad (21)$$

and

$$P^{ac}(G_n,x) = x^n\left\{g_n\left(\frac{x^2 - 1}{x}\right) - g_{n-2}\left(\frac{x^2 - 1}{x}\right)\right\} \qquad (22)$$

where G_n stands for the molecular graph of n-radialene. Using eq 13 we have

$$x_{i\mp} = \cos \frac{2i\pi}{n} \mp \left(1 + \cos^2 \frac{2i\pi}{n}\right)^{1/2} \qquad i = 1, ..., n - 1 \qquad (23)$$

and

$$x_{i\mp}^{ac} = \cos \frac{(2i + 1)\pi}{2n} \mp \left(1 + \cos^2 \frac{(2i + 1)\pi}{2n}\right)^{1/2} \qquad i = 1, ..., n - 1 \qquad (24)$$

Consequently

$$\begin{aligned} \text{TREPE} &= (E_\pi - E_\pi^{ac})/2n \\ &= \beta\sum_{i=0}^{n-1}\left[\left(1 + \cos^2 \frac{2i\pi}{n}\right)^{1/2} - \left(1 + \cos^2 \frac{(2i + 1)\pi}{2n}\right)^{1/2}\right]\Big/ n \end{aligned} \qquad (25)$$

$$\eta = \begin{cases} (1 - \sqrt{2})\beta & \text{if } n \text{ is even} \\ \left[1 - \sqrt{2} + \cos \frac{\pi}{n} - \left(1 + \cos^2 \frac{\pi}{n}\right)^{1/2}\right]\beta/2 & \text{if } n \text{ is odd} \end{cases} \qquad (26)$$

and

$$\eta_r = \begin{cases} \left[1 - \sqrt{2} - \cos \frac{\pi}{2n} + \left(1 + \cos^2 \frac{\pi}{2n}\right)^{1/2}\right]\beta & \text{if } n \text{ is even} \\ \left[1 - \sqrt{2} + \cos \frac{\pi}{n} - \left(1 + \cos^2 \frac{\pi}{n}\right)^{1/2} - 2 \cos \frac{\pi}{2n} + 2\left(1 + \cos^2 \frac{\pi}{2n}\right)^{1/2}\right]\beta/2 & \text{if } n \text{ is odd} \end{cases} \qquad (27)$$

Note that $\eta_r < 0$ in both cases, so we predict that all radialenes are antiaromatic (nonaromatic if n is very large). This agrees with the predictions of Hess and Schaad.[4] TREPE values for n-radialenes are positive when $n = 4m$, negative otherwise.

Finally we point out that by using Hess and Schaad's parameters[4] we can also obtain analytical formulas for the REPE of Hess and Schaad for annulenes and radialenes.

IX. Concluding Remarks

Absolute hardness as an indicator for aromaticity has the advantage that it does not depend on the subtleties of a reference structure. Also, in principle it does not depend on a quantum mechanical model for molecules, because ideally one would simply use experimental ionization potential and electron affinity to determine hardness (eq 2). However, absolute hardness does not provide of itself the prediction that all acyclic polyenes are nonaromatic, or the prediction that some cyclic molecules are antiaromatic, for which purposes relative hardness appears to be useful.

Given that the hardnesses are composed from experimental I and A values, they incorporate, in principle, information about σ electrons as well as about π electrons. This reminds one of the corresponding characteristic of successful semiempirical electronic structure theories. The quantity $I - A$ is the one-center parameter in PPP theory;[26] for an atom or species as a whole it is twice the hardness.[11] For the species as a whole it now appears also to be, in essence, the aromaticity. There is no problem extending the concept to homoaromatic and general nonplanar systems.

The agreement, at least rough agreement, with ring-current ideas is straightforward to demonstrate, and accords with the arguments of Haddon.[9] The "paramagnetic" contributions to magnetic susceptibilities and chemical shifts are second-order-perturbation contributions, the approximate evaluation of which can be accomplished by factoring out an "average energy denominator", and hence these quantities vary inversely as hardness (at least roughly). Alternatively, one sees from the exact density-functional formula for the so-called linear response function in terms of softness kernel[27] that such second-order quantities must have inverse dependence on hardness.

The maximum hardness principle of section V merits careful study. If it can be suitably generalized, it could be of considerable importance.

In summary, in chemical hardness one has a simply defined and straightforwardly determined molecular parameter that measures molecular stability, molecular reactivity, and ring-current effects. We therefore commend hardness and relative hardness as defining measures of aromaticity.

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(26) Pariser, R. *J. Chem. Phys.* **1953**, *21*, 568–569.

(27) Berkowitz, M.; Parr, R. G. *J. Chem. Phys.* **1988**, *88*, 2554–2557; eq 36.

Stereoelectronic Effects in the Gas Phase. 2. Negative Ion Reactions of 1,3-Dithianes and 1,3-Dithiane 1-Oxides

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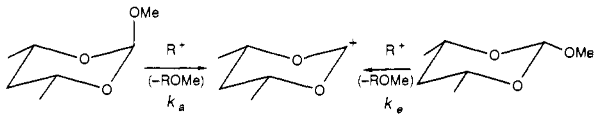
Abstract: Reactions of gaseous anions (methoxide, hydroxide, and thermal electrons) with *cis*-4,6-dimethyl-1,3-dithiane and the corresponding axial and equatorial 1-oxides have been investigated using the techniques of ion cyclotron resonance (ICR) spectroscopy and pulsed positive–negative ion chemical ionization (PPNICI) spectroscopy. Deprotonation to $(M-H)^-$ ions *and* extensive fragmentation to ions of m/z 99 and 101 were observed for all three compounds with all three reactant anions. When compounds labeled with deuterium specifically at the C2 position were used, it was found that deprotonation occurred at C2 *and* elsewhere in the molecule. The axial hydrogen at C2 was removed as readily or more so than the equatorial hydrogen, depending on the reactants and conditions of ion generation. (These results differ from the corresponding condensed-phase reactions, which show strong selectivity for C2 equatorial deprotonation.) Deuterium isotope effects were estimated to be 1.2 and 1.3 for ions generated by MeO^- and e, respectively. Exchange (H/D) between hydroxide and *cis*-4,6-dimethyl-1,3-dithiane-*2-d_2* was insignificant, although exchange was observed in comparable reactions of hydroxide with 1,3-dithiane-d_2 and bis(methylthio)methane-d_2. Stereoelectronic effects that may contribute to selectivity in solution do not account for the gas-phase results. Ab initio calculations at the 3-21G(*) level applied to methanedithiol and the anion $(HS)_2CH^-$ (as models for the 1,3-dithiane system) provide insight into the nature of the gas-phase reactions. Possible reaction pathways are discussed.

There is much evidence, largely through the work of Deslongchamps,[1] that certain reactions have demanding stereoelectronic requirements. Yet it is difficult to isolate stereoelectronic effects from effects due to the reaction medium, counterions, and leaving groups, and it remains controversial as to how important they really are.[2] In an earlier investigation, we sought evidence of stereoelectronic control in the gaseous ionic dissociation of cyclic orthoesters **1a** and **1e** using ion cyclotron resonance (ICR) techniques.[3] Eliel and Nader[4] had shown previously that cyclic orthoesters **1** react selectively with Grignard reagents to cleave the *axial* OMe bond (**1e** is unreactive). The axial selectivity is possibly a stereoelectronic effect involving n → σ^* delocalization of nonbonding electrons of the ring oxygens into the σ^* orbital of the axial C–O bond. It is also possible that axial selectivity may be due entirely to reagent and solvent effects.[5] We reasoned that a study of related gas-phase reactions of **1a** and **1e** where perturbations by solvent and counterions are absent might permit isolation of the stereoelectronic effect. However, no significant differences in the rates of ionic cleavage of the exocyclic OMe group of **1a** and **1e** were observed under the conditions of the ICR experiment (eq 1, $k_a = k_e$).[3] A similar result has been found for the related thioorthoesters.[6]



(1)

1a **1e**

$R^+ = C_3H_7^+$
$= CH_3SCH_2^+$

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