

ABSOLUTE HARDNESS AND AROMATICITY: MNDO STUDY OF BENZENOID HYDROCARBONS

ZHONGXIANG ZHOU* AND HIMANSHOO V. NAVANGUL†

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599, U.S.A.

Absolute hardness calculated by the MNDO method has been shown to be a good measure of aromaticity for 14 benzenoid hydrocarbons. Comparisons among hardnesses at different levels of approximation are given. The parallelism of the aromaticity and hardness concepts in benzenoids is elaborated.

INTRODUCTION

The characterization and quantification of aromaticity have long been goals of both physical and organic chemists. The aromaticity of a molecule can be considered as the complex of properties associated with the cyclic conjugation in the molecule. Among many facets of aromaticity, high stability, low reactivity and sustained induced ring current are the most important characteristics for aromatic compounds.¹ Therefore, it has been possible to quantify aromaticity by emphasizing one or the other of these three aspects²⁻¹⁰ (note that the definition of resonance energy in this paper has a different sign convention from the original definition of Dewar and de Llano²). There exist unified theories which characterize more than one aspect of aromaticity.¹¹⁻¹⁴ Recently, Zhou and co-workers^{10,14} have shown that absolute hardness and relative hardness can also well serve as measures of aromaticity because they also unify, at least in principle, the three main aspects of aromaticity mentioned above.

In this paper we calculate absolute hardness at the MNDO level (η_{MNDO}) for some selected benzenoid hydrocarbons and use it as a measure of aromaticity in comparison with hardnesses calculated using two other levels of approximation: HMO hardness (η_{HMO}) and experimental hardness (η_{EXP}). We then discuss the correlation of hardnesses with other criteria of aromaticity, such as Dewar's resonance energy per π -electron (REPE) [REPE(D)],² Hess and Schaad's REPE [REPE(HS)]³ and Aihara's⁴ and Gutman *et al.*'s⁵ REPE (or topological REPE: TREPE). Finally, we

attempt to establish hardness as a measure of aromaticity that unifies the three main aspects of aromaticity concept.

CALCULATION OF ABSOLUTE HARDNESS AT THE MNDO LEVEL

Absolute hardness, η , is defined as¹⁵

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

where E is the electronic energy, N is the number of electrons and v is the external potential. The corresponding finite difference equation is

$$\eta = (I - A)/2 \quad (2)$$

where I is the ionization potential and A the electron affinity. If molecular orbital theory is used,¹⁶ the absolute hardness can be defined as

$$\eta = (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})/2 \quad (3)$$

where ϵ_i are the orbital energies. We shall use equation (3) as our operational equation.

The standard AMPAC package¹⁷ was used to calculate η and the geometric optimization procedure (with restriction of planarity) was employed for all the molecules considered here. The initial geometries were set up assuming all rings to be hexagons and all angles to be 120° , and with the following fixed values of bond lengths: all C—C bonds, $r = 1.39 \text{ \AA}$; all C—H bonds, $r = 1.08 \text{ \AA}$. The output ϵ_{LUMO} and ϵ_{HOMO} gives η_{MNDO}

* Author for correspondence.

† Permanent address: Department of Chemistry and Physical Science, North Carolina Wesleyan College, Rocky Mount, North Carolina 27804, USA.

Table 1. Hardnesses and REPEs for selected benzenoid hydrocarbons

No. Compound	$\eta_{\text{HMO}}^{\text{a}}$	$\eta_{\text{MNDO}}^{\text{b}}$	$\eta_{\text{Exp}}^{\text{c}}$	TREPE ^d	REPE(HS) ^e	REPE(D) ^f
1 Benzene	1.000	4.879		0.046	0.065	0.145
2 Naphthalene	0.618	4.121	3.985	0.039	0.055	0.132
3 Anthracene	0.414	3.603	3.430	0.034	0.047	0.114
4 Naphthacene	0.295	3.268	2.900	0.031	0.042	0.101
5 Pentacene	0.220	3.034		0.029	0.038	0.091
6 Hexacene	0.169	2.869		0.027		
7 Biphenyl	0.705	4.143		0.042	0.060	0.142
8 Phenanthrene	0.605	3.999	3.805	0.039	0.055	0.138
9 Pyrene	0.445	3.568	3.570	0.037	0.051	0.114
10 Benzo[c]phenanthrene	0.568	3.812	3.825	0.038	0.053	0.138
11 Benz[a]anthracene	0.452	3.641	3.415	0.036	0.050	0.127
12 Chrysene	0.520	3.771	3.795	0.038	0.053	0.138
13 Triphenylene	0.684	3.974	3.955	0.041	0.056	0.147
14 Perylene	0.347	3.348		0.037	0.048	0.131

^aIn $-\beta$. Values are from Ref. 10.

^bIn eV. Values are calculated by using equation (3).

^cIn eV. Values are from Ref. 18.

^dIn β . Values are from Ref. 19.

^eIn β . Values are from Ref. 20.

^fIn $-eV$. Values are from Ref. 2.

via equation (3). Calculated η_{MNDO} results and η_{HMO} , η_{Exp} and REPEs are reported in Table 1.

HARDNESSES AS A MEASURE OF AROMATICITY

Hardnesses at different levels of approximation are given in Table 1. Previously η_{HMO} and η_{Exp} were shown

to correlate well with both TREPE and REPE(HS).¹⁴ Figure 1 demonstrates that hardnesses at different levels of approximation are linearly correlated. The results shown in Figure 2 demonstrate that η_{MNDO} serves well as a measure of aromaticity. The correlation between η_{MNDO} and TREPE or REPE(HS) is linear. It is clear from Figure 2 that the harder the cyclic conjugated molecule, the more aromatic it is. The correlation of

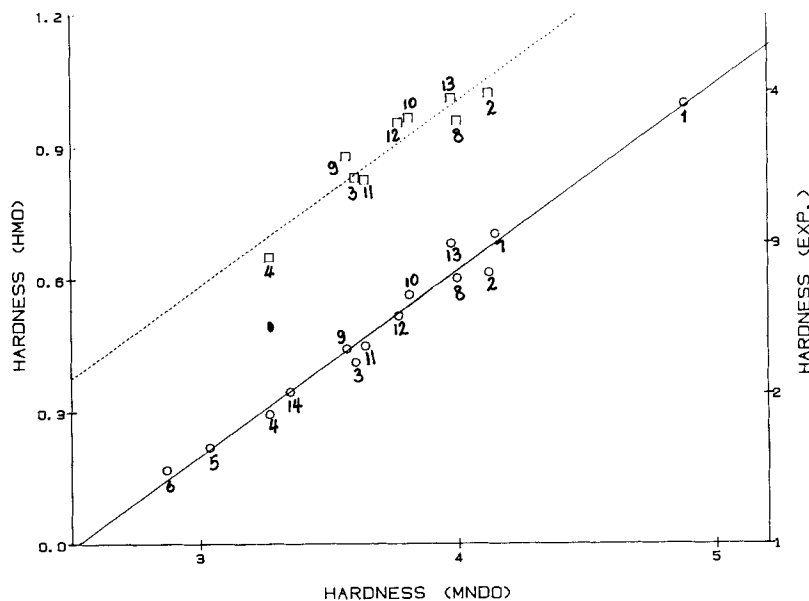


Figure 1. Correlation of η_{MNDO} (in eV) with η_{HMO} (in $-\beta$) and η_{Exp} (in eV). (○) HMO hardness; (□) experimental hardness. The straight lines are the corresponding linear least-square fits. For compound numbers, see Table 1

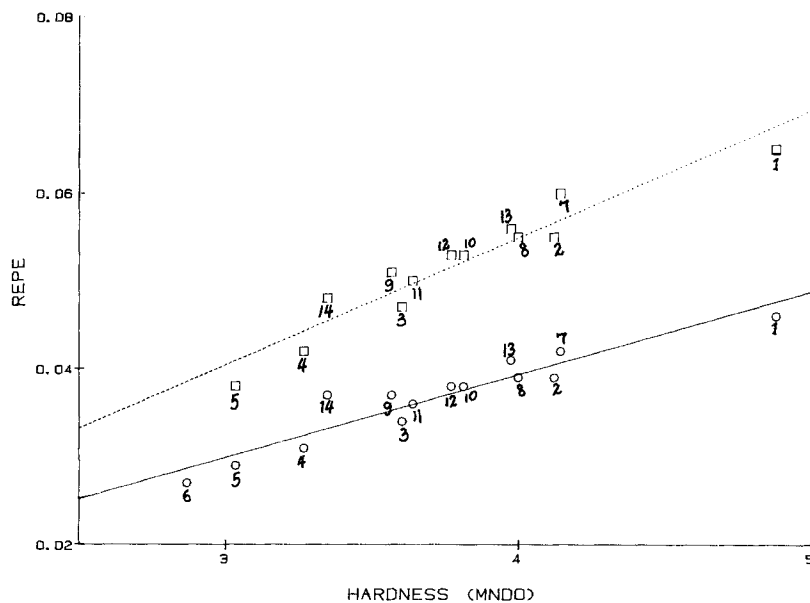


Figure 2. Correlation of η_{MNDO} (in eV) with REPE (in β). (○) TREPE; (□) indicate REPE(HS). The straight lines are the corresponding linear least-square fits. For compound numbers, see Table 1

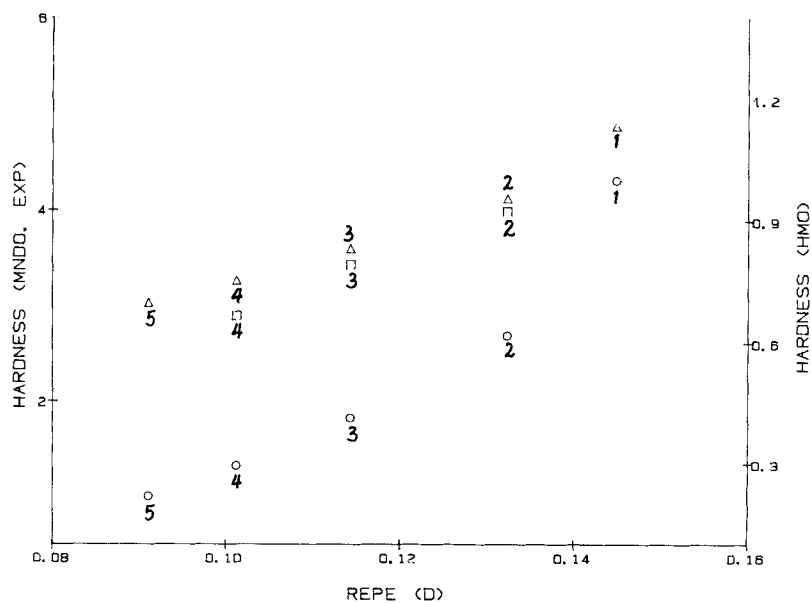


Figure 3. Correlation of Dewar REPE (in $-eV$) with η_{HMO} (in $-\beta$), η_{EXP} (in eV) and η_{MNDO} (in eV). (○) HMO hardness; (□) experimental hardness; (Δ) MNDO hardness. For compound numbers, see Table 1

REPE(D) with hardness is not always as good as TREPE or REPE(HS). However, for some particular types of molecules, it can be very good. Figure 3 shows the correlation of REPE(D) with η_{HMO} , η_{MNDO} and η_{Exp} for acenes. Again, in all cases harder implies more aromatic. This agrees with the known fact that acenes show decreasing stability as the number of rings increases. Hence the MNDO calculations here are in complete agreement with the previous results.¹⁴

About 25 years ago Clar²¹ noted that highly colored benzenoid hydrocarbons are generally less stable. Hess and Schaad²⁰ even plotted their REPE vs the p band of benzenoid hydrocarbons and found a very good linear correlation. The p band is due to an electron transition from the HOMO level to the LUMO level. The transition energy (ΔE_p) of the p band is related but not equivalent to twice the hardness because of the electron-electron repulsion. As an approximation, if we neglect electron-electron repulsion or assume that it remains the same for different numbers of electrons, we find that hardness is $0.5\Delta E_p$. Hence the linear correlation of REPE(HS) with ΔE_p shown by Hess and Schaad²⁰ really reveals the correlation of REPE(HS) with hardness.

It should be noted that equation (3) assumes the validity of Koopman's theorem for both ionization potential and electron affinity.¹⁶ This introduces some errors because of the neglect of the rearrangement of the electron distribution. However, these errors partially cancel each other when equation (3) is used to calculate hardness. It seems that the differences among hardnesses are mainly due to the different treatment of the electron-electron interactions in different calculation schemes. It is interesting that the linear least-square fit of η_{HMO} to either η_{MNDO} or η_{Exp} gives β , the resonance integral, with a value of about -2.5 eV. This value is comparable to those obtained by other methods²² (note that the β value from the η value fitting should be the average of β values from the ionization potential fitting and the electron affinity fitting).

HARDNESS AS A UNIFYING MEASURE OF AROMATICITY

Zhou and Parr¹⁴ have recently argued that relative hardness is a parallel concept to aromaticity because it measures in principle the three main aspects of aromaticity. Here we elaborate the conclusion that hardness measures the sustained induced ring current effect of an aromatic compound. For simplicity we consider the effects of sustained induced ring current on the diamagnetic susceptibility χ of a species. The z-component of the diamagnetic susceptibility χ for a molecule can generally be written as²³

$$\chi_z = -\frac{Ne^2}{4mc^2} \sum_i \langle 0 | x_i^2 + y_i^2 | 0 \rangle + \frac{Ne^2}{2m^2c^2} \sum_{n \neq 0} \frac{|\langle 0 | m_z | n \rangle|^2}{E_n - E_0} \quad (4)$$

where N is Avogadro's number, m_z is the z-component of the angular momentum, $|n\rangle$ are eigenstates of the molecule and E_n are the corresponding energies, where the subscript 0 corresponds to the ground state. The first summation in equation (4) is over the electrons and the second is over all excited eigenstates. The effects of the induced ring current on χ_z of an aromatic compound are contained in the second term of equation (4). This can be seen from the following argument.²⁴ For a free atom, the second term in equation (4) equals zero, which represents a maximum induced circulation current. In a molecule the existence of the other atoms will resist this induced circulation current. The second term of equation (4) represents this resistance. Other things being equal, this resistance is inversely proportional to the induced ring current in a cyclic conjugated molecule. Therefore, this resistance is smaller for an aromatic molecule than for its acyclic analog, and larger for an antiaromatic molecule than for its acyclic analog. This is in accordance with the hardness index of aromaticity. Applying the Unsöld approximation²⁵ to the second term of equation (4) we arrive at a common denominator of energy gap Δ which is roughly proportional to hardness. The harder the compound is, the smaller the second term of equation (4) will be. This implies that for a cyclic conjugated molecule harder means more aromatic.

ACKNOWLEDGEMENTS

Thanks are due to Professor Robert G. Parr for his constant encouragement and helpful discussions. This research was supported by grants from the National Science Foundation and the National Institutes of Health.

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