JOC Article

Topology-Driven Physicochemical Properties of π-Electron Systems. 1. Does the Clar Rule Work in Cyclic π-Electron Systems with the Intramolecular Hydrogen or Lithium Bond?[†]

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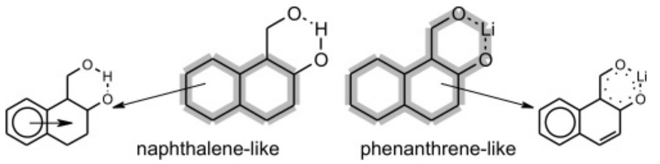

The Clar model predicting stability and electron distribution in benzenoid hydrocarbons seems to be also a good predictor for related properties in lithium *o*-acylphenolates and to a lesser extent in the phenols themselves. This conclusion is based on analysis of geometry changes in the analogues of naphthalene, phenanthrene, anthracene, and triphenylene, where benzene rings are systematically replaced with a quasi-ring formed as a β-ketoenol or β-ketoenolate complex with a lithium cation, i.e., where CH−CH−CH fragments are replaced with O···Li···O or O···H···O fragments. These systems were optimized at the MP2/6-31G(2d,p) level of theory. The energy of bond separation reactions in line with aromaticity indices HOMA and NICSs supported the above statement.

Introduction

Benzene, the archetypic aromatic compound,[1,2] has served as the basis for formulation of all of the most important criteria of aromaticity.[3] Benzene is a six-membered, cyclic, and planar π-electron system, which is chemically[2] and thermodynamically stable.[4] The benzenoid bonds do not display a pattern of long−short alternation[5] and have lengths between those observed for typical single and double Csp^2-Csp^2 bond lengths.[6] Typically, benzene is involved in reactions in which the π-electron system is maintained, for example, in electrophilic substitution.[7]

β-Ketoenols may exist in two conformations−linear and cyclic.[8] The linear form is observed primarily in the crystalline state as chains linked by intermolecular H-bonds. The cyclic form may be stable in the gas, liquid, and crystalline phases due to an intramolecular H-bond.[9] The cyclic structure is planar and, inclusive of the bridging proton, may be considered as a six-membered "quasi-ring". Analogous cyclic conformations are known for β-ketoenolate complexes with metal cations.[10] Numerous literature studies, in fact, focus on quasi-ring-type systems, since they appear to exhibit substantial chemical stability[11] and in many cases follow electrophilic substitution rather than addition.[12] Additionally, these systems often exhibit a symmetry in which the two C−O bonds as well as the two C−C bonds are rendered equivalent (Scheme 1).[10] To rationalize chemical behavior in quasi-ring systems, the concept of

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[†] Dedicated to Professor A. J. Sadlej on the occasion of his 65th birthday.

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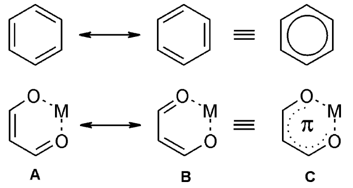
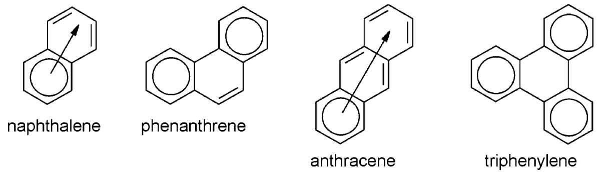
SCHEME 1



SCHEME 2



resonance between A and B has been employed,[11] which has been more recently replaced with a concept of π-electron delocalization represented by conformation C in Scheme 1.[13]

Thus, to an approximation, the β-ketoenolate complexation with metal cations may be considered analogous to that of the π-electron structure in benzene. These types of π-electron chelate systems with metal cations are occasionally referred to as "quasiaromatic".[14]

The question arises as to how the π-electrons of such a quasi-ring affect the π-electron structure of benzene and benzenoid hydrocarbons to which the β-ketoenolate complex with metal cation is fused. Does the quasi-ring, with a proton or metal cation, act equivalently to that of the carbocyclic parent ring?

To answer the above question, it is useful to recall the empirical rule introduced by Clar[15] describing π-electron delocalization in benzenoid hydrocarbons. The Clar rule states that many physicochemical properties of polycyclic aromatic hydrocarbons may be well understood in terms of the localization of the aromatic sextet present in the molecule. The idea is to "assign the π-electrons that can participate in aromatic sextets to particular rings and to do so in such a way as to obtain the maximum number of π-electron sextets".[16] In this way, π-electron delocalization of a particular ring within a benzenoid hydrocarbon is qualified by the Clar rule as (i) the "empty" ring, as in the case of central ring in triphenylene, (ii) containing localized double bond(s), as in the case of the central ring in phenanthrene and alike, or (iii) containing a localized or migrating aromatic sextet, as in triphenylene or naphthalene, and is quantified in terms of the magnitude of an aromaticity index (Scheme 2).[17]

The Clar rule belongs to the graph-topological models of π-electron delocalization in large, polycyclic—mostly carbocyclic—systems.[18] The aim of the present study is to verify whether the Clar rule may be applied to systems with quasi-rings.

Methodology

We have analyzed the analogues of naphthalene (**1**), phenanthrene (**2**, **3**), anthracene (**4**), and triphenylene (**5**), where benzene rings were systematically replaced with a quasi-ring (Figure 1).

The quasi-ring is formed as a β-ketoenol (**a**, **b**) or β-ketoenolate complex with a lithium cation (**c**). Moreover, in the case of triphenylene, three external benzene rings were replaced with H-bonded quasi-rings (**6**). Then successively, each H-bonded quasi-ring was replaced with a Li-bonded ring. In three cases, **1**, **2**, and **4**, the keto form was not stable and the proton transferred immediately to the oxygen atom.

Full geometry optimizations have been carried out using the GAMESS[19] and GAUSSIAN[20] software packages. Structural computations were performed using Møller−Plesset perturbation theory (MP2).[21] The 6-31G(2d,p) basis set[22] was used. Full geometry optimizations were performed and uniquely characterized by calculating and diagonalizing the matrix of energy second derivatives (Hessian) to determine the number of imaginary frequencies (0 = minima; 1 = transition state).

Bond separation reaction (BSR) energies[23] were determined as one comparative method for assessment of aromatic character in the described systems. The BSRs are a subgroup of isodesmic reactions that compare potentially aromatic systems against a

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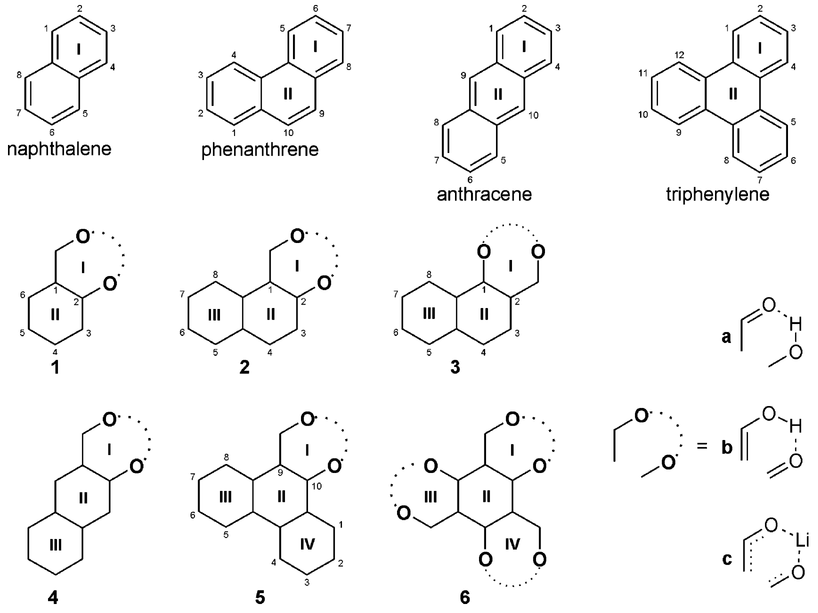
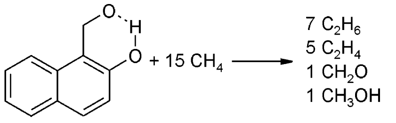


FIGURE 1. Labeling of the studied systems.

SCHEME 3. Example Bond Separation Reaction for a Quasi-ring Phenanthrene System



set of smallest prototype molecules that make up the ring structure. In this regard, the BSRs represent formal transformations in which all bonds between heavy (non-hydrogen) atoms in the molecule are separated into the simplest two-heavy-atom molecules containing the same kind of bond. The set of prototype molecules that would be compared against the quasi-ring systems above involving H, C, O, and Li consists of ethane, ethylene, methanol, lithium methanolate, and formaldehyde. Stoichiometric balance is obtained by addition of CH_4 as shown in Scheme 3. The energetics of the BSRs are calculated as the energy difference of the two sides of the reaction equation. Positive values would imply that the ring compounds are more stable than the prototype reference compounds.

As an assessment of the overall total change in geometry for a single π-electron system, a geometry-based index, HOMA (harmonic oscillator model of aromaticity), is used. HOMA is defined[24] as

$$\mathrm{HOMA} = 1 - \frac{1}{n}\sum_{j=1}^{n}\alpha_i(R_{\mathrm{opt},i} - R_j)^2 \qquad (1)$$

TABLE 1. Selected Bond Lengths for Studied Systems

system	bond	bond length/Å
naphthalene	C(1)−C(2)	1.381
phenanthrene	C(9)−C(10)	1.365
1-formyl-2-naphthol (**2a**)	C(3)−C(4)	1.371
lithium 1-formyl-2-naphtholate (**2c**)	C(3)−C(4)	1.363
2-formyl-1-naphthol (**3a**)	C(3)−C(4)	1.372
lithium 2-formyl-1-naphtholate (**3c**)	C(3)−C(4)	1.364
triphenylene	C(4a)−C(12b)	1.422
9-formyl-10-phenanthrol (**5a**)	C(9)−C(10)	1.392
(10*Z*)-10-(hydroxymethylene)-phenanthr-9-one (**5b**)	C(9)−C(10)	1.446
lithum 9-formyl-10-phenanthrolate (**5c**)	C(9)−C(10)	1.415

where n represents the total number of bonds in the molecule and α_i is a normalization constant (for C−C and C−O bonds $\alpha_{\mathrm{C-C}} = 257.7$ and $\alpha_{\mathrm{C-O}} = 157.38$) fixed to give HOMA = 0 for a model nonaromatic system, e.g., Kekulé structure of benzene and HOMA = 1 for the system with all bonds equal to the optimal value $R_{\mathrm{opt},i}$, assumed to be realized for fully aromatic systems.[6] For C−C bonds, $R_{\mathrm{opt,C-C}} = 1.388$ Å, and for C−O bonds $R_{\mathrm{opt,C-O}} = 1.265$ Å. The higher the HOMA value, the more "aromatic" is the ring in question and, hence, the more delocalized the π-electrons of the system.

We have also calculated the nuclear independent chemical shift, NICS$(1)_{zz}$, the perpendicular to the ring component of negative value of the absolute shielding estimated 1 Å above the geometrical center of the ring.[25] The NICS computations were performed using the GIAO[26] method at the Hartree−Fock level of theory with the 6-31G(2d,p) basis set.

Results and Discussion

Comparison across selected bond lengths for the molecular systems studied is very illustrative (Table 1).

The most dramatic results are associated with the bonds that, according to the Clar rule, are either "single" or "double" bonds. In the case of phenanthrene, the C(9)−C(10) bond is considered as a double bond, and at the optimized geometry this bond length is 1.365 Å. For the derivatives **2c** and **3c**, with Li-bonded quasi-

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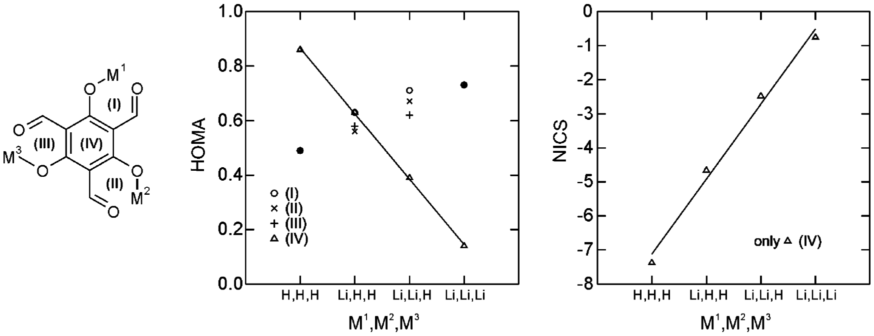

FIGURE 2. Dependences of HOMA and NICS on the number of Li$^+$ replacing H$^+$ in the quasi-ring.

TABLE 2. Calculated BSR Energies for Studied Systems

system	total energy/ hartree	BSE/ kcal·mol^{-1}
naphthalene	−384.615	139.3
salicylaldehyde (**1a**)	−419.575	115.8
lithium salicylate (**1c**)	−426.538	144.8
phenanthrene	−537.781	207.3
1-formyl-2-naphthol (**2a**)	−572.735	180.1
lithium 1-formyl-2-naphtholate (**2c**)	−579.700	210.3
2-formyl-1-naphthol (**3a**)	−572.739	182.9
(2*Z*)-2-(hydroxymethylene)-naphthalen-1-one (**3b**)	−572.726	174.3
lithium 2-formyl-1-naphtholate (**3c**)	−579.706	214.5
anthracene	−537.771	200.9
2-formyl-3-naphthol (**4a**)	−572.735	180.1
lithium 2-formyl-3-naphtholate (**4c**)	−579.695	207.1
triphenylene	−690.946	274.4
9-formyl-10-phenanthrol (**5a**)	−725.902	249.1
(10*Z*)−10-(hydroxymethylene)-phenanthr-9-one (**5b**)	−725.893	243.7
lithium 9-formyl-10-phenanthrolate (**5c**)	−732.868	280.6

TABLE 3. HOMA and NICS(1)$_{zz}$ (*Italics*) Values for Individual Rings in Studied Systems[a]

	ring			
system	I	II	III	IV
salicylaldehyde (**1a**)	0.32	0.94		
		−27.1		
lithium salicylate (**1c**)	0.63	0.73		
		−20.5		
1-formyl-2-naphthol (**2a**)	0.42	0.69	0.82	
		−23.7	*−31.6*	
lithium 1-formyl-2-naphtholate (**2c**)	0.73	0.40	0.86	
		−15.5	*−30.5*	
2-formyl-1-naphthol (**3a**)	0.43	0.74	0.83	
		−24.2	*−31.3*	
(2*Z*)-2-(hydroxymethylene)-naphthalen-1-one (**3b**)	0.68	0.25	0.91	
		−7.1	*−30.0*	
lithium 2-formyl-1-naphtholate (**3c**)	0.76	0.45	0.87	
		−15.0	*−30.5*	
2-formyl-3-naphthol (**4a**)	0.17	0.78	0.74	
		−28.2	*−29.4*	
lithium 2-formyl-3-naphtholate (**4c**)	0.43	0.65	0.72	
		−24.5	*−24.2*	
9-formyl-10-phenantrol (**5a**)	0.49	0.39	0.87	0.89
		−14.2	*−30.7*	*−30.7*
(10*Z*)-10-(hydroxymethylene)-phenanthr-9-one (**5b**)	0.68	−0.06	0.91	0.93
		2.3	*−27.9*	*−28.4*
lithum 9-formyl-10-phenanthrolate (**5c**)	0.82	0.11	0.89	0.91
		−7.8	*−29.0*	*−29.8*
naphthalene	0.79			
	−32.3			
phenanthrene	0.86	0.51		
	−32.6	*−22.5*		
anthracene	0.68	0.69		
	−28.4	*−39.0*		
triphenylene	0.89	0.17		
	−29.9	*−10.6*		

[a] For quasi-rings, NICS(1)$_{zz}$ values were not estimated.

ring in place of the carbocycle, the analogous bond lengths to C(9)$-$C(10) in phenanthrene are 1.363 and 1.364 Å, respectively. For naphthalene itself, the length of the C(1)$-$C(2) bond is 1.381 Å. Thus, placement of the quasi-ring with Li-bonding in **2c** and **3c** results in ring II being more similar to that of phenanthrene with a typical shorter C(9)$-$C(10) bond than that of the C(1)$-$C(2) bond in naphthalene. The situation found for the enol forms of the H-bonded systems **2a** and **3a** gives rise to geometries between those for the C(1)$-$C(2) bond in naphthalene and the C(9)$-$C(10) bond in phenanthrene. The analogous bond lengths are 1.371 and 1.372 Å, respectively.

When the system with a fused quasi-ring simulates the topology of anthracene the situation is less clear, since according to the Clar rule the aromatic sextet in anthracene is of a migrating type. Another good illustration is the changes of the C(9)$-$C(10) bond length in structures **5**. Since these systems are the derivatives of phenanthrene, the C(9)$-$C(10) bond length should be close to the value for the double bond. In the case of **5a**, the C(9)$-$C(10) bond length is 1.392 Å, whereas for **5c** the C(9)$-$C(10) bond length is 1.415 Å. The latter value is longer than a typical value for the double bond and resembles the situation in triphenylene (1.422 Å).

For three cases (**1**, **2**, and **4**), the keto form, **b**, was not stable and did not lead to an optimized geometry. Only two keto forms, **3b** and **5b**, were obtained as minima, with the proton attached to the vinyl-like oxygen atom. In these cases, a possible conjugation between the neighboring benzo-ring and the $-$C$=$O π-electrons provides as a plausible explanation for stabilization of these two conformers. These results are in line with the recent analysis of changes in aromaticity due to the fusion of the quasi-rings in *o*-hydroxylaryl aldehydes with intramolecular H-bonding.[27]

Considering the energetics aspects by the use of BSR energies, we have found that for the isomeric structures (phenanthrene and anthracene analogues **2**$-$**4**) **3c** is the structure with the highest BSR energy among all Li-bonded systems, while **3a** has the highest BSR energy among the H-bonded systems.

Table 2 shows calculated results for BSR energies for the studied systems. Systems **2**$-$**4** are isomeric naphthalene deriva-

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tives. The results indicate that analogues of phenanthrene in which one carbocylic ring is replaced with a Li-bonded quasi-ring are more stable than the respective analogue of anthracene. This is in line with the situation for benzenoid hydrocarbons—phenanthrene is more stable than anthracene, since in the first case, two Clar sextets can be drawn.

For all cases studied, the systems with Li-bonded quasi-rings fused to the benzenoid hydrocarbons exhibit much higher stability than the H-bonded ones.

Very different results have been obtained when H^+ is replaced with Li^+, since the lithium is almost symmetrically placed in the ring while the hydrogen has one short and one long bond within the ring. Moreover, it is known that ionic/covalent contributions in the respective interactions are very different. From the calculations, it would appear that the Li-bonded quasi-rings exhibit higher π-electron delocalization than that observed in H-bonded ones. This may be due not only to a stronger ionic character of the lithium bond but also to possible participation of unoccupied 2p lithium orbital in delocalization since the energy of this orbital is significantly lower than that for hydrogen.[28]

The above results are well supported by the HOMA aromaticity index[24] as well as by NICS$(1)_{zz}$ (Table 3).[29]

In all cases, the Li-bonded quasi-ring system has a greater value of HOMA than in the respective H-bonded system. The values of HOMA for the carbocyclic ring and the quasi-ring in the Li-bonded **1** (0.73 and 0.63, respectively) are very similar to that found for naphthalene (0.79). The HOMA values for ring II in Li-bonded **2** and **3** (phenanthrene analogues) are 0.40 and 0.45, respectively, which is similar to the HOMA value of 0.51 found for the central ring in phenanthrene.

The most striking result involves the Li-bonded analogue of **5**, where ring II has a very low HOMA value, 0.11, almost exactly the same as the value found for the central ring in triphenylene (0.17, Clar's empty ring). The case of Li-bonded **4** is less striking; the HOMA values for the ring and the quasi-ring have some similarity to the values found for anthracene. The analogous comparison for H-bonded systems shows that the HOMA values for the rings are more similar to the values found for the respective parent molecules: naphthalene in the case of **2**−**4** and phenanthrene for **5**.

Similar observations were found for NICS$(1)_{zz}$ values as presented in Table 3.

We have also investigated the case where more than one carbocyclic π-electron ring within a single structure is replaced with a six-membered H- or Li-bonded quasi-ring (**6**). This example illustrates that extension of the Clar rule also works for such systems. Figure 2 shows the studied system and variation of HOMA and NICS values for the central benzenoid ring for cases when the hydrogen atoms are replaced, one after another, with lithium atoms. From either index, we observe a progressive decrease of aromaticity within the central ring. In fact, the central ring (IV) becomes essentially "empty", as in the case of triphenylene, according to the Clar rule.

The scatter plots in Figure 2 show evidence of a dependence of HOMA and NICS values on the number of Li^+ replacing the H^+ in the quasi-ring.

Conclusions

The most important conclusion is that Li-bonded β-ketoenolate quasi-ring attached to benzene (or other aromatic system) simulates fairly well the aromatic nature of the ring (or aromatic system), and the extension of the Clar rule to π-electron systems with quasi-ring seems to be well justified. The Clar rule, predicting stability and structural features of benzenoid hydrocarbons, is also a good predictor for related properties in lithium *o*-acylphenolates and, to a lesser extent, on the *o*-acylphenols themselves. Moreover, this also applies in the case when more than one benzene ring in a benzenoid hydrocarbon is replaced with a quasi-ring. These conclusions result from more than one gauge for aromatic character, including energetics, NICS$(1)_{zz}$, and geometry-based analyses across the set of studied systems. The changes in geometry and π-electron delocalization of the central ring in systems analogous to triphenylene provide excellent support for the idea of correlation between physicochemical properties and topology. In general, it may be concluded that topology of the benzenoid hydrocarbon determine π-electron properties of their analogues in which the CH−CH−CH fragment is replaced with O···Li···O or O···H···O.

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Supporting Information Available: Cartesian coordinates of optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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