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On the Intrinsic Difference between Topological Aromaticity and So-Called Quasi-Aromaticity

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In an attempt to understand the intrinsic difference between topological aromaticity and so-called quasi-aromaticity, the authors examined the potential energy and the kinetic energy of electrons in 6-π-acyclic polymethine-like molecules (**5**—**7**), benzene (**8**), and hexatriene (**9**) as a reference structure. Protonation interrupts π conjugation; the energetic difference from the non-protonated structure depends on the conjugative stabilization energy. Such a difference from the reference system corresponds to extra stabilization. Analysis of this difference showed that benzene increases the kinetic energy by interrupting its conjugation more than hexatriene while polymethine-like molecules increase the potential energy by doing so. This indicates that extra stabilizaion in benzene is produced by lowering the kinetic energy of electrons. In marked contrast with this that in polymethine-like molecules is due to lowering the potential energy. Analogous results were obtained in the ten-π-electron systems (**10**—**13**). The authors discussed the inappropriateness of the term "quasi-aromatic" for polymethinic resonance stabilization.

Aromatic compounds have been characterized by the tendency to undergo substitution reactions.[1] Such a characteristic is really applicable to many cyclic conjugated compounds and has been studied topologically[2] as well as by a variety of molecular orbital methods.[3–5] Atoms are arranged in an aromatic compound in such a manner that they induce an appreciable amount of so-called topological resonance energy. This kind of aromaticity will be referred to as topological aromaticity.

It is noteworthy that substitution reactions take place not only in many cyclic but also in some acyclic systems, e.g. some of which not only undergo very easily electrophilic substitution but also nucleophilic substitution followed by a cleavage of the C–C bond.[6] Lloyd and Marshall proposed that molecules should be called quasi-aromatic if they are acyclic conjugated π electron systems with chemical properties typical of aromatic compounds.[7] At the same time Daehne et al. showed that conjugated chain-shaped molecules consisting of n atoms and $n\pm1$ π electrons have unique features which are not comparable to those of aromatic compounds.[8] Therefore, they introduced the term ideal polymethine state to describe the typical properties of resonance stabilized molecular chains. The quantum chemical foundation of this ideal state was given by Fabian and Hartmann.[9] Among such "quasi-aromatics" or "polymethinic" compounds are the 2,3-dihydro-1*H*-1,4-diazepinium salts (**1**),[7,10] α,ω-diazapolymethinium ions (**2**),[8a,11] and transition-metal chelates of diketones (**3**).[12] Noteworthy, however, is that extra stabilization energy scarcely arises from these systems: So-called topological resonance energy is negligible.[13] Recently, Aihara[14] as well as Klein[15] pointed out that quasi-aromatic compounds can be rationalized in terms of Gimarc's topological charge stabilization rule.[16] Our problem is what then is the intrinsic difference between topological aromaticity on the one hand and quasi-aromaticity or polymethinic resonance stabilization or "polymethinicity" on the other hand.

Theory

Molecular energy (E) consists of the electronic energy and the energy of nuclear motion. The kinetic energy of nuclear motion may be treated separately as far as the Born–Oppenheimer approximation operates.[17] Therefore, important energies are the potential energy (V) and the kinetic energy of electrons (T). Those energies can be easily obtained by the ab initio Hartree–Fock theory.

At the optimized structure the system holds the virial relationship, $V=-2T$, as far as all bond lengths, with which the geometry is determined together with bond angles, are optimized with respect to the total energy. As a matter of fact, it is not easy to obtain such a wave function without artificially scaling it. Fortunately, this is not necessary in most case, since we only need the changes of the energy components. For example, the energy difference (by an MO method with any split-valence basis set) between any two sets of geometry-optimized conformations was shown to satisfy the relationship, $\Delta V=-2\Delta T$ (the virial theorem of difference), where ΔT and ΔV are the differences of the kinetic energy and the potential energy.[18c] This shows that the virial errors caused by an inappropriate wave function are cancelled in the differences. The effectiveness of the use of these differences has been discussed in detail[18] and successfully applied in the analyses of π bond formation and conjugations between a π electron system and its substituent.

Now consider a perturbed state such that a proton is loosely put on one of the carbon atoms of the conjugated system. Such a perturbation leads to changes in the total energy and its components, where the simple virial relationship of difference no longer holds, since the system is not in the state of the optimized geometry. Our strategy is to analyze those energy changes by protonation. The basis sets adopted here are 6-31G[19] and 4-31G,[20] which are suitable for the practical analysis of such large molecular systems as those studied here.[18c]

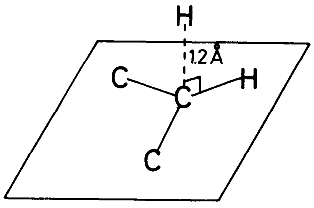
Results and Discussion

Intrinsic Difference of Resonance Stabilizations. We examined the effect of protonation on individual energy terms of π conjugated acyclic compounds (**4**—**7**, **10**, **11**) as well as benzene (**8**) and naphthalene (**12**). Protonation interrupts π conjugation; the difference from the non-protonated structure (ΔE) may depend on the resonance stabilization energy. Analysis of the energy changes in ΔE may reveal the origin of resonance stabilization. In determining the degree of resonance stabilization, e.g. topological aromaticity, of a given compound, one needs the reference structure. The reference structure is considered to have the *standard* conjugation and can be a measure of any type of π conjugation. For cyclic unsaturated hydrocarbons, the linear unsaturated hydrocarbon with the same number of double bonds has once been used as the reference structure.[4] Such a reference structure has later been replaced by a hypothetical structure constructed with bonds of an appropriate infinitely large conjugated system.[2] Although the latter reference structure is desirable, it is not applicable to the present problem. Therefore, we adopted hexatriene (**9**) and decapentaene (**12**) as the reference structures for the six-π-electron and ten-π-electron systems, respectively.

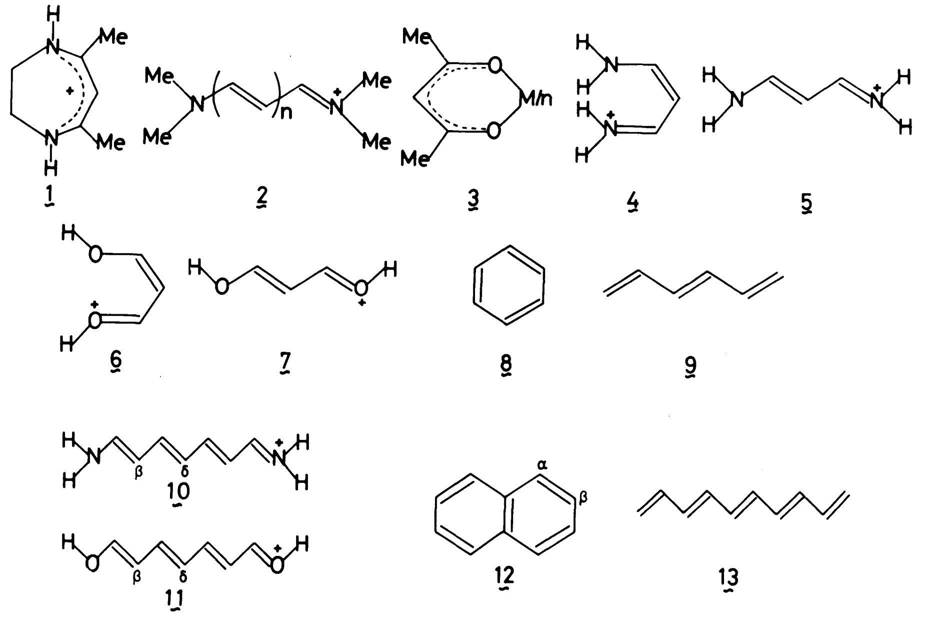
The proton can be placed at any distance from the carbon atom to give a perturbation with shorter distances leading to larger energy changes. Shown in tables are the case where proton was placed 1.2 Å vertically above a carbon atom on the molecular plane (Scheme 2).

Table 1 shows the total energy and its components in the six-π-electron systems. As for the protonated systems only the deviation from the intact systems is recorded. The last column shows the difference in energy from the reference system. In all cases protonation increases the kinetic energy and decreases the potential energy. The latter is larger, resulting in lower total energy by protonation. This is a natural consequence that reflects a localization of π electrons by a broken conjugation.

The energy difference from the reference system is important as is true for determining the degree of aromaticity. Namely, the difference from the reference system corresponds to *extra* stabilization. As shown in



Scheme 2.



Scheme 1.

the last column of Table 1, benzene increases the kinetic energy by interrupting its conjugation more than hexatriene while acyclic conjugated molecules increase the potential energy by doing so. This indicates that resonance stabilization in benzene is produced by the kinetic energy of electrons. In marked contrast with this, that in polymethine-like molecules is due to the potential energy.

Table 1. Change of Total Energy and Its Components by Protonation in 6π Electron Systems

	Intact[a]	Protonated[b]	Difference[c]
Benzene (**8**)			
E	−230.624489	−0.265263	20
T	230.903329	0.537919	42
V	−461.527818	−0.803182	−22
cis-α,ω-Diaminotrimethinium ion (**4**)			
E	−226.267783	−0.095677	465
T	226.453696	0.399686	−321
V	−452.721480	−0.495463	786
trans-α,ω-Diaminotrimethinium ion (**5**)			
E	−226.285304	−0.100065	454
T	226.479256	0.408643	−297
V	−452.764560	−0.508708	751
cis-α,ω-Dihydroxytrimethinium ion (**6**)			
E	−265.841417	−0.052270	579
T	265.949952	0.352943	−443
V	−531.791369	−0.405213	1022
trans-α,ω-Dihydroxytrimethinium ion (**7**)			
E	−265.843424	−0.046499	594
T	265.969946	0.347787	−457
V	−531.813370	−0.394286	1051
Hexatriene (**9**)[d]			
E	−231.725518	−0.272877	
T	232.011570	0.521786	
V	−463.737088	−0.794663	

a) By 6-31G in terms of au. b) Difference from the intact structure. c) Difference from the hexatriene system (kJ mol^{-1}). d) Proton was put on C_3.

Analogous results for the ten-π-electron systems are presented in Table 2. Possible sites of protonation in **10** and **11** are at β and δ carbons. In harmony with the six-π-electron systems, ten-π-electron polymethines give higher potential energy than the corresponding reference structures by protonation while naphthalene gives higher kinetic energy by protonation.

Concluding Remarks

Ichikawa and Ebisawa reported that thermodynamic stability of a topological aromatic system is given by the lowered kinetic energy of π electrons.[5c] The present results for benzene and naphthalene are in good accord with this interpretation of topological aromaticity. From the present study, we come to the conclusion that the resonance stabilization of acyclic conjugated molecules is intrinsically different from that of topological aromatics. Stabilization of topological aromatics is given by the lowered kinetic energy of π electrons whereas that of acyclic polymethine-like molecules by the potential energy. From the above reason the term "quasi-aromatic" connected with resonance-stabilized chain-shaped molecules seems to us misleading, whereas designation such as ideal polymethine state, polymethinic resonance stabilization, or "polymethinicity" much better describe the situation. We caution, however, against over-emphasizing the charge stabilization rule, because there are

Table 2. Change of Total Energy and Its Components by Protonation in 10π Electron Systems

	Intact[a]	Protonated[b]	Difference[c]	Protonated	Difference
Naphthalene (**12**)		α-Protonation		β-Protonation	
E	−382.810012	−0.286775	−13	−0.280042	5
T	383.334234	0.520290	38	0.518230	33
V	−766.144246	−0.807065	−51	−0.798272	−28
α,ω-Diaminoheptamethinium ion (**10**)		β-Protonation		δ-Protonation	
E	−379.612764	−0.169398	295	−0.176990	275
T	380.035021	0.423839	−215	0.427294	−206
V	−759.647785	−0.593237	510	−0.604284	481
α,ω-Dihydroxyheptamethinium ion (**11**)		β-Protonation		δ-Protonation	
E	−419.155002	−0.127994	404	−0.139094	375
T	419.492695	0.371604	−352	0.387287	−311
V	−838.647697	−0.499597	756	−0.526381	686
Decapentaene (**13**)		C_5-Protonation			
E	−385.036761	−0.282039			
T	385.549432	0.505638			
V	−770.586193	−0.787677			

a) By 4-31G in terms of au. b) Difference from the intact structure. c) Difference from the decapentaene system (kJ mol^{-1}).

two basic phenomenological preconditions of maximum resonance stabilization of chain-shaped molecules,[8,9] i.e., not only certain charge alternation but also maximum bond order equalization.

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