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Topological Charge Stabilization Rule and Quasi-Aromaticity

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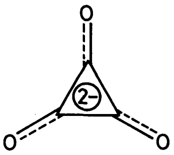
Synopsis. Stabilities of the oxocarbon dianions and some quasi-aromatic compounds can be rationalized in terms of Gimarc's topological charge stabilization rule. The term "quasi-aromatic" is recommended for describing those non-aromatic compounds which behave like aromatics owing to the operation of this rule.

Monocyclic oxocarbon dianions with the general formula $C_nO_n^{2-}$ (**1**—**4**) are fairly stable substances.[1,2] West et al.[1,3] and Herndon[4] considered them as a kind of aromatic species, stabilized by π electron delocalization around the ring. Two research groups, however, showed that extra stabilization energy scarcely arises from the cyclic conjugation in these ions.[5,6] So-called topological resonance energy (TRE) is very small except the deltate dianion (**1**).[5] Only $C_3O_3^{2-}$ seems to be aromatic with large TRE. Associating bond orders with aromaticity, Jug showed that for the oxocarbon dianions the aromaticity decreases rapidly as the ring size increases.[7]

In 1964 Lloyd and Marshall proposed that molecules should be called quasi-aromatic only if they contain an acyclic conjugated π-electron system and show chemical properties typical of aromatic compounds, especially reaction by substitution with retention of the original conjugated system.[8] They first used the term "quasi-aromatic" with this meaning to describe the behavior of the 2,3-dihydro-1,4-diazepinium salts (**5**).[8,9] The α,ω-diazapolymethinium salts (**6**)[10] and the transition-metal chelates of β-diketones (**7**)[11] can also be classified as quasi-aromatics. Although the metal chelates of acetylacetone apparently have a cyclic conjugated system, Musso et al. demonstrated that no ring currents are induced in these complexes.[12] This indicates that the π-electron conjugation is interrupted at the metal atom. All these quasi-aromatic species have no TRE since there are no cyclic paths for π electrons.

What then is the main origin of stability of the monocyclic oxocarbon dianions and the quasi-aromatic compounds? It is very true that their aromatic behavior and stability cannot be related to the cyclic conjugation of π electrons. The purpose of this note is to solve this problem using Gimarc's topological charge stabilization rule.[13-15]



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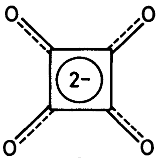

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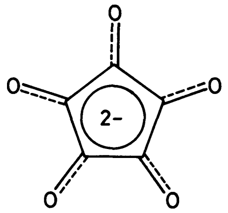

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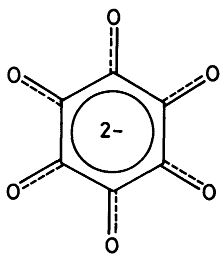

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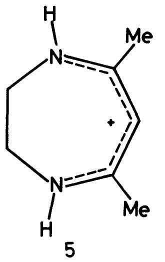

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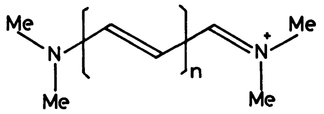

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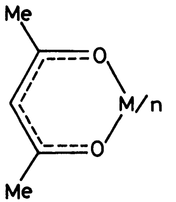

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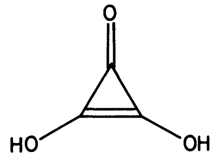

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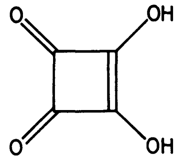

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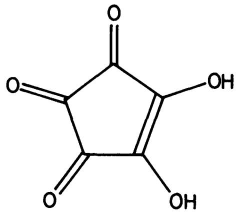

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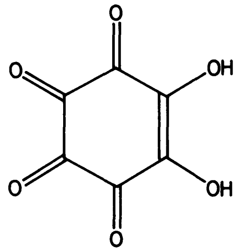

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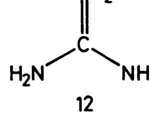

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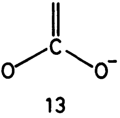

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In 1983 Gimarc stressed that the pattern of charge densities in a molecule is determined primarily by the connectivity or topology of the molecule.[13,14] Many examples showed that nature prefers to place atoms of greater electronegativity in those positions where the topology of the structure tends to pile up extra charge in the isoelectronic hydrocarbon.[13,15] Since such heteroatomic systems are preferentially stabilized by molecular topology, Gimarc called the effect the rule of topological charge stabilization.[13]

Oxocarbon Dianions

An oxocarbon dianion with n carbonyl groups is referred to as [n]oxocarbon dianion. Radialene with n exomethylenes is likewise referred to as [n]radialene. The [n]radialene dianion is iso-π-electronic with the [n]oxocarbon dianion. Such an iso-π-electronic hydrocarbon has been called a uniform reference frame (URF).[13] The [n]oxocarbon dianion and its URF have the same geometry with the same number of π electrons ($2n+2$). Charge densities were calculated for the URF's of **1**—**4**, (i.e., four radialene dianions) using the simple HMO model. They are shown in Fig. 1.

It is noteworthy that these radialene dianions have maximum charge densities at the exomethylene carbons. The oxocarbon dianions are formed by replacing all these carbons by more electronegative oxygens. Thus, the framework of every oxocarbon dianion is favored from the standpoint of the topological charge stabilization rule.[13] In other words, the stability of most oxocarbon dianions is largely due to the presence of oxygens at positions where, for purely geometrical reasons, the π electrons congregate.[13,14] This possibly constitutes the primary reason why the oxocarbon dianions have often been regarded as aromatics.

Many oxocarbon analogues have been synthesized by replacing one or more oxygens by other hetero atoms, such as nitrogens and sulfurs.[1,2] The topological charge stabilization rule necessarily operates in these compounds.

Oxocarbon acids of the general formula $C_nO_nH_2$ (**8**—**11**)[1,2] are acids conjugate to the oxocarbon dianions. The URF of each oxocarbon acid is identical with that of the corresponding oxocarbon dianion. A given oxocarbon acid is formed by replacing two of the exomethylene carbons in the URF by hydroxyl oxygens and the remaining ones by carbonyl oxygens. Thus, the carbons of maximum charge density in the URF are all replaced by electronegative oxygens. All oxocarbon acids are known indeed.

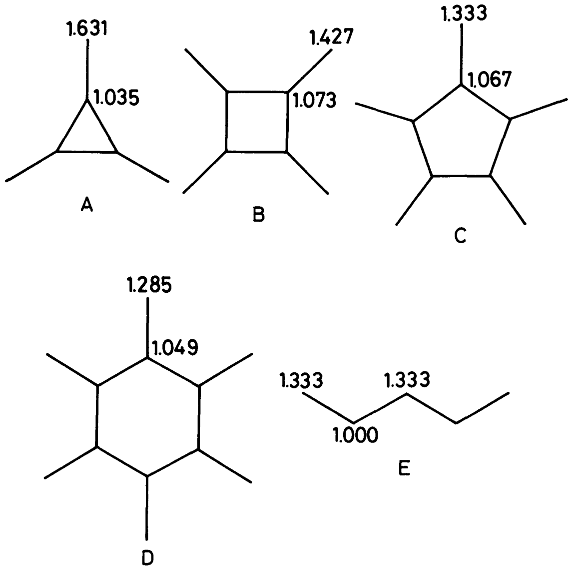

Fig. 1. Charge densities in: (A) the [3]radialene dianion (the URF of **1**); (B) the [4]radialene dianion (the URF of **2**); (C) the [5]radialene dianion (the URF of **3**); (D) the [6]radialene dianion (the URF of **4**); and (E) the pentadienide anion (the URF of **5** and **7**).

Unfortunately, the topological charge stabilization rule is not applicable to the neutral oxocarbons (C_nO_n). The URF of neutral [$2m$]oxocarbon is [$2m$]radialene. Since this is an alternant hydrocarbon, the charge distribution is uniform over the entire conjugated system. A similar situation is seen in the case of the URF of neutral [$2m+1$]oxocarbon. Although [$2m+1$]radialene is not an alternant hydrocarbon, the charge distribution is fairly uniform. These facts may not account for the instability of neutral oxocarbons, but coincide with it.

Quasi-Aromatic Compounds

Pentadienide ion ($C_5H_7^-$) is iso-π-electronic with the conjugated systems of the quasi-aromatic compounds **5** and **7**. As shown in Fig. 1, this URF has the maximum charge densities at one central and two edge carbons. If the two edge carbons are replaced by electronegative nitrogens, in such a manner that the entire conjugated system preserves the number of π electrons, we obtain the conjugated system of the 2,3-dihydro-1,4-diazepinium ion (**5**). If they are replaced by oxygens, we obtain the conjugated subsystem of the β-diketonate ion in **7**. Therefore, the stability of these quasi-aromatic systems can again be rationalized by the topological charge stabilization rule. A similar explanation applies to the quasi-aromaticity of other α,ω-polymethinium ions (**6**). We might safely say that the tendency of these compounds to retain the original conjugated system[8] arises primarily from such topological charge stabilization in the ground electronic state.

Concluding Remarks

The oxocarbon dianions and some acyclic systems have been classified as aromatics or quasi-aromatics although they have essentially zero TRE. It was shown that chemical behaviors and stability of these compounds can be rationalized well in terms of the topological charge stabilization rule. These compounds are thermodynamically favored since the constituent atoms are arranged such that their electronegativities match the pattern of charge densities of the iso-π-electronic hydrocarbon.[13,14] Considering that there have been no other widely accepted theories for the stability of these compounds, the present simple rationale seems to be the best one available.

It is suggested that to avoid confusion the term "aromatic" be restricted to compounds with relatively large TRE.[5] The term "quasi-aromatic" is instead recommended for describing those essentially nonaromatic conjugated compounds which tend to retain their own conjugated systems. The quasi-aromatic compounds defined here are those which are stabilized by the operation of the topological charge stabilization rule but not by cyclic conjugation. The oxocarbon dianions with $n>3$ should be classified as quasi-aromatic compounds, rather than as aromatic compounds.

As already pointed out by Gimarc,[13] Y-aromaticity in guanidinium (**12**) and carbonate (**13**) ions[16] can also be rationalized in terms of the topological charge stabilization rule. These Y-aromatic compounds should again be classified as quasi-aromatic species.

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