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Quasi-aromaticity—what does it mean?

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1. Introduction

Aromaticity is one of the most popular and useful concepts in organic chemistry. Every day more than 30 papers appear in which the term 'aromaticity' is used either in the title, key words or in the abstract.[1] However, apart from applying this term in its original form and sense, the term 'aromaticity' has recently been used with a lot of different prefixes[2–5] such as anti-,[2] pseudo-,[2] hetero-,[6] homo-,[7] σ-,[8] spherical-,[9,10] Mobius-,[11] all-metal-,[12] three-dimensional-,[13] and many others. A common feature of these *prefixed-aromaticities* is that some (but not all) typical properties of the 'proper' (in other words, classical) aromatic compounds appear in many, sometimes very different, kinds of molecules. Hence it is necessary to apply prefixes to specify a particular kind of various applications of the term 'aromaticity'.

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Quasi-aromaticity is probably the only one of these *prefixed-aromaticities* that has not yet been reviewed, despite a very long history of its existence. Almost seventy years ago Calvin and Wilson[14] documented an increased stability of chelating substances of the kind presented in Fig. 1 in which hydrogen was replaced by the metal cation. This observation was related to the resonance effect, which now we could call an increased π-electron delocalization in the chelating chain.
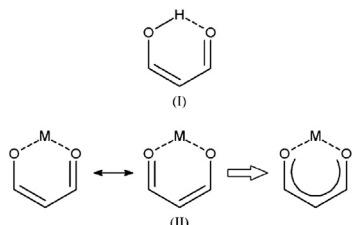

Fig. 1. Schemes of quasi-aromatic systems with chelating proton (I) and metal cation (II). CH bonds are not shown.

For the first time the term *quasi-aromaticity* was applied to describe[15] the chelating structure of phenylosazone in which '*sharply defined azo- and hydrazo structures disappear*'. In other words, due to the resonance effect within the chelating chain some kind of π-electron delocalization occurred and no typically single or double bonds were observed. Finally, at The Jerusalem Symposia on Quantum Chemistry and Biochemistry 'Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity'[16] the following definition of quasi-aromaticity was suggested: '… **the 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 type. The significant mesomeric stability is implied**.'[17] In the lecture by Lloyd and Marshall[16] many examples of this kind of reactivity are presented.[18–24] Thus, one of the most important criteria of aromaticity was already fulfilled at that time. In order to have a deeper insight into the problem of relations between different behaviour of chelating systems and aromaticity it is advisable to start from the definition of aromaticity. It is enumerative in nature and hence there are a few criteria, which have to be fulfilled to accept a given molecule as aromatic. Its classical definition was presented in Tetrahedron Report 520:[25] aromatic are planar, cyclic π-electron compounds, which fulfill the following qualitative criteria:

  i) they are more stable than their acyclic unsaturated analogues,
  ii) they have less alternated bond lengths than their acyclic unsaturated analogues,
  iii) the external magnetic field induces in them diatropic ring currents,
  iv) they have a tendency to retain π-electron structure in chemical reactions

The purpose of this review is to discuss how the above criteria of aromaticity are fulfilled in chelated systems named *quasi-aromatic*. From the formal and structural viewpoint cyclic π-electron systems in which three units as CH−CH−CH are replaced by −Y···M(+)···X−, where X and Y are electronegative atoms that are able to chelate atoms/ions as proton or cations of the first and second group of the Periodic Table behave as if they were aromatic (see Fig. 1). It should be noted that **quasi-aromaticity differs from metalloaromaticity[26] by the nature of the coordination centre involved: in quasi-aromatic systems it is either hydrogen or the atoms, which do not participate in π-electron delocalization that operate in the chelate part of the system.** A good example of formation of the quasi-aromatic system is shown in Fig. 2, where open and closed conformers of malonaldehyde exhibit completely different properties: the closed conformer is more stable by 12.96 kcal/mol[27] (estimated at B3LYP/6-311+G(d,p) level of theory), and its bonds are less alternated than in the open one. The absolute values of differences between CO and CC bond lengths in the closed form are 0.082 and 0.074 Å as compared with 0.129 and 0.118 Å in the open form. Obviously, a smaller alternation in the closed form is observed, and hence the name of quasi-aromatic ring may be used here.
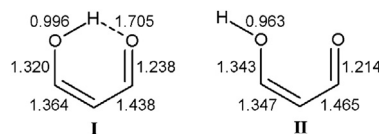

Fig. 2. Schemes of malonaldehyde in 'closed' (I) and 'open' form (II). ΔE for I and II equals 12.96 kcal/mol.[27]

In general, π-electron delocalization is observed in a sequence of bonds between atoms, which are π-centres whereas the chelated ion does not participate in this process except some electrostatic influence on chelating atoms and then further on the whole ring.[28]

As fundamental ideas, the criteria (i)–(iv) are clear. Nevertheless, it should be noted that:

(a) none of the above-presented criteria and numerical indices resulting from them is sufficient in their description of aromaticity, therefore it is most useful to apply many of them to get the most reliable result.[29–31]

(b) in many cases of various series of the analyzed compounds a statistical multidimensionality is observed. This means that the applied indexes of aromaticity do not always speak with one voice.[32–37]

(c) Finally, it should be noted that in many cases the application of the above-mentioned criteria and the indexes resulting from them have limited applications. In what follows some aspects of these limitations will be presented, to warn the reader that in many cases no absolute conclusion can be drawn. Now let us look at and present shortly some details showing the limitations of the application of criteria (i)–(iv).

Ad (i) The concept of resonance energy (RE) introduced by Pauling et al.[38] and Kistiakovsky et al.[39] works for simple hydrocarbons, but it is difficult to be applied in the case of more complex systems.[40] Apart from the complexity of the systems in question, (too big systems, strain, various heteroatoms involved), there are a few sources of limitation. Firstly, in a virtual reaction defining aromatic stabilization energy (named ASE) it is necessary to find a way to compensate additional effects, which appear in the reference system and, which are not due to the lack of aromaticity itself. Depending on the kind of reference systems and nature of the hypothetical reaction stabilization energies computed for benzene are in the range 18.4–66.9 kcal/mol[40]—if all side effects are eliminated (protobranching, hyperconjugation, strain etc.)[41] the stabilisation energy lies in the range 64.9–69.0 kcal/mol. This result is very important for any use of the energetic criterion of aromaticity, but the procedure is difficult to be applied for complex systems particularly those, which contain heteroatoms. Nevertheless, it is an interesting field for further exploration, and recently great progress was made,[42] but unfortunately only in the field of π-electron hydrocarbons. Despite the above-presented reservations, the energetic criterion of aromaticity seems to be accepted as the most important one.