Paradoxes and Paradigms: Are Maleimides Antiaromatic, Aromatic, or Neither?

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Abstract: The maleimide moiety is present in numerous species of commercial or theoretical interest. The resemblance of maleimide to aromatic pyrrole raise the question of the aromaticity of the former. Are maleimides aromatic or antiaromatic, or neither? Should they be described as N-substituted derivatives of (2,5-dihydro)pyrrole-2,5-dione or as pyrrole-2,5-dioxy biradical? Through an analysis of the energetics of neutral and ionic species alike, the former description is to be preferred with only minimal antiaromaticity associated with its 4 π electrons.

Keywords: Antiaromaticity, aromaticity; enthalpy of formation; maleimides; N-substituted (2,5-dihydro)pyrrole-2,5-dione; pyrrole-2,5-dioxy biradical

The maleimide (pyrrole-2,5-dione) moiety (**1**) is present in numerous molecules of commercial or theoretical interest, including pharmaceuticals [1-4], fluorescent probes [5-8], fluorophores [9-14] and photoswitches [15-17]. Maleimide is also employed as bioconjugatable reactive group, due to the great reactivity of its C=C bond towards nucleophiles. [18]. Maleimide derivatives are useful building blocks and structural motifs utilized in, for example, helicenes [19,20] and multichromophoric arrays [21, 22]. In addition, maleimide is a powerful dienophile in Diels-Alder reaction, which is justified by the presence of olefin substituted by two electron-withdrawing carbonyl groups [for selected examples of applications of maleimide in the Diels-Alder reaction, see [23-28].

The resemblance of maleimide to aromatic pyrrole raise the question on the aromaticity of the former. Particularly intriguing is the question on extent in which aromatic pyrrole-2,5-dioxy biradical (**2**) contributes to the structure of maleimide. In this regard, maleimide can be considered as an analog of quinone. The biradical character has been postulated for more elaborated quinoidal pyrrole derivatives. [29,30] We, thus analyzed here the maleimide, as a simplest quinoidal pyrrole derivative. Note, that simple quinodimethane pyrrole derivatives (**3**) received only limited attention [31], although this motif is present in porphyrins, [32] and the related chlorins, [33] corrins, [34, 35] and other cyclic [36] and acyclic [37,38] oligopyrrolic compounds. We thereby will ignore all quinodimethane derivatives. [39, 40]. We limit our analyses to maleimide derivatives, and therefore exclude the analogous five membered dicarbonyl compound (i.e., maleic anhydride), as well as phthalimide, due to the importance and the prevalence of the maleimide, discussed above, and due to the potential importance of our discussion to the chemistry of porphyrins and related species.

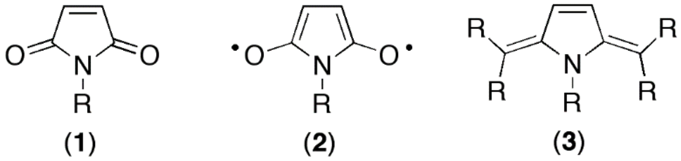
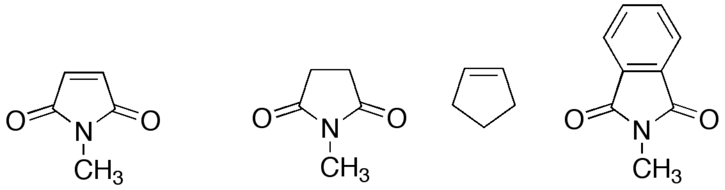


Figure 1. Structures of maleimide (**1**), pyrrole-2,5-dioxy biradical (**2**), and quinodimethane pyrrole derivative (**3**).

In the current study we briefly discuss the electronic description and energetics of maleimides. Should they be understood as N-substituted 2,5-dihydropyrrole-2,5-diones, **1**, and hence antiaromatic and therefore destabilized because of 4π electrons in the heterocyclic ring? Or should these species be understood as pyrrole-2,5-dioxy biradicals, **2**, and therefore stabilized because of 6π electrons in its ring? Let us start with our discussion with a brief return to the measurement of the enthalpy of formation of a particularly simple maleimide, the N-methyl derivative **4** (Figure 2) [41]. We now acknowledge that species is the sole maleimide for which there is a measured enthalpy of combustion and accompanying enthalpy of formation. We also note that our thermochemical discussion emphasizes gas phase species. While this is rarely the phase that most organic chemists consider, absent are any intermolecular interactions that characterize the condensed phase, whether it be a solution or the pure liquid or solid. More precisely, we now give the enthalpies of formation of gaseous N-methylmaleimide, the species of interest as a solid, and for the enthalpy of sublimation that connects these two quantities: -329.3 ± 1.4, -256.0 ± 1.5 and 73.3 ± 0.5 kJ mol^{-1} respectively. [41] (These values, and all others in the current paper, are in kJ mol^{-1}, where by definition 1 kJ mol^{-1} = 1/4.184 kcal mol^{-1}. Furthermore, we will always implicitly refer to the gaseous species of interest at the "standard conditions" of 25°C and 1 atm.) In ref. [41] we find considerations of the hydrogenation of N-methylmaleimide resulting in N-methylsuccinimide **5** (Figure 2). Comparison was explicitly made with the nonaromatic cyclopentene and the resultant cyclopentane. In that the value of the hydrogenation enthalpy of N-methylmaleimide (137 kJ mol^{-1}) is 27 kJ mol^{-1} larger than the nonaromatic cyclopentene **6** (110 kJ mol^{-1}), suggests that N-methylmaleimide is antiaromatic by 137 – 110 = 27 kJ mol^{-1}.

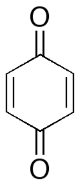


(**4**) (**5**) (**6**) (**7**)

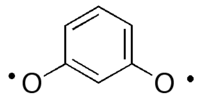
Figure 2. Structures of *N*-methyl maleimide (**4**), N-methylsuccinimide (**5**), ceclopentene (**6**), and N-methylphthalimide (**7**).

Alternatively, from the enthalpy of formation values in ref. [39] we find that the formal benzo-annelation of N-methylmaleimide to form N-methylphthalimide **7** is accompanied by an almost zero change. By contrast, the increase from cyclopentadiene to its benzo-analog indene is ca. 27 kJ mol^{-1} endothermic. The enthalpy of formation change associated with the unequivocally aromatic benzene to form naphthalene is endothermic by ca. 70 kJ mol^{-1}. The aforementioned ca. 30 kJ mol^{-1} difference of cyclopentene and N-methylmaleimide may be ascribed to the antiaromaticity of the latter species, in encouraging agreement with that suggested by our benzo-annelation logic. (For general discussions of aromaticity within the context of the energetics associated with benzo-annelation, see [42, 43])

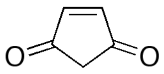
It Is tempting to compare N-methyl-2,5-dihydropyrrole-2,5-dione, **1**, and N-methyl-2,5-pyrrole-2,5-dioxy biradical, **2**, with cyclo-1,4-hexadiene-2,5-dione **8** (Joel,is this a correct name? Do you mean 1,4-hexadiene3,6-dione?) and benzene-1,3-dioxy biradical **9** (Figure 3). More precisely, the first entry for both pairs of compounds is a dione affixed to a nonaromatic backbone, while the second entry shows an aromatic backbone with two affixed oxy radicals. Let us now use more common names for cyclo-1,4-hexadiene-2,5-dione and benzene-1,3-dioxy biradical, species better known as p-benzoquinone and m-benzoquinone. Let us adopt the findings of ref. [44] or both species. The former isomer is considerably more stable than the latter, the recommended enthalpies of formation are -116 ± 13 and 28 ± 17 kJ mol^{-1}, a difference of 144 ± 20 kJ mol^{-1}. Relatedly, the enthalpy of hydrogenation to the corresponding p- and m-benzenediols (hydroquinone and resorcinol respectively) are 160 ± 13 and 313 ± 17 kJ mol^{-1}. This results in a difference of 153 ± 21 kJ mol^{-1}, that of m-benzoquinone that much higher. For the reader who is much more comfortable with results from classical calorimetric measurements than those using the analysis of ion-molecule reactions, and thereby deprived of all information about m-benzoquinone, the recommended enthalpies of formation of (gas phase) p-benzoquinone [43] and hydroquinone [44] are -119 ± 1 and -261 ± 1 kJ mol^{-1} respectively. This corresponds to a hydrogenation enthalpy of p-benzoquinone of 142 ± 2 kJ mol^{-1} . It is thus found that the values of the enthalpies of formation and hydrogenation of p-benzoquinone found by two methodologically independent studies are consistent within recommended error bars.



(**8**)



(**9**)

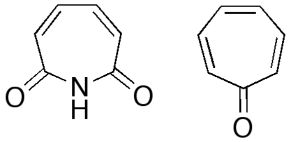


(**10**)

Figure 3. Structures of *p*-benzoquinone (**8**), benzene-1,3-dioxy biradical (**9**), and cyclopentene-3,5-dione (**10**).

This encourages us to trust the corresponding values for m-benzoquinone. As such, we trust the values for N-methyl-2,5-dihydropyrrole-2,5-dione and N-methyl-2,5-pyrrole-2,5-dioxy biradical and the derived conclusion that the former is much more stable. In other words, the description of maleimide as the classical 4 π and so possibly antiaromatic species **1** is more correct than the plausible 6 π and so possible aromatic diradical **2**. Gaining the conventionally high degree of aromaticity of benzene, and the lessened aromaticity of pyrrole, upon diradical formation are insufficient to overcome the loss of two carbonyl π bonds upon "conversion" of **1** into **2**.

Another study of the energetics of quinones involved gas phase electron affinity measurements. Perhaps not surprisingly the electron affinity of the m-isomer is found to be greater than that of the p-isomer by ca 95 kJ mol^{-1} [43, 47]. Upon formation of the isomeric semiquinone, less carbon-oxygen π bonding is lost for the m- than its p-isomer. This discussion of electron affinities returns us to the electron affinity of N-methylmaleimide. The aforementioned high dienophilicity of maleimides in [4 + 2] cycloaddition reactions suggests a high electron affinity. The electron affinity of a variety of N-substituted maleimides have been studied [48] and the value is ca. 110 kJ mol^{-1} regardless of the group on nitrogen. This invariance is quite surprising. Even more so is that roughly the same value is found for the isoelectronic carbocycle cyclopentene-3,5-dione **10** (Figure 3) in which >CH_2 has replaced the various >NR groups. These findings would be hard to reconcile if the maleimides were, in fact, pyrrole-2,5-dioxy radicals.



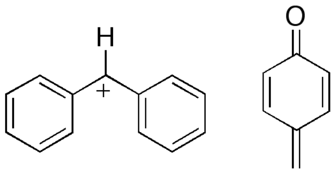
(11) (**12**)

Figure 4. Structures of azepine-2,7-dione (**11**) and tropone (**12**).

Now, should maleimides have only minimal antiaromaticity, then the related ring-expanded species with 6 π electrons, alternatively named azepine-2,7-dione and muconimides **11** (Figure 4), would be expected to be but weakly aromatic. Indeed, the

N-methyl derivative muconimide has been suggested [49] to have less aromatic character than the π-isoelectronic tropone **12** (Figure 4), a carbocyclic species long documented to be but weakly aromatic [50, 51, 52]. We would relatedly suggest that maleimides should be less antiaromatic than the π-isoelectronic tropone and muconimide are aromatic. In turn, the aromaticity of tropone would be expected to be less than the antiaromaticity of cyclopentadienone [52]. Using methodologies analogous to that earlier employed for the isomeric benzoquinones, cyclopentadienone has been suggested to have negligible antiaromaticity [53]. Once again, we conclude that maleimides enjoy little antiaromatic character.

Yet another probe of the aromaticity/antiaromaticity of maleimides is shown by reactions with diversely substituted benzhydrylium ions **13** and quinone methides **14** (in aprotic solvents, Figure 5) the nucleophilicity of a large variety of N-based anions has been determined [54]. These studies showed that the anions of maleimide and succinimide, as their potassium salts, have very nearly the same nucleophilicity, the former slightly higher suggested therein to be due to “the higher electronegativity of sp^2 - compared to sp^3 -hybridized carbon atoms.”. No effect arising from any difference in the aromaticity/antiaromaticity of the two anions was suggested.



(**13**) (**14**)

Figure 5. Structures of benzhydrylium ions (**13**), and quinone methide (**14**).

We thus conclude that N-maleimides exhibit only a small degree of aromaticity or antiaromaticity, and that these species are not to be understood as pyrrole-2,5-dioxy biradical derivatives.

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Author contribution

J. F. L. designed the study and wrote the manuscript, M. P. wrote the introduction and contributed to the study design.

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Code applicability

Not applicable

Data availability

Not applicable.

Declarations

Ethical approval

We did not perform any experiments when preparing this article, so neither ethics review nor informed consent was necessary.

Consent to participate

Both authors agreed with participation in research and publication of the results.

Consent to publish

Both authors have approved the manuscript before submission, including the names and order of authors.

Competing interests

The authors declare no competing interests

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