Quantification of Aromaticity in Oxocarbons: The Problem of the Fictitious “Nonaromatic” Reference System

David Quiñonero, Carolina Garau, Antonio Frontera,* Pablo Ballester, Antonio Costa, and Pere M. Deyà*[a]

Abstract: Despite the extensive research reported in the literature, the concept of aromaticity has eluded rigorous quantification. The main reason for this undesirable reality is the fact that aromaticity is a differential property. While bond orders, atomic charges and electronegativity differences are properties of the molecule under analysis, the aromaticity concept often refers to the difference between some property of the molecule and that of an artificial “nonaromatic” reference system. A rigorous definition of such a reference system is non-existing and therefore constituting the main barrier to obtain a satisfactory quantification of the aromatic concept. Oxocarbon acids and their anions are examples where the criteria of aromaticity that use reference systems are unsuccessful, only NICS criterion gives satisfactory results. Wiberg bond indexes and ^{17}O NMR chemical shifts are also useful to study such compounds.

Keywords: ab initio calculations · aromaticity · NMR chemical shifts · oxocarbons

Introduction

Quantification of aromaticity involves the evaluation of properties that are exclusively characteristic of aromatic systems. The most widely used measures of the degree of aromaticity[1] are energetic,[2] structural[3] and magnetic properties.[4] First of all, estimates of aromatic stabilization energies (ASE) by means of homomolecular differential bond separation reactions vary significantly and are strongly dependent not only on the equation type used (isodesmic, homodesmotic, hyperhomodesmotic, etc.),[5] but also on reference systems adopted and computational levels and basis sets. Furthermore, aromatic stabilization energies do not measure aromaticity itself but rather energy nonadditivities due to all nontransferable effects.[6] The determination of ASEs in five-membered organic heterocycles involving the use of homodesmotic reactions are examples of the above mentioned restrictions; whereas values reported by Schleyer et al.[6] and by Chesnut and Davis[5] are in a reasonably agreement, the results published by Nyulaszi et al.[7] differ by an average of 8.5 kcal mol^{-1}. Moreover, ASEs of strained and complicated systems are difficult to evaluate.[8]

Several structural criteria have been proposed based on bond length (e.g., Julg[9] aromaticity index) and on bond order considerations (e.g., Bird[10] and Jug[11] indexes). The Bird index[10] (I) uses bond orders computed from the bond length by means of an empirical formula, and then averaged. It has been applied to five (I_5) and six-membered (I_6) heterocycles. However, some discrepancies are inherent to this method, namely, it assumes the same I_6 value for benzene, 1,3,5-triazine and the cyclic N_6 molecule and this regardless of the striking differences in stability of those molecules. The Jug index[11] is based on the smallest bond order within the ring following the idea that the weaker the bond, the more significant the diminution of the ring current.

Magnetic criteria based on magnetic susceptibilities have also been used as a measure of aromaticity. The crucial characteristic of an aromatic ring is the existence of a permanent diatropic ring current. Since the magnitudes of the diamagnetic susceptibility along the three axes in a molecule are not equal—the magnetic susceptibility perpendicular to the ring plane is much greater than that in the ring plane—most diamagnetic molecules are anisotropic. As a result, the difference between the magnetic susceptibility anisotropy of an aromatic compound (χ_M) and a corresponding hypothetical analogue lacking cyclic delocalization (χ_M') is the magnetic susceptibility exaltation ($\Lambda = \chi_M - \chi_M'$). It has been proposed as a measure of aromaticity. It has been shown that it is highly dependent on the ring size and requires calibration standards.[12]

It should be emphasized that none of the aromaticity indexes hitherto defined is by itself completely satisfactory. In fact, it is generally assumed, for example, that geometric criteria must be considered along with others.

The characteristic ^{1}H NMR chemical shifts of aromatic molecules are usually ascribed to the existence of ring current

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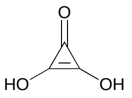
effects.[13] Following this reasoning, Schleyer et al.[14] have recently proposed the use of the negative of the computed magnetic shielding at the ring centers, referred to "nucleus-independent chemical shift" (NICS) as an effective criterion for aromaticity and antiaromaticity. NICS does not require reference systems and is also not dependent on the ring size. Other groups[15] have also applied satisfactorily the NICS method to study different kinds of romatic compounds, for example: heterocyclic 2π electron aromatic systems,[16] pyridone derivatives,[17] 4-silaltriafulvene,[18] *N*-heterocyclic carbene, sililene and germilene complexes.[19]

In spite of this, some aspects of the problem remain unanswered. Schleyer claimed[6] to have demonstrated the quantitative relationship among the magnetic, energetic and geometric criteria of aromaticity for a wide ranging set of five-membered heterocycles. In contrast, Katrizky et al. affirmed[20] and reaffirm[21] the multidimensional characteristic of the aromaticity showing that the linear relationship between the aforementioned properties is invalid for any representative set of heteroaromatic compounds in which the number of heteroatoms varies. Particularly, Katrizky reported that no linear relationship ($R^2 = 0.034$) exists between Λ and ASE using a set of 19 aromatic and heteroaromatic compounds. As a matter of fact, since both Λ and ASE need the use of artificial "nonaromatic" reference systems, it is not surprising that the plot of one versus the other leads to an uncorrelated scatterplot.

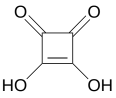
Oxocarbons and their derivatives have attracted the attention of many theoretical and experimental researchers. In 1960 West et al.[22] recognized cyclic oxocarbon dianions as aromatic systems, stabilized by the delocalization of π-electrons and suggested that they constitute a series of aromatic compounds. The latter generalization was questioned by Aihara[23] proposing that only deltate dianion is diatropic and aromatic. Subsequently, Jug,[11] following the geometric criterion based on his bond order index, stated that no aromaticity is expected for rings with six or more atoms, and concluded that the aromaticity decreases with the ring size, considering croconate, squarate and deltate as moderately aromatic. Recently, Schleyer et al.[24] considered three types of equations to evaluate the ASEs of oxocarbon dianions but none of them was able to give satisfactory results, due to the difficult design of equations free from other influences. Similar behaviour was observed for Λ, where the obtained results were also contradictory. Finally, by considering the NICS calculations along with other bond length criteria[25] we explained the remarkable hydrogen bond acceptor character of squaramide derivatives, acting as binding units in several tripodal receptors,[26–28] promoted by the gain in aromaticity of the corresponding squaramide ring on complexation with ammonium cations.

These highly functionalized small rings are representative examples where homodesmotic equations are not applicable and, consequently, it is not possible to measure accurately ASE, Λ, and other aromatic indexes where nonaromatic reference systems are needed.

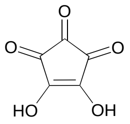
The aim of this paper is to review the aromaticity criteria using previously reported data, as well as, our own calculations on aromatic compounds. We are also interested in the study concerning the aromaticity of oxocarbons and its derivatives to continue our recent experimental[26–28] and theoretical[25, 29] findings on this interesting class of compounds. Our study will be carried out using NICS, but also Wiberg bond indexes (WBI) and ^{17}O NMR calculated chemical shifts.



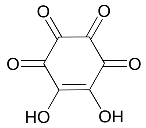
deltic acid



squaric acid



croconic acid



rhodizonic acid

Computational Methods

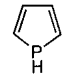
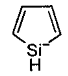
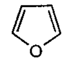
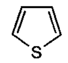
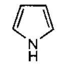
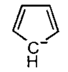
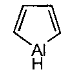
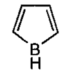
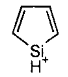
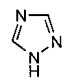
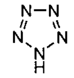
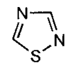
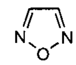
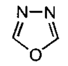
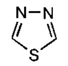
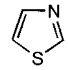
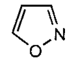
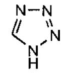
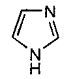
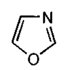
Geometries were optimized first at the HF/6-311+G** level and further reoptimized at MP2/6-311+G** level by using the Gaussian 98 program package.[30] Absolute NMR shieldings were calculated using the GIAO method[31] at both HF/6-311+G**//MP2/6-311+G** and MP2/6-311+G**//MP2/6-311+G** levels in order to evaluate the effect of including electron correlation, which is expected to become more significant in unsaturated compounds.[32] NICS values were obtained by calculating the absolute NMR shielding at the ring centers and at 0.6 Å above them in order to reduce the local shielding of nearby σ-bonds which complicates the analysis for small rings. The maximum diatropic ring current effect for benzene is in the center of the ring, but is offset by the paratropic contribution of the C–H and C–C σ-bonds. These paratropic effects decrease more rapidly than the diatropic ones away from the center. Therefore, NICS values at 0.6 Å above the ring minimize the paratropic effect and give a more reliable indication of aromaticity. The NICS values present in Table 1 were calculated at HF/6-31+G** in order to be comparable with those previously published by Schleyer et al.[14] Wiberg bond indices[33] were computed at HF/6-311+G**//MP2/6-311+G** level of theory using the NBO program[34] implemented in Gaussian 98.

Results and Discussion

As previously mentioned, Katrizky[21] claimed that the plot of magnetic susceptibility exaltation Λ versus ASE for a set of 19 aromatic and heteroaromatic compounds does not show a linear relationship, as the corresponding R^2 factor equals to 0.034; this indicates the multidimensionality of the aromaticity. Conversely, Schleyer[6] insisted to have shown that linear relationships exist among the energetic, geometric and magnetic criteria of aromaticity and that these relationships extend from highly antiaromatic to highly aromatic compounds. Since both Λ and ASE are dependent of reference systems, we have calculated the NICS values for the compounds shown in Table 1 apart from those previously reported by Schleyer, which are also included in the Table.[14] Since NICS does not need increment systems or reference molecules for evaluation, the plot of NICS versus ASE reveals an acceptable linear correlation ($R = 0.944$) for this representative set of heteroaromatic compounds in which the number of heteroatoms varies, thus supporting the idea that NICS is an effective aromaticity criterion (Figure 1).

Aimed with the preliminary results, NICS will be used to study the aromaticity of oxocarbon acids and their derivatives, namely squaramide and its complex with ammonium cation. Other energetic, magnetic and geometric criteria will be used for comparison purposes. Among them, ^{17}O NMR chemical

Table 1. ASE [kcal mol^{-1}], Λ (ppm cgs) and NICS (ppm) calculated values for some five-membered heteroaromatic compounds.

Name	Structure	ASE	Λ	NICS
phosphole		7.0[a]	– 3.3[a]	– 5.3[b]
silacyclopentadienyl anion		13.8[a]	– 7.7[a]	– 6.7[b]
furan		19.8[a]	– 9.1[a]	– 12.3[b]
thiophene		22.4[a]	– 10.0[a]	– 13.6[b]
pyrrole		25.5[a]	– 12.1[a]	– 15.1[b]
cyclopentadienyl anion		28.8[a]	– 17.2[a]	– 14.3[b]
cyclopentadiene		3.7[a]	– 2.4[a]	– 3.2[b]
alumol		– 6.8[a]	11.2[a]	6.5[b]
borol		– 19.3[a]	12.8[a]	17.5[b]
silolil cation		– 24.1[a]	13.2[a]	12.8[b]
1H-1,2,4-triazole		26.2[c]	– 3.8[c]	– 13.9[d]
pentazole		10.8[c]	– 3.0[c]	– 16.3[d]
1,2,4-thiadiazole		19.1[c]	– 6.6[c]	– 14.0[d]
1,2,5-oxadiazole		26.4[c]	– 1.5[c]	– 12.2[d]
1,3,4-oxadiazole		14.9[c]	– 3.2[c]	– 10.6[d]
1,3,4-thiadiazole		13.3[c]	– 9.5[c]	– 12.9[d]
thiazole		21.3[c]	– 4.8[c]	– 13.8[d]
isoxazole		24.1[c]	– 4.3[c]	– 12.2[d]
1H-1,2,3,4-tetrazole		27.4[c]	– 1.2[c]	– 14.6[d]
imidazole		25.2[c]	– 7.5[c]	– 14.1[d]
oxazole		18.1[c]	– 3.8[c]	– 11.8[d]

[a] From ref. [6]. [b] From ref. [14]. [c] From ref. [21]. [d] This work.

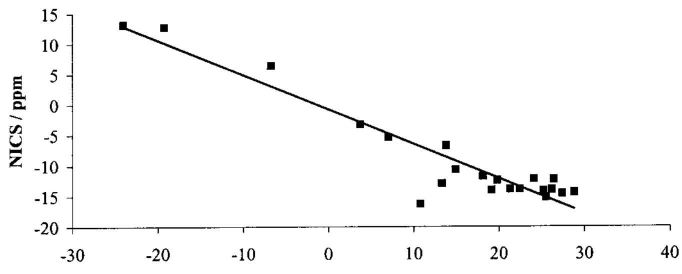


Figure 1. Plot of the aromatic stabilization energy versus NICS for the five-membered heteroaromatic compounds considered in Table 1, $R = 0.944$.

shifts were used since they allowed us to clearly differentiate between doubly (=O) and singly (–O–) bonded oxygen atoms, as well as, between doubly bonded oxygen atoms placed in different electronic environments.[35, 36]

First, we have computed ASE values for the oxocarbon acids and corresponding dianions by using Equations (1) and (2). The values shown in Table 2 are consistent with earlier

$$C_nO_{n-2}H_4 + 2x(\text{ethenoxide}) \rightarrow C_nO_n^{2-} + \text{ethane} + \text{ethene} \qquad (1)$$

$$C_nO_{n-2}H_4 + 2x(\text{ethenol}) \rightarrow C_nO_nH_2 + \text{ethane} + \text{ethene} \qquad (2)$$

conclusions on aromaticity of oxocarbon dianions which point out that only deltate dianion is aromatic.[3, 23] A moderate ASE value is obtained for squarate (– 11.39 kcal mol^{-1}) while negligible values are obtained for croconate and rhodizonate. Positive ASE values for oxocarbon acids indicate that they are not aromatic.

Despite this concordance with reported general conclusions, our values are in contrast with those recently reported by Schleyer et al.[14] for oxocarbon dianions using three different series of reactions for ASE evaluation. However, as pointed out by the authors, all equation types have drawbacks. Indeed, all reported ASE values are largely negative and, generally, do not show any regular trend with the ring size. At this point, we consider that oxocarbon derivatives are examples where the use of ASE as a criterion of aromaticity is not applicable due to the difficulty in finding suitable equations free from other influences.

Evaluation of the magnetic susceptibility exaltation of oxocarbon dianions by means of Equation (1) yields small and positive values thus indicating lack of aromaticity even for deltate dianion, in striking contrast with the calculated ASE using the same equation. In the same way, Λ values of $C_nO_n^{2-}$ reported by Schleyer, using different sets of equations, were in some cases positive and in some cases negative. These results prevent any use of Λ values to measure the degree of aromaticity, due to the large dependency on the type of equations used for its evaluation.

The uncertainties concerning ASE and Λ as suitable aromaticity criteria, led us to analyze the possible aromaticity of oxocarbon acids and its derivatives by calculating the nucleus-independent chemical shifts (NICS). NICS(0.6) values—calculated at 0.6 Å over the ring plane—for both oxocarbon acids and their corresponding dianions are shown in Table 2 together with the computed ^{17}O NMR chemical

Table 2. Computed NICS (ppm), aromatic stabilization energies ASE [kcal mol^{-1}], ^{17}O chemical shifts (ppm, relative to water), Wiberg bond indexes (WBI), magnetic susceptibilities (χ, ppm cgs) and magnetic susceptibility exaltations (Λ, ppm cgs).

Molecule	NICS(0.6)	ASE	^{17}O NMR	WBI (CO)	Λ	χ
$C_3O_3^{2-}$	−25.0 (HF) −21.3 (MP2)	−49.19	121	1.256	4.83	−44.5
$C_4O_4^{2-}$	−11.0 (HF) −7.1 (MP2)	−11.39	304	1.403	7.23	−50.0
$C_5O_5^{2-}$	−4.3 (HF) −0.5 (MP2)	−0.6	385	1.491	0.60	−50.8
$C_6O_6^{2-}$	−4.2 (HF) −0.3 (MP2)	−4.24	452	1.551	2.09	−58.4
$C_3O_3H_2$	−23.2 (HF) −20.5 (MP2)	6.47	218 (C=O) 97 (OH)	1.586	3.13	−40.5
$C_4O_4H_2$	−7.0 (HF) −5.7 (MP2)	14.89	463 (C=O) 109 (OH)	1.736	2.80	−43.2
$C_5O_5H_2$	1.2 (HF) 0.7 (MP2)	17.04	599, 521 (C=O) 87 (OH)	1.872	1.88	−49.8
$C_6O_6H_2$	2.2 (HF) 1.9 (MP2)	12.52	612, 533 (C=O) 99 (OH)	1.884	2.98	−56.9

shift values and the Wiberg bond indexes (WBI) that will be also used in the following discussion. From the comparison of NICS values at HF and MP2 levels of theory, one can conclude that HF values tend to overestimate the aromatic character of a molecule. Henceforth, NICS values at the MP2 level will be used for the discussion of the results.

Deltic acid and deltate dianion: The appreciable NICS(0.60) value for deltate dianion ($\delta = -21.3$) confirms its aromaticity. Even more, the computed ^{17}O NMR chemical shift for $C_3O_3^{2-}$ is $\delta = 121$, close to the value of phenolate ($\delta = 158$), in line with the general assumption that deltate dianion is aromatic. In contrast to ASE and Λ values, the NICS value for the corresponding acid $C_3O_3H_2$ is also large and negative ($\delta = -20.5$), which indicates that deltic acid is also aromatic. This fact can be related with the high stability of cyclopropenones,[37] despite their high ring strain[38] and in contrast to cyclopropanones and cyclopropenes, attributed to resonance stabilization by its polar formula which represents a pseudoaromatic system. The computed ^{17}O NMR chemical shift corresponding to the carbonyl oxygen atom of deltic acid is $\delta = 218$, far from the standard carbonyl oxygen atoms, namely, acetone shows signal at $\delta = 569$, and close to diphenylcyclopropenone ($\delta = 248$)[39] confirming the contribution of the pseudoaromatic Hückel form. Such a high shielding is only observed for the exocyclic oxygen atom of sydnone ($\delta = 232$)[40] and related mesoionic compounds which are currently formulated with −O$^-$ in the place of =O. Finally, the X-ray analysis[41] of deltic acid shows nearly equal C−C lengths in the ring (r(C=C) = 1.373 Å, r(C−C) = 1.397 Å, difference = 0.024 Å) which are on average of standard values for single and double bonds, following a general characteristic of aromatic molecules. The calculated Wiberg bond indexes (WBI) for carbonyl CO bonds in deltic acid and its dianion are 1.586 and 1.256, respectively, (compared with WBI = 1.778 for acetone), which indicates delocalization in agreement with their NICS(0.6) values and ^{17}O NMR chemical shifts.

Squaric acid and squarate dianion: The different criteria for squarate dianion indicate a lesser aromatic character than deltate, since NICS (0.6), being also negative, is only −7.1[42] and the ^{17}O NMR chemical shift shows high shielding of the oxygen atom ($\delta = 304$), but less than in deltate. Analogously, deltic acid is more aromatic than squaric acid as deduced by the smaller NICS(0.6) negative value of $\delta = -5.7$ thus showing only a moderate aromatic character. Conclusions based on both ^{17}O NMR chemical shift—the computed value of $\delta = 463$ is comparable to a standard ketone—and X-ray findings,[37] where the difference between carbon−carbon single and double bonds is 0.048 Å (twice the value for deltic acid), confirm the small degree of aromaticity for squaric acid. A recent theoretical study[43] on squaric acid has concluded that it is aromatic, based on its values of ASE and Λ, although the reported Λ value was very small ($\delta = -2.07$ ppm cgs). The calculated WBI values for carbonyl CO bonds in squaric acid and its dianion are 1.736 (close to acetone) and 1.403, respectively, in agreement with previous conclusions based on NICS(0.6) and ^{17}O NMR results.

Larger rings of the oxocarbon series: As derived from NICS(0.6) values, ^{17}O NMR chemical shifts and WBIs (see Table 2) five- and six-membered ring compounds of the series are clearly nonaromatic. Even more, rhodizonic acid is not planar at MP2/6-311+G** theoretical level.

Oxocarbon derivatives: The values corresponding to the three criteria that we have found to be useful to evaluate aromaticity are listed in Table 3 for some oxocarbon derivatives of our interest. Particularly, an estimation of the aromaticity of squaric acid derivatives (squaramide and dimethylsquarate) and their complexes with ammonium cation were compared with the corresponding di-O-protonated species. Results shown in Table 3 predict that the squaramide complex is more aromatic (NICS(0.6) = −8.1 ppm, ^{17}O NMR chemical shift $\delta = 379$ and WBI(CO) = 1.298) than squaramide (NICS(0.6) = −6.3 ppm, ^{17}O NMR chemical shift $\delta = 448$ and WBI(CO) = 1.712). Therefore the gain in aromaticity of the squaramide ring is a possible explanation for its remarkable proton affinity and hydrogen bond acceptor character. Indeed

Table 3. Computed NICS (ppm), ^{17}O chemical shifts (ppm, relative to water) and Wiberg bond indexes (WBI).

Molecule	NICS(0.6), HF	NICS(0.6), MP2	^{17}O NMR	WBI (CO)
squaramide	−8.1	−6.3	448	1.712
squaramide-NH_4^+ complex	−11.1	−8.1	379	1.298
di-O-protonated squaramide	−12.8	−10.0	173	1.208
dimethylsquarate	−10.2	−7.8	468	1.720
dimethylsquarate-NH_4^+ complex	−10.6	−7.9	403	1.575
di-O-protonated dimethylsquarate	−13.7	−10.5	190	1.216
squaric acid	−7.0	−5.7	463	1.736
squaric acid-NH_4^+ complex	−10.3	−7.8	411	1.383
di-O-protonated squaric acid	−13.8	−10.7	208	1.269

we have observed such a behaviour in the molecular recognition of ammonium cations by squaramido-based model receptors.[27, 28] Di-O-protonated squaramide has more aromatic character (NICS(0.6) = – 10.0 ppm, ^{17}O NMR chemical shift $\delta = 173$ and WBI(CO) = 1.208) than squaramide complex; this indicates that the aromaticity of the four-membered ring of squaramide is successively enhanced by hydrogen bonding and by protonation of the carbonyl oxygen atoms. This is also corroborated by the progressive equalization of the covalent bond lengths in the four-membered ring (see Figure 2). Similar behaviour has been observed for squaric acid and dimethylsquarate: a continuous enhancement of the aromatic character of the four-membered ring by hydrogen bonding and by protonation of the carbonyl oxygen atoms (see Table 3). Consequently, squaramide isoelectronic compounds are good candidates for hydrogen-bond acceptors due to the enhancement of the aromaticity of the four-membered ring.

Conclusion

Aromaticity is a differential property and often the criteria to evaluate it need an artificial “nonaromatic” reference system. A rigorous definition of such reference system is fundamental to obtain a satisfactory quantification of the aromatic concept. However, such definition is unfortunately not existing at present. Even the dimensionality of aromaticity is still under discussion,[21c] so much remains to be done to clarify this issue.

NICS criterion does not need reference systems to be computed and, although it has been criticized and it is not verifiable experimentally, we have demonstrated a significant linear relationship between NICS values and ASEs for a wide range of five-membered heteroaromatic compounds. Oxocarbon acids and their dianions are examples where traditional criteria, that is Λ and ASE, are not satisfactory to evaluate aromaticity. However, we have found that the NICS criterion is adequate for the study of oxocarbon acids and its derivatives, together with ^{17}O NMR chemical shifts and Wiberg bond indexes.

Finally, the remarkable proton affinity and hydrogen bond acceptor character of squaramide has been explained by means of the gain in aromaticity of the four-membered ring that it is enhanced by hydrogen bonding of the carbonyl oxygen atoms to ammonium cation or by protonation of the carbonyl oxygen atoms. Parallel behaviour is observed for squaric acid and dimethylsquarate compounds.

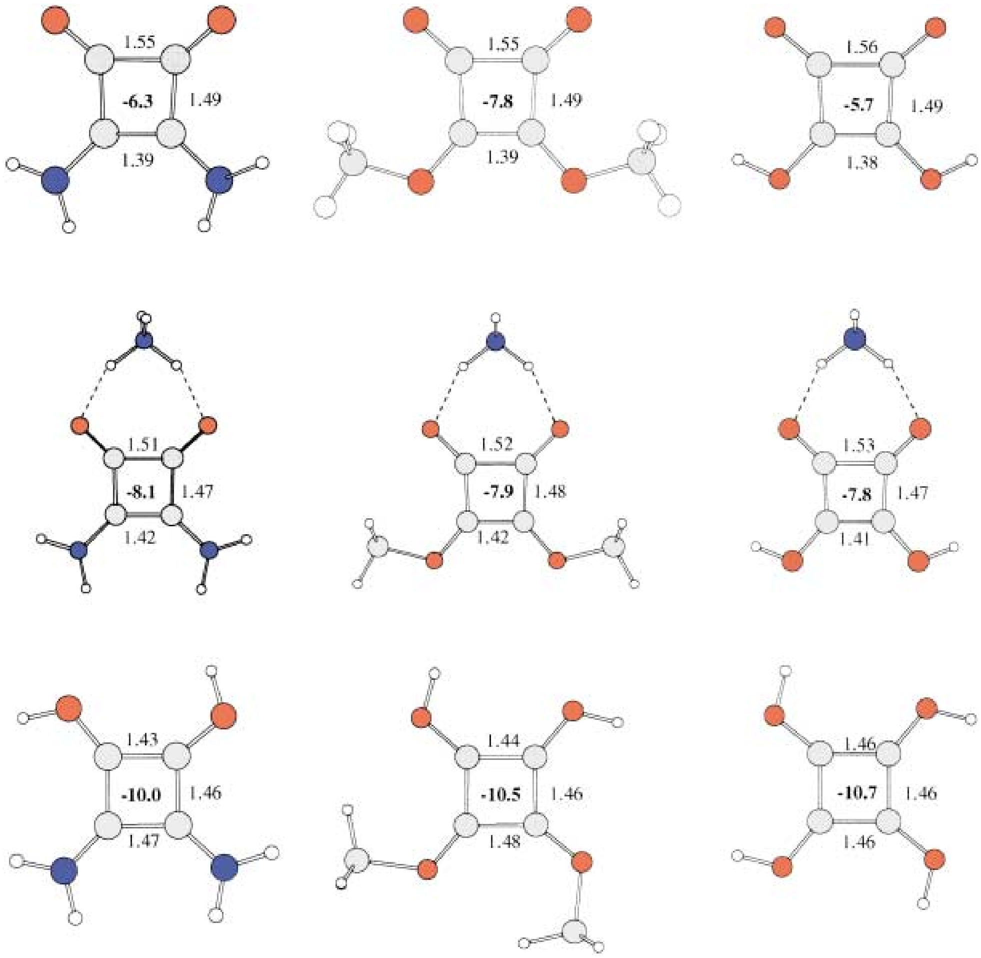


Figure 2. MP2/6-311+G** optimized structures of squaramide, squaric acid and dimethylsquarate, their complexes with ammonium cation and their di-O-protonated derivatives. Bond lengths are in Å. NICS(0.6) values are indicated at ring centers in ppm.

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