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LETTERS

## A theoretical study of aromaticity in squaramide and oxocarbons

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### Abstract

A systematic estimation of aromaticity in oxocarbon acids, their dianions, squaramide and its complex with the ammonium cation have been studied using structural and magnetic criteria. Results based on Nucleus Independent Chemical Shift (NICS) predict that deltic and squaric acids and their dianions are aromatic, while croconic and rhodizonic acids and their dianions are non-aromatic. Squaramide is less aromatic than its complex with the ammonium cation. Therefore, the gain in aromaticity in the squaramide ring is a possible explanation for the remarkable hydrogen bond acceptor character of squaramide. © 2000 Elsevier Science Ltd. All rights reserved.

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Due to their highly functionalized and interesting structures, the cyclic oxocarbon acids ( $C_nO_nH_2$ ) and their conjugated bases, the oxocarbon dianions ( $C_nO_n$ )<sup>2-</sup>, have been widely investigated both theoretically and experimentally.<sup>1</sup> In 1960 West et al.<sup>2</sup> recognized cyclic oxocarbon dianions as aromatic systems, stabilized by the delocalization of  $\pi$ -electrons and suggested that they constitute a series of aromatic compounds. The latter generalization has been questioned by Aihara<sup>3</sup> for the oxocarbons in general, although there are arguments in favor of aromaticity in the smallest member of the oxocarbon dianions series, the deltate dianion.<sup>4</sup>

Several criteria for aromaticity are known.<sup>5</sup> The most widely used quantitative measures of the degree of aromaticity are energetic (aromatic stabilization energies),<sup>6</sup> structural (nearly equal bond lengths in the ring),<sup>7</sup> and magnetic properties such as magnetic susceptibilities.<sup>8</sup> Estimates of aromatic stabilization energies (ASE) vary significantly and depend strongly on the equations used (isodesmic, homodesmotic, hyperhomodesmotic),<sup>9</sup> the reference molecules adopted, and the computational levels and basis sets. The major characteristic of an aromatic species 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, most diamagnetic molecules are anisotropic. The magnetic susceptibility perpendicular to the plane of the ring is much greater than that in the ring. Therefore magnetic susceptibility anisotropy ( $\chi_{anis}$ ) is a valid criteria for aromaticity. However,  $\chi_{anis}$  is only applicable to planar or nearly planar molecules.

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Recently, Schleyer et al.<sup>10</sup> proposed the use of the negative of the computed magnetic shieldings at the ring centers, referred to as 'Nucleus Independent Chemical Shift' (NICS) as an effective criteria for aromaticity. NICS agrees well with the energetic (ASE), geometric and magnetic criteria and does not require increment systems for other references.<sup>11</sup> NICS also is an adequate probe of the individual rings in polycyclic systems. Negative NICS values denote aromaticity whereas small NICS values indicate non-aromaticity. In contrast to the magnetic susceptibility exaltation,<sup>12</sup> NICS values have the advantage that they are less dependent on ring size.

In this letter we study the aromatic character of cyclic oxocarbon acids (**1–4**) and their conjugated bases (**5–8**), squaramide (3,4-diamino-3-cyclobutene-1,2-dione) (**9**), a complex between squaramide and ammonium cation (**10**), and di-*O*-protonated squaramide (**11**) (Fig. 1).<sup>13</sup> Following both structural and magnetic criteria, the remarkable hydrogen bond accepting character of squaramide, that we have observed in the molecular recognition of ammonium cations,<sup>14</sup> will be explained by means of the aromaticity of the four-membered ring in its complex. The aromatic character of deltic and squaric dianions will be confirmed but will be questioned for the oxocarbons in general. Geometries<sup>15</sup> were optimized first at the HF/6-311+G\*\* level and further reoptimized at MP2/6-311+G\*\* level by using the Gaussian 98<sup>16</sup> program package. Absolute NMR shieldings were calculated using the GIAO method<sup>17</sup> 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.<sup>18</sup> NICS values (Table 1) 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  $\sigma$ -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  $\sigma$ -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.

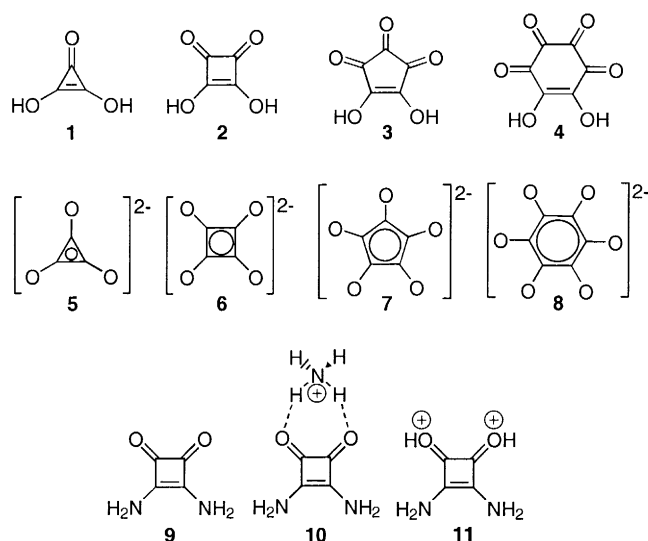


Fig. 1. Oxocarbons (**1–4**), their dianions (**5–8**), squaramide **9**, a complex between squaramide and ammonium cation **10** and di-*O*-protonated squaramide **11**

The results shown in Table 1 indicate that the smallest member of the oxocarbon acids, the deltic acid (**1**), is aromatic. This is in agreement with an X-ray analysis<sup>4b</sup> of **1** where the covalent bond lengths

Table 1  
Nucleus Independent Chemical Shifts (NICS, ppm) computed at the geometrical centers (NICS(0)) and 0.6 Å above (NICS(0.6)) of **1–11** and benzene at two levels of theory

compound	HF/6-311+G**		MP2/6-311+G**	
	NICS(0)	NICS(0.6)	NICS(0)	NICS(0.6)
<b>1</b>	-34.0	-23.2	-32.4	-20.5
<b>2</b>	-2.9	-7.0	-2.4	-5.7
<b>3</b>	7.6	1.2	7.4	0.7
<b>4</b>	6.4	2.2	6.5	1.9
<b>5</b>	-36.1	-25.0	-35.2	-21.3
<b>6</b>	-6.0	-11.0	-3.3	-7.1
<b>7</b>	2.6	-4.3	6.2	-0.5
<b>8</b>	0.8	-4.2	4.0	-0.3
<b>9</b>	-2.5	-8.1	-1.9	-6.3
<b>10</b>	-6.7	-11.1	-5.3	-8.1
<b>11</b>	-10.6	-12.8	-9.1	-10.0
benzene	-9.6	-11.5	-7.9	-10.1

in **1** showed a remarkable degree of conjugation ( $r(\text{C}=\text{C})=1.373$  Å,  $r(\text{C}-\text{C})=1.397$  Å, difference=0.024 Å). The squaric acid (**2**) has a smaller NICS (0.6) value than **1**, also in agreement with X-ray findings, where the difference in bond lengths between the C–C single and the C=C double bonds is 0.048 Å,<sup>4b</sup> suggesting that **1** is more aromatic than **2**, as predicted by NICS values. Higher members of the series of oxocarbon acids are clearly non-aromatic, the highest member, rhodizonic acid is not even a planar structure at MP2/6-311+G\*\* level.

A study of the vibrational spectra of the oxocarbon dianions carried out by West et al.<sup>19</sup> showed that they have symmetric  $D_{nh}$  structures and C–C stretching force constants that indicate large delocalization energies. The latter arguments were used to support the aromaticity of oxocarbon dianions, although  $\pi$ -electron delocalization cannot be used as the only measure of aromaticity.<sup>20</sup> Aihara, using the graph theory of aromaticity,<sup>21</sup> concluded that the deltate dianion **5** is highly aromatic while the other members of the series **6–8** are non-aromatic. The NICS value obtained for **5** (–21.3 ppm), twice the value of benzene at the same level, is in agreement. However, NICS values presented in Table 1 also indicate that squaric dianion **6** is aromatic (NICS (0.6)=–7.1 ppm) while the other members of the series, croconic and rhodizonic dianions, are non-aromatic compared with benzene.<sup>22</sup>

An estimation of the aromaticity of squaramide (**9**) and its complex with the ammonium cation (**10**) was studied using structural and magnetic (NICS) criteria and compared with di-*O*-protonated squaramide (**11**). Results shown in Fig. 2 predict that complex **10** is more aromatic (NICS (0.6)=–8.1 ppm) than **9** (NICS (0.6)=–6.3 ppm) and similar to benzene (NICS (0.6)=–10.1 ppm). Therefore the gain in aromaticity of the squaramide ring is a possible explanation for the remarkable proton affinity and hydrogen bond acceptor character of **9**. Indeed we have observed such a behavior in the molecular recognition of ammonium cations by squaramido-based model receptors.<sup>14</sup> Di-*O*-protonated squaramide **11** has more aromatic character (NICS (0.6)=–10.0 ppm) than **10**, indicating that the aromaticity of the four-membered ring of squaramide is successively enhanced by hydrogen bonding<sup>23</sup> 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 Fig. 2). Similar behavior has been observed for cyclopropenones and has been used<sup>24</sup> to justify the more basic character of these species than other  $\alpha,\beta$ -unsaturated ketones.

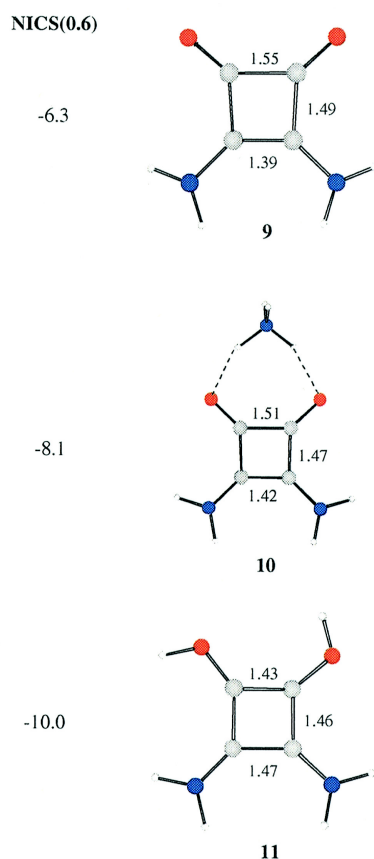


Fig. 2. MP2-optimized structures and NICS (0.6) values for **9–11**. Distances in Å and NICS values in ppm

In summary, high-level GIAO-MP2 computations (GIAO-MP2/6-311+G\*\*) show that the oxocarbon acids **3** and **4** are non-aromatic. In contrast, deltic acid (**1**) is highly aromatic, consistent with X-ray measurements and squaric acid (**2**) is very weakly aromatic (NICS (0.6) = -5.7). The aromatic character of the oxocarbon dianions has been confirmed for **5** and **6** but cannot be extended to the entire series, in contrast to what has been suggested in the literature.<sup>1</sup>

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.

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