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^{13}C NMR and *ab Initio*/IGLO Study of Protonated Oxocarbons: Poly-O-protonated Squaric, Croconic, and Rhodizonic Acids and Their Aromatic Nature. Preparation and Study of Tetrahydroxy- and Diaminodihydroxyethene Dications[1]

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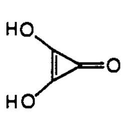
Abstract: The protonation of oxocarbons in superacidic solutions has been studied. Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, **2**), croconic acid (4,5-dihydroxy-4-cyclopentene-1,2,3-trione, **3**), and rhodizonic acid (5,6-dihydroxy-5-cyclohexene-1,2,3,4-tetraone, **4**) were poly-O-protonated with Magic Acid (1:1 SbF_5 + FSO_3H) or fluorosulfuric acid at low temperatures and characterized by ^{13}C NMR spectroscopy. The protonation of oxalic acid and oxamide has also been studied in $HSO_3F/SbF_5/SO_2$ solution at -78 °C and the resulting ethene dications were characterized by ^{13}C NMR spectroscopy. Dimethyl oxalate was also methylated under stable-ion conditions with CH_3F/SbF_5 in SO_2 solution but gave only the corresponding monomethylated cation. Comparison of experimental with ab initio/IGLO calculated ^{13}C NMR chemical shifts gives insight into the nature of the protonated oxocarbons. Similar comparisons in the studied ethene dications show their preferred planar geometry.

Introduction

The term "oxocarbon", first suggested by West in 1963, designates compounds in which all carbon atoms are bonded to carbonyl or enolic oxygens or their hydrated or deprotonated equivalents.[2] Cyclic oxocarbon anions were recognized as aromatic systems, stabilized by delocalization of π-electrons.[3] 2,3-Dihydroxy-2-cyclopropenone (deltic acid, **1**), 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid, **2**), 4,5-dihydroxy-4-cyclopentene-1,2,3-trione (croconic acid, **3**), and 5,6-dihydroxy-5-cyclohexene-1,2,3,4-tetrone (rhodizonic acid, **4**) are thus considered to be acids. Indeed, **2** was found to be a remarkably strong acid, having a p*K* value close to that of sulfuric acid.[4]



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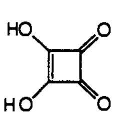

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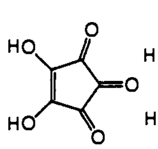

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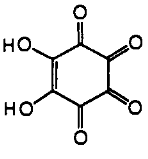

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Mono-O-protonated deltic acid (**1**), di-O-protonated squaric acid (**2**), tri-O-protonated croconic acid (**3**), and tetra-O-protonated rhodizonic acid (**4**) would formally be Hückeloid [4*n* + 2] aromatic systems with significant delocalization of the positive charge from the oxygen into the ring. Lien and Hopkinson have calculated the structure and energetics of mono-O-protonated deltic acid (**1**) at the HF/3-21G level and found aromatic trihydroxy cyclopropenium structure.[5] Poly-O-protonated polycations can also be considered as homoaromatic species.[6]

Theoretical study of the doubly ionized ethene dication $C_2H_4^{2+}$ has shown the global energy minimum species to be perpendicular ethene dication.[7] The planar form of $C_2H_4^{2+}$ is a transition state for the rotation around the C–C bond, and the rotational barrier for the process is 28.1 kcal/mol. Bock et al. have found by X-ray diffraction that the chloro and bromo salts of tetrakis(dimethylamino)ethene dications have perpendicular geometry.[8] The planar (D_{2h}) geometry for substituted ethene dications was calculated for the $C_2F_4^{2+}$ dication.[9] This result has been explained by back-donation of the fluorine lone-pair electrons into the formally empty carbon p-orbitals. Recently, Frenking studied the structure of substituted ethene dications[10] by theoretical calculations using *ab initio* quantum theoretical methods. His calculations indicated that the doubly charged, substituted ethene dications $C_2(OH)_4^{2+}$ and $C_2(OH)_2(NH_2)_2^{2+}$ should have planar geometries.

In continuation of our studies on carbocations and onium ions, we report now the poly-O-protonation of squaric, croconic, rhodizonic, and oxalic acids under superacidic conditions. Furthermore, diprotonation of oxamide was also explored. The

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[1] Stable Carbocations. 287. For 286, see: Prakash, G. K. S.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. *J. Am. Chem. Soc.* **1992,** *114,* 3076.

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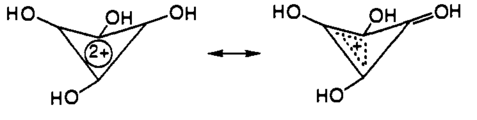
resulting carboxonium ions were characterized by ^{13}C NMR spectroscopy. The geometries and ^{13}C NMR chemical shifts of these polyprotonated systems were also investigated by high-level *ab initio*/IGLO (Individual Gauge for Localized Orbitals) methods. Recently the *ab initio*/IGLO method has become a very powerful tool for structure elucidation of carbocations.[11,12] By comparison of the calculated IGLO ^{13}C NMR chemical shifts with the experimentally observed data, structural aspects of the studied polycations can be better inferred.

Results and Discussion

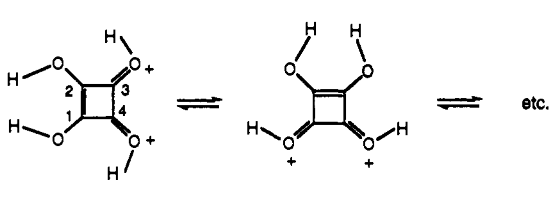
Di-O-protonated Squaric Acid (5). Olah et al. studied originally the protonation of squaric acid in Magic Acid (FSO_3H/SbF_5)/SO_2 solution by ^{1}H NMR spectroscopy.[13] The results were inconclusive, and the observed deshielded NMR shift was interpreted as an equilibrating protonated system but not a stabilized cyclobutadiene dication system.

We carried out now the preparation and characterization of di-O-protonated squaric acid (**5**) in the even stronger, superacidic, $FSO_3H/SbF_5/SO_2ClF$ system. When a saturated solution of FSO_3H/SbF_5 in SO_2ClF was added with vigorous stirring at −78 °C to a suspension of squaric acid **2** in SO_2ClF, a solution of **5** was obtained. The ^{13}C NMR (75 MHz) spectrum of the solution consists of a single sharp peak at a chemical shift of δ 183.4 and shows no temperature dependence.

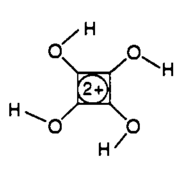
The data indicate the equivalency of the carbon atoms. The possible predominant resonance forms of diprotonated squaric acid are depicted as **5a–c**. Besides planar 2π-aromatic structure **5c**, we also considered carboxonium ion structures **5b** as well as puckered aromatic and homoaromatic structures **5a**.



5a



5b

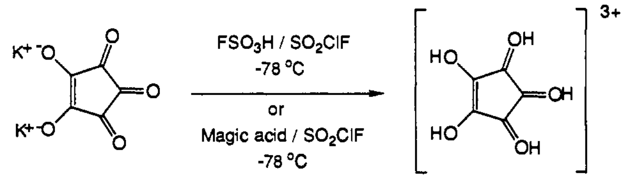


5c

Schleyer et al. calculated the structure of the parent cyclobutadiene dication and found that a puckered structure with a D_{2d} geometry is a minimum.[14] Schleyer et al. later confirmed[15] that the preferred geometry for tetramethylcyclobutadiene dication is also puckered by comparing the IGLO calculated ^{13}C chemical shifts with the experimental ^{13}C chemical shift values. We calculated the puckered structure **5a** with D_{2d} geometry at the HF/6-31G* level but could not find an energy minimum for it.

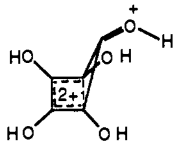
When we optimized the planar structures **5b** (E = −452.47374 hartrees) and **5c** (E = −452.48089 hartrees), with C_{2v} and C_{4h} symmetry, respectively, at the HF/6-31G* level, we found the latter to be more stable by 4.5 kcal/mol. IGLO calculation of the planar form **5c** at the II//HF/6-31G* level gave a chemical shift of δ(^{13}C) 186.4, in good agreement with the observed experimental value of δ(^{13}C) 183.4, indicating the predominant planar tetrahydroxycyclobutadiene dication nature of **5c**. IGLO calculation on **5b** at the II//HF/6-31G* level gave an average chemical shift at δ(^{13}C) 187.1, close to the calculated chemical shift of **5c**. However, energetically this species is less stable than **5b** and consequently may make only a relatively minor contribution to the overall structure.

Tri-O-protonated Croconic Acid (6). The potassium salt of croconic acid **3a** was prepared by treating the potassium salt of rhodizonic acid **4a** with potassium carbonate.[16] A suspension of dipotassium croconate (**3a**) in SO_2ClF was treated with FSO_3H/SO_2ClF under vigorous stirring at −78 °C.

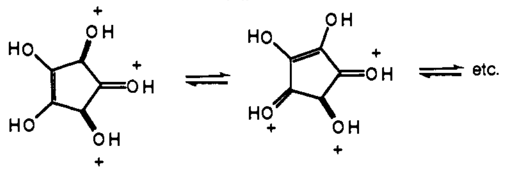


3a 6

The ^{13}C NMR spectrum (75 MHz) of the resulting yellow solution consists of a singlet at δ 174.4. The singlet indicates the equivalence of the five carbon atoms on the NMR time scale, in accord with croconic acid (**3**) being protonated with rapid proton exchange equilibrating all carbons under the acidic conditions. The extent of protonation in FSO_3H is, however, not clear as rapid exchange of less than fully protonated species on the NMR time scale is possible. Subsequently, **3** was also protonated with Magic Acid under similar conditions. The observed ^{13}C NMR spectra showed three singlets at δ 162.5, 174.3, and 192.9 (in the ratio 2:2:1, average δ 173.3). In Magic Acid, a much stronger superacid than FSO_3H, proton exchange seems to be frozen out at −78 °C, resulting in the observation of the three signals.



6 a



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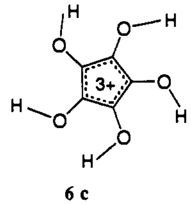
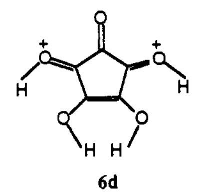


6 c



6d

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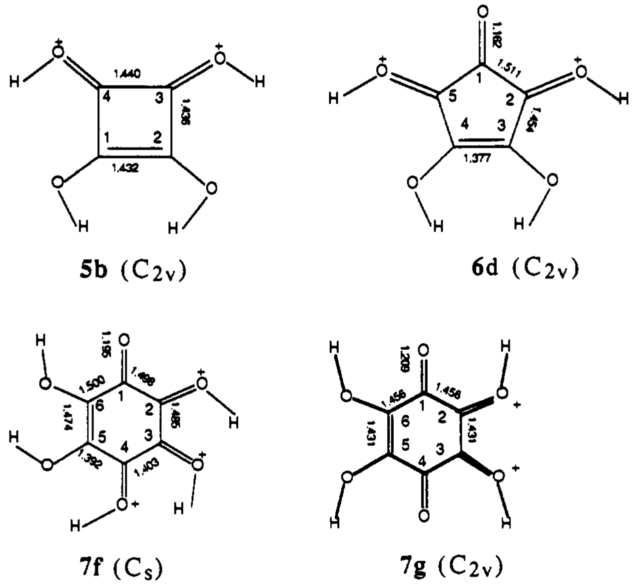
Table I. ^{13}C Chemical Shifts of Poly-O-protonated Oxocarbons (in ppm from TMS)[a]

basis	5b	5c	6c	6d	7a	7f	7g
DZ//3-21G		203.9	187.4		177.5	177.2 (C1) 186.7 (C2) 178.2 (C3) 148.4 (C4) 178.4 (C5) 186.6 (C6) 175.9 (ave)	172.4 (C1) 177.9 (C2) 176.1 (ave)
DZ//6-31G*	199.5 (C1) 202.7 (C3) 201.1 (ave)	199.5	186.0	150.2 (C1) 210.7 (C2) 160.7 (C3) 178.6 (ave)			
II//6-31G*	184.1 (C1) 190.1 (C3) 187.1 (ave)	186.4	181.1	138.7 (C1) 203.0 (C2) 155.8 (C3) 171.3 (ave)			
experimental		183.4	174.4[b] 173.3[c]		164.4[b] 166.5[c]		

[a] ave means average of all carbon chemical shifts. [b] In FSO_3H acid medium. [c] In Magic Acid medium; average of the all carbon chemical shifts.



5b (C_{2v}) 6d (C_{2v})

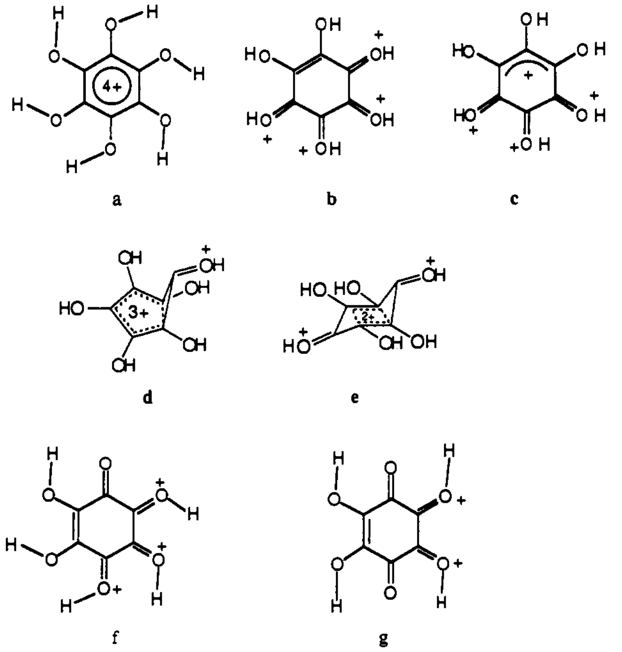
7f (C_s) 7g (C_{2v})

Figure 1. Selected parameters of optimized **5b** (HF/6-31G*), **6d** (HF/6-31G*), **7f** (HF/3-21G), and **7g** (HF/3-21G).

However, in both systems, the extent of protonation appears to be similar as indicated by the ^{13}C NMR data. To determine the extent of protonation, as well as the nature of triprotonated species, we have also carried out *ab initio*/IGLO calculations on both diprotonated as well as triprotonated structures **6a** and **6c**. The triprotonated carboxonium type structures **6b** were not considered in our calculations because of the possible large number of *syn* and *anti* isomers involved.

No energy minimum was found for the triprotonated homoaromatic structure **6a**. The triprotonated planar C_{5h} structure **6c** was optimized at the HF/6-31G* level, and we carried out IGLO calculations. At the II//HF/6-31G* level, the calculated ^{13}C NMR chemical shift δ 181.1 (Table I), 6.7 ppm more shielded than the experimentally observed value in FSO_3H/SO_2ClF and 7.8 ppm more shielded than the average shift observed in Magic Acid solution. We also considered diprotonated symmetrical structure **6d** (C_{2v}) for comparison. The calculated, average ^{13}C NMR chemical shift of δ 171.3 at the II//HF/6-31G* level is closer to the observed experimental value. However, the calculated, individual chemical shifts do not match with those observed in Magic Acid solution (see Table I for the individual shifts). Thus, *ab initio*/IGLO calculations are unable to resolve the extent of protonation. However, considering the Magic Acid is at least 10^7–10^8 times stronger than FSO_3H, we are forced to conclude that triprotonation has indeed taken place in both acid systems.

Tetra-O-protonated Rhodizonic Acid (7). The 5,6-dihydroxy-5-cyclohexene-1,2,3,4-tetrone cation **7** was prepared by reacting the dipotassium salt of rhodizonic acid (**4a**) with Magic Acid in sulfur dioxide at −78 °C (dry ice/acetone bath). The obtained ^{13}C NMR spectrum showed absorptions at δ 151.7, 163.8, 165.2, and 176.5 (1:1:2:2), indicating protonation leading to a carboxonium ion species. The average shift is δ(^{13}C) 166.5. We also prepared **7** by treating a suspension of dipotassium rhodizonate (**4a**) in SO_2 with a solution of FSO_3H in SO_2 under vigorous stirring at −78 °C. A dark orange solution was obtained, which is stable at this temperature for up to a month. The ^{13}C NMR spectrum of this solution shows a singlet with a chemical shift of δ 164.7. We suggest that the observations are similar to those made in the case of **6** and the tetraketone is tetraprotonated in both acid systems. The possible resonance structures for cation **7** are as depicted. In this case, five structural possibilities exist which include two types of homoaromatic structures (**7d** and **7e**).

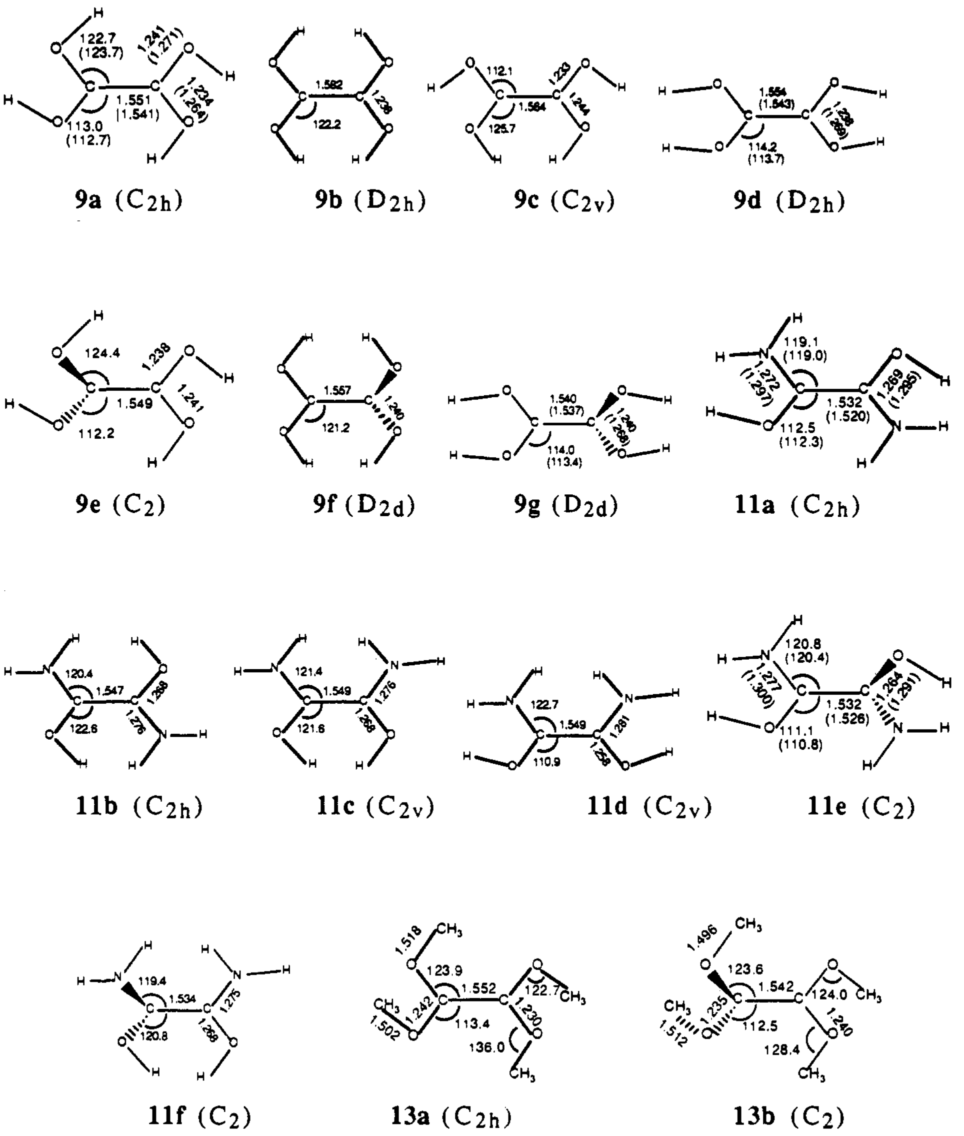


a b c

d e

f g

The IGLO calculated chemical shift of the C_{6h} geometry structure **7a** is δ(^{13}C) 177.0 at the DZ//HF/3-21G level, in reasonable agreement with the observed value of δ(^{13}C) 164.7. Larger basis sets for geometry optimization and IGLO calculations could not be employed for cation **7a** or other low-symmetry structures because of the large number of heavy atoms involved. However, we also considered triprotonated structure **7f** and



9a (C_{2h}) 9b (D_{2h}) 9c (C_{2v}) 9d (D_{2h})

9e (C_2) 9f (D_{2d}) 9g (D_{2d}) 11a (C_{2h})

11b (C_{2h}) 11c (C_{2v}) 11d (C_{2v}) 11e (C_2)

11f (C_2) 13a (C_{2h}) 13b (C_2)

Figure 2. Selected parameters of diprotonated oxalic acid 9, oxamide 11, and tetramethoxyethene dication 13 at HF/6-31G* (MP2/6-31G* optimized parameters are given in parentheses).

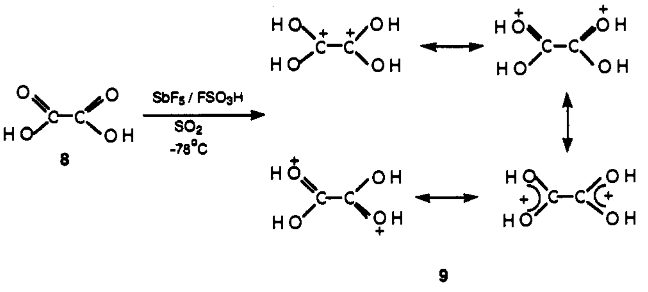
Table II. HF/3-21G Optimized Parameters of Poly-O-protonated Oxocarbons (HF/6-31G* optimized parameters)

parameter	5c (C_{4h})	6c (C_{5h})	7a (C_{6h})
C–C (Å)	1.446 (1.435)	1.452 (1.457)	1.465
C–O (Å)	1.261 (1.251)	1.250 (1.237)	1.246
O–H (Å)	0.985 (0.966)	0.999 (0.997)	1.011
C–O–H (deg)	124.8 (118.7)	129.2 (122.6)	132.7

diprotonated structure **7g** at the DZ//3-21G level (other isomers of diprotonated and triprotonated forms are less stable). The calculated, average chemical shifts are $\delta(^{13}C)$ 175.9 and 176.1, respectively (see Table I for the individual shifts). However, the individual chemical shifts do not match well with the experimentally observed data in Magic Acid (Table I). Again, the *ab initio*/IGLO method is unable to unequivocally decide on the extent of protonation. On the basis of the similar behavior of the tetraketone in both FSO_3H as well as Magic Acid, it is very likely that that tetraprotonation has taken place.

Diprotonation of Oxalic Acid and Oxamide. The diprotonation of aliphatic dicarboxylic acids was studied by Olah and co-workers in $FSO_3H/SbF_5/SO_2$ solution.[17] In the case of oxalic acid (**8**), they observed an ^1H NMR chemical shift of δ 15.7. This large deshielding was considered to indicate diprotonation of **8**. ^{13}C NMR spectroscopic studies of protonated mono- and dicarboxylic acid esters were also carried out in FSO_3H/SbF_5 solution.[18] The diethyl ester of oxalic acid gave a well resolved ^{13}C NMR spectrum with a chemical shift of δ 166.5 for the carbocationic carbon. From these studies, however, it was not possible to establish the planar or perpendicular nature of the diprotonated ester.

To a suspension of oxalic acid (**8**) in SO_2 was added with vigorous stirring at −78 °C (using a dry ice/acetone bath) a solution of excess FSO_3H–SbF_5 (Magic Acid) in SO_2.



The 75-MHz ^{13}C NMR spectrum of the solution obtained at

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Table III. Calculated Energies (in hartrees) of Substituted Ethylene Dications (relative energies in kcal/mol)

cation	HF/6-31G*// HF/6-31G*	MP2/6-31G*// HF/6-31G*	MP2/6-31G*// MP2/6-31G*
	Tetrahyroxyethene Dications		
planar			
9a (C_{2h})	−376.76638(0.2)	−377.70018(0.0)	−377.70747(0.1)
9b (D_{2h})	−376.70429(39.1)	−377.63988(37.8)	
9c (C_{2v})	−376.74749(12.0)	−377.68179(11.5)	
9d (D_{2h})	−376.76666(0.0)	−377.70000(0.1)	−377.70756(0.0)
perpendicular			
9e (C_2)	−376.75471(7.5)	−377.68843(7.4)	
9f (D_{2d})	−376.71995(29.3)	−377.65728(26.9)	
9g (D_{2h})	−376.76456(1.3)	−377.69608(2.6)	−377.70309(2.8)
	Diaminodihydroxyethene Dications		
planar			
11a (C_{2h})	−337.20431(0.0)	−338.11174(0.0)	−338.11723(0.0)
11b (C_{2h})	−337.16669(23.6)	−338.07537(22.8)	
11c (C_{2v})	−337.16563(24.3)	−338.07433(23.5)	
11d (C_{2v})	−337.18479(12.3)	−338.09212(12.3)	
perpendicular			
11e (C_2)	−337.19222(7.6)	−338.09900(8.0)	−338.10433(8.1)
11f (C_2)	−337.18031(15.1)	−338.08994(13.7)	
	Tetramethoxyethene Dications		
planar			
13a (C_{2h})	−532.96892(0.0)		
perpendicular			
13b (C_2)	−532.96610(1.8)		

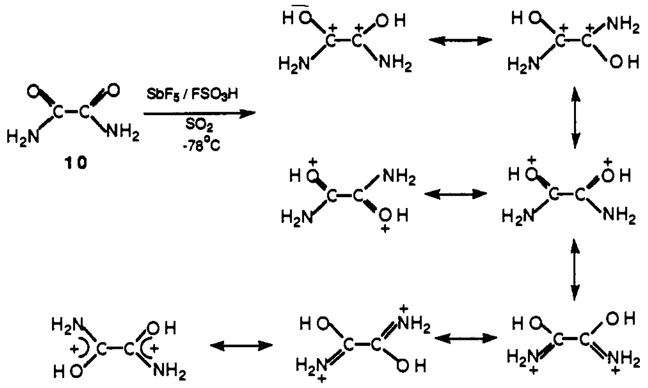
Table IV. Cationic Carbons' ^{13}C NMR Chemical Shifts (δ) of Substituted Ethylene Dications (in ppm from TMS)

	DZ//		II//		
cation	HF/ 6-31G*	MP2/ 6-31G*	HF/ 6-31G*	MP2/ 6-31G*	exptl
	Tetrahydroxyethene Dications				
planar					
9a	172.1	185.5	160.5	172.1	163.8
9b	169.6		157.6		
9c	170.8		159.7		
9d	170.3	184.3	159.7	171.3	
perpendicular					
9e	177.3		164.7		
9f	182.8		166.2		
9g	172.6	185.7	162.6	173.8	
	Diaminodihydroxyethene Dications				
planar					
11a	164.5	173.0	158.0	165.7	157.9
11b	165.7		158.8		
11c	165.1		158.2		
11d	166.3		158.8		
perpendicular					
11e	169.4	178.1	163.4	171.4	
11f	171.2		164.3		
	Tetramethoxyethene Dications				
planar					
13a	170.8		160.2[a]		
perpendicular					
13b	180.8		167.2[a]		

[a] II′//6-31G* value.

−78 °C showed only one sharp resonance at δ 163.8. We assigned the signal to the oxalic acid dication $(C_2H_4O_4)^{2+}$ **9**. We also prepared the diprotonated oxamide dication **11** by adding an excess of $SbF_5/FSO_3H/SO_2$ solution to a suspension of oxalic acid diamide (**10**) at −78 °C. The ^{13}C NMR (75 MHz) of **11** in $SbF_5/FSO_3H/SO_2$ solution consists again of only one singlet at δ 157.9.

There are several possible planar and perpendicular geometric structures to be considered for diprotonated **9** and **11** (see Figure 2). However, on the basis of the ^{13}C NMR data alone, it is not possible to decide which of the structures **9a–g** or **11a–f** is preferred under superacidic conditions. Thus, *ab initio* theoretical calculations were carried out to help resolve the question.



We have fully optimized the planar structures **9a–d** and perpendicular structures **9e–g** of diprotonated oxalic acid at the HF/6-31G* level. The optimized geometries can be compared to the reported[10] HF/3-21G* geometries by Frenking (Figure 2). At the MP2/6-31G*//6-31G* level, planar **9a** is 2.6 kcal/mol more stable than perpendicular **9g**. Frequency calculations at the HF/6-31G*//HF/6-31G* level show that **9g** is a transition state on the potential energy surface as it contains one imaginary frequency. However, at the MP2/6-31G*//MP2/6-31G* level, planar **9d** becomes the most stable isomer which is 2.8 kcal/mol more stable than perpendicular **9g** (Table III).


9a-d, 11a-d **9e-f, 11e, 11f**

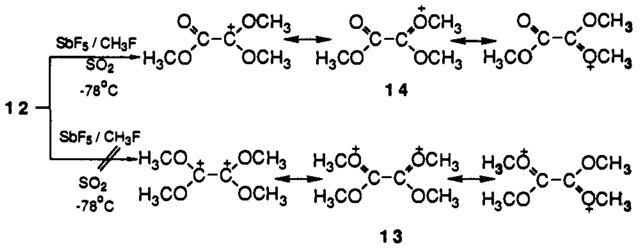
9a-g, R=R$_1$=OH; **11a-f**, R=OH, R$_1$=NH$_2$

Furthermore, we have carried out IGLO calculations on these substituted ethene dications. Using MP2/6-31G* geometry and a lower IGLO level (DZ//MP2/6-31G*), the calculated ^{13}C NMR chemical shift for the planar form of diprotonated oxalic acid (**9d**) is δ 184.3, only 1.4 ppm shielded, in comparison with the chemical shift of perpendicular **9g** (Table IV). The calculated chemical shift at a higher IGLO level (II//MP26-31G*) for **9d** is δ(^{13}C) 171.3. At the same level, we found for **9g** a chemical shift of δ(^{13}C) 173.8. Although no clear conclusion could be made from IGLO calculations, *ab initio* energy and frequency calculations favor the planar **9d** form of diprotonated oxalic acid over perpendicular **9g**. The stability of planar form **9d** is probably due to the strong pπ–pπ-interaction of the oxygen lone pairs to the formally empty carbon p-orbitals, which in turn indicates that the strong electronic effect overcomes the steric interactions. The ^{13}C NMR chemical shifts of other isomers (**9a–c**, **9e**, and **9f**) are also calculated, and these are listed in Table IV.

Similarly, we have also investigated diprotonated oxamide **11**, i.e., diaminodihydroxyethene dications. In this case, the planar form **11a** is 8.1 kcal/mol more stable than the perpendicular form **11e** at the MP2/6-31G*//MP2/6-31G* level (Table III). **11e** was found to be a transition state in the frequency calculation at the HF/6-31G*//HF/6-31G* level. These studies are also in agreement with Frenking's theoretical studies[10] at a lower level. IGLO calculations (II//MP26-31G*) of **11a** showed a chemical shift of δ(^{13}C) 165.7 which matches the experimental value of δ(^{13}C) 157.9 better than the calculated value of **11e** (δ(^{13}C) 171.4). The data on other less favorable isomers are listed in Table IV.

We also studied the methylation of dimethyl oxalate (**12**). Attempts to prepare the tetramethoxyethene dication **13** by adding **12** to a solution of $CH_3F/SbF_5/SO_2$ at −78 °C led to monomethylation. The ^{13}C NMR (75 MHz) spectrum in $SbF_5/CH_3F/$

SO_2 solution consists of five singlets at δ 57.2, 61.2, 65.5, 152.2, and 169.7, indicating only mono-O-methylation to **14**.



We have calculated the two possible isomers of dication **13** at the HF/6-31G*//6-31G* level and found the planar form to be more stable than the perpendicular form by only 1.8 kcal/mol. The IGLO value at II′//HF/6-31G* for the planar structure of **13** showed a chemical shift of δ(^{13}C) 160.2. A chemical shift of δ(^{13}C) 167.2 was calculated for the perpendicular structure of **13** at the same level.

The tetramethoxyethene dication, however, may become accessible by two-electron oxidation of tetramethoxyethene. Tetrakis(dimethylamino)ethene, an electron-rich olefin, has been readily oxidized to the corresponding ethene dication,[19] and, as mentioned earlier, these dication salts have been investigated by X-ray crystallography.[8]

Conclusions

Experimental ^{13}C NMR and *ab initio*/IGLO study indicate that poly-O-protonated squaric acid has a preferred symmetrical, planar aromatic structure. On the other hand, polyprotonated croconic and rhodizonic acids have carboxonium type structures. No indication was obtained for any significant contributing homoaromatic structures. Similar investigation of diprotonated oxalic acid and oxamide supports their planar ethene dication structures **9d** and **11a**. The main reason for the planar conformation appears to be conjugative nonbonded electron-pair back-donation to the cationic center (pπ–pπ-interaction) from the hydroxy or the amino group.

Experimental Section

Squaric acid, dipotassium salt of rhodizonic acid, oxalic acid, and all derivatives were commercially available (Aldrich). They were used without further purification. Dipotassium croconate (**3a**) was prepared by the literature method.[16]

General Procedure for the Preparation of Cations. The corresponding substance (0.8 mmol) was placed in an NMR tube, and 0.87 g (8.7 mmol) of FSO_3H dissolved in SO_2 at −78 °C was added with vigorous vortex stirring at −78 °C.

For studies in Magic Acid, to the above described mixture at −78 °C with vigorous vortex stirring was added 0.30 g (1.4 mmol) of SbF_5 dissolved in SO_2 at −78 °C.

The resultant mixtures were directly analyzed by ^{13}C NMR. In indicated cases, SO_2ClF instead of SO_2 was used as a solvent.

Methylation of Dimethyl Oxalate (12). Dimethyl oxalate, 0.8 mmol, was placed in an NMR tube, and a mixture of CH_3F/SbF_5 dissolved in SO_2 at −78 °C was added rapidly with vigorous vortex stirring. The resultant mixture was directly studied by NMR.

Calculational Method, Basis Set, and Geometry. IGLO calculations were performed according to Schindler's reported method.[11] Huzinaga[20] Gaussian lobes were used for the three different basis sets as follows. Basis DZ: C, O, or N, 7s 3p contracted to [4111, 21]; H, 3s contracted to [21]. Basis II: C, O, or N, 9s 5p 1d contracted to [51111, 2111, 1]; d exponent, 1.0; H, 5s 1p contracted to [311, 1]; p exponent, 0.70. Basis II′: C, O, or N, same as basis II; H, same as basis DZ.

Geometries of the cations were optimized by using Spartan[21] and GAUSSIAN90[22] programs on IBM RISC/6000 Model 560 and Alliant FX/40 computers, respectively.

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