6212 *J. Org. Chem.* **1996,** *61,* 6212−6217

Cyclobutene-1,2-diones. A Theoretical and Spectroscopic Study

Giovanni Cerioni*

Dipartimento di Scienze Chimiche, Università, Via Ospedale 72, I-09124 Cagliari, Italy

Rudolf Janoschek

Institut für Theoretische Chemie, Universität Graz, Graz, Austria

Zvi Rappoport

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Thomas T. Tidwell

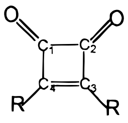
Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6

Received March 11, 1996[⊗]

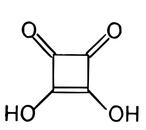
The properties of substituted cyclobutene-1,2-diones **1** are examined by the use of ^{17}O NMR spectroscopy and theoretical calculations and compared to those of cyclopropenones **2** and other models. Cyclobutene-1,2-diones have less negative charge per oxygen compared to cyclopropenones, and electron donation by substituents enhances the negative charge on oxygen. Calculated ^{17}O chemical shifts reproduce the measured trends. The dianions of squaric and deltic acids are highly stabilized by negative charge delocalization to the oxygens.

Introduction

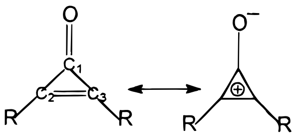
Cyclobutene-1,2-diones **1** are an important and interesting class of compounds. The 3,4-dihydroxy derivative **1a**, first reported in 1959,[1a] is usually known as squaric acid and its structure and reactions have been widely studied.[1,2] Recently, cyclobutene-1,2-diones have been extensively utilized[3] in the synthesis of complex polycyclic aromatic compounds by the sequence of nucleophilic addition of an unsaturated unit to one of the carbonyl groups of the cyclobutene-1,2-dione, and thermal ring opening to a vinylketene which cyclizes to a six-membered ring. Compounds in the squaric acid series are also of considerable biological interest.[4] The stability of cyclobutene-1,2-dione and some of its derivatives compared to those of the isomeric 1,3-butadiene-1,4-diones (bisketenes) has recently been examined,[5] and the photochemical conversion of cyclobutene-1,2-diones **1** to cyclopropenones **2** has also been reported.[6] Cyclobutene-1,2-diones are also isomeric to the commercially important squaraines **3**,[7] and the structure and stability of **1** and **3** have been compared.[7e]



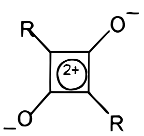
1



1a



2 **2a**



3

Cyclobutene-1,2-diones are remarkably stable species, and the origin of this property is a question of some interest.[8,9] Cyclopropenones **2** are also stable, and this may be explained by the aromatic structure shown in **2a**. There is evidence[10a] for the high degree of negative charge on oxygen in **2** from the ^{17}O NMR chemical shifts. This

---

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

(1) (a) Cohen, S.; Lacher, J. R.; Park, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 3480. (b) Park, J. D.; Cohen, S.; Lacher, J. R. *J. Am. Chem. Soc.* **1962**, *84*, 2919. (c) West, R.; Powell, D. L. *J. Am. Chem. Soc.* **1963**, *85*, 2577. (d) Cohen, S.; Cohen, S. G. *J. Am. Chem. Soc.* **1966**, *88*, 1533. (e) Schwartz, L. M.; Howard, L. O. *J. Phys. Chem.* **1971**, *75*, 1788. (f) Sprenger, H. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 530.

(2) (a) Ried, W.; Schmidt, A. H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 997. (b) Schmidt, A. H.; Ried, W. *Synthesis* **1978**, 1. (c) Knorr, H.; Ried, W. *Synthesis* **1978**, 649. (d) Schmidt, A. H.; Ried, W. *Synthesis* **1978**, 869. (e) Schmidt, A. H. *Synthesis* **1980**, 961.

(3) (a) Moore, H. W.; Yerxa, B. R. *Adv. Strain Org. Chem.* **1995**, *4*, 81. (b) Lee, K. H.; Moore, H. W. *J. Org. Chem.* **1995**, *60*, 735. (c) Koo, S.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1995**, *117*, 3389. (d) Danheiser, R. L.; Casebier, D. S.; Huboux, A. H. *J. Org. Chem.* **1994**, *59*, 4844. (e) Yamamoto, Y.; Ohno, M.; Eguchi, S. *J. Am. Chem. Soc.* **1995**, *117*, 9653.

(4) (a) Cole, R. J.; Kirksey, J. W.; Cutler, H. G.; Doupnik, B. L.; Peckham, J. C. *Science* **1973**, *179*, 1324. (b) Tietze, L. F.; Arlt, M.; Beller, M.; Glüsenkamp, K. H.; Jähde, E.; Rajewsky, M. F. *Chem. Ber.* **1991**, *124*, 1215.

(5) (a) Tidwell T. T. *Ketenes*; Wiley: New York, 1995. (b) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 7233. (c) Allen, A. D.; Lai, W.-Y.; Ma, J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 2625. (d) Allen, A. D.; Colomvakos, J. D.; Egle, I.; Lusztyk, J.; McAllister, M. A.; Tidwell, T. T.; Wagner, B. D.; Zhao, D.-C *J. Am. Chem. Soc.* **1995**, *117*, 7552.

(6) (a) Maier, G.; Reisenauer, H. P.; Sayrac, T. *Chem. Ber.* **1982**, *115*, 2192. (b) Hochstrasser, R.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 181.

(7) (a) Chen, H.; Law, K.-Y.; Perlstein, J.; Whitten, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 7257. (b) McKerrow, A. J.; Buncel, E.; Kazmaier, P. M. *Can. J. Chem.* **1995**, *73*, 1605. (c) Keil, D.; Hartmann, H. *Liebigs Ann.* **1995**, 979. (d) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449. (e) Gheorghiu, M. D.; Tidwell, T. T. 208th National American Chemical Society Meeting, August 21−25, 1994, Washington, D.C.; Abstract COMP, 0083.

(8) (a) West, R.; Ed. *Oxocarbons*; Academic Press: New York, 1980. (b) Cava, M. P.; Mitchell, M. J. *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1967.

(9) Rathna, A.; Chandrasekhar, J. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1661.

(10) (a) Dahn, H.; Ung-Truong, M.-N. *Helv. Chim. Acta* **1987**, *70*, 2130 and references therein. (b) Cerioni, G.; Culeddu, N.; Saba, A. *J. Phys. Org. Chem.* **1992**, *5*, 424 and references therein. (c) Cerioni, G.; Culeddu, N.; Saba, A. *Magn. Reson. Chem.* **1993**, *31*, 829 and references therein.

S0022-3263(96)00484-7 CCC: $12.00

Table 1. Carbonyl ^{17}O NMR Shifts for 1, 2, 4−6

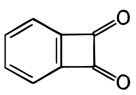
compound	R	R′	solvent	δ (ppm)	$\nu_{1/2}$(Hz)
1a	OH	OH	H_2O	263	182
1b	$O^- K^+$	$O^- K^+$	H_2O	273	156
1c[a]	OMe	OMe	$CDCl_3$	433.2	270
1d[b]	OEt	OEt	$CDCl_3$	430.8	365
1e	$SiMe_3$	$SiMe_3$	$CDCl_3$	499.1	526
1f	NMe_2	NMe_2	$CDCl_3$	368.3	220
1g	Me	Me	$CDCl_3$	477.1	222
1h	Cl	Cl	$CDCl_3$	499.3	194
1i[c]	NEt_2	OEt	$CDCl_3$	357.7 (β R)	410 (β R)
				418.2 (β R′)	520 (β R′)
1j[d,e]	$OSiMe_3$	$OSiMe_3$	CCl_4	456.3	540
1k	SPh	SPh	$CDCl_3$	457.9	860
1l	Ph	Ph	$CDCl_3$	479.8	950
2b[f]	Me	Me	CCl_4	234	190
2c[f]	Ph	Ph	CCl_4	246	500
4			$CDCl_3$	508.6	183
5a	OH	OH	H_2O	254.2	203
5b	$O^- NH_4^+$	$O^- NH_4^+$	H_2O	264.9	119
6[f]			CCl_4	502	100

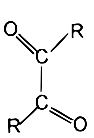
[a] OMe = 90.2 ppm, $\nu_{1/2}$ = 305 Hz. [b] OEt = 122.2 ppm, $\nu_{1/2}$ = 425 Hz. [c] OEt = 115.1 ppm, $\nu_{1/2}$ = 470 Hz. [d] $OSiMe_3$ = 123.1 ppm, $\nu_{1/2}$ = 560 Hz. [e] Measured by Dr. V. V. Toan (Lausanne). [f] From ref 10a, **2b** and **2c** measured at 66 °C, **6** at 78 °C.

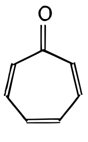
method is a valuable tool to study the carbonyl group[11] and its electronic charge,[10] and we have now extended this technique to the study of cyclobutene-1,2-diones and have also used theoretical studies to understand their properties.

Results

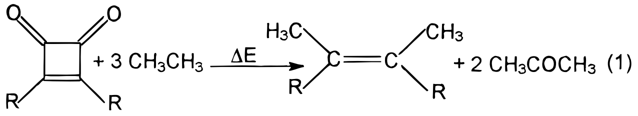
Cyclobutene-1,2-diones **1** and **4** and oxalic acid and its dianion **5** (R = O^-) were prepared by reported methods, or obtained from commercial suppliers, while data for the reference compounds **2** and **6** were taken from the literature. Measured ^{17}O NMR data are given in Table 1. There is a remarkably large range of shifts (263−508.6 ppm) of the 1,2 carbonyl groups of compounds **1a**−**l** and **4** depending on the 3,4 substituents.


4


5

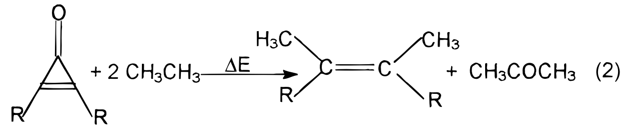

6

Also a series of cyclobutene-1,2-diones **1** as well as cyclopropenones **2** have been investigated theoretically by means of *ab initio* calculations. The optimization of geometries was carried out at the correlated MP2/6-31G-(d,p) level of theory. Natural net atomic charges have been calculated at the basis of the RHF/6-311G(d) density employing the NBO (natural bond orbitals) analysis[12] which seeks to represent the electronic structure of a molecule in terms of the best possible Lewis resonance structure. NMR chemical shifts have been calculated at the GIAO/6-311++G(2d,2p) level of theory. All these calculations have been performed on an SGI computer employing the program package GAUSSIAN 94.[13] Geometries of the cyclobutene-1,2-diones **1** and cyclopropenones **2** are given in Tables 2 and 3, along with calculated and observed ^{17}O chemical shifts. Homodesmic energy changes are shown for the reactions of eqs 1 and 2.



1

ΔE (kcal/mol) = -8.6 (R=OH), -14.8 (R=CH_3), 98.3(R=O^-)

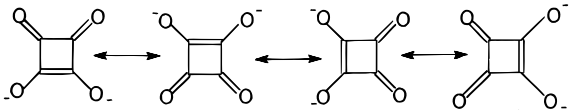


2

ΔE (kcal/mol) = -34.7 (R=OH), -37.6 (R=CH_3), 38.7 (R=O^-)

Discussion

It is known that squaric acid is an unusually strong organic acid (pK_1 = 1.2, pK_2 = 3.48),[14] its strength being comparable to that of oxalic acid **5a** (pK_1 = 1.28, pK_2 = 4.27).[15,16] Both compounds, as well as their salts, are completely ionized in aqueous solutions. Evidence of this fact is given by our observation of only one signal for the four oxygens of squaric acid in aqueous solution. The structure of the squarate dianion may be represented as a combination of the four degenerate resonance structures **7a**−**d**.


7a **7b** **7c** **7d**

The exceptional properties of the dianions of the deltic acid (**2**, R = OH) and squaric acid molecules can be seen from their calculated geometries in Tables 2 and 3. Such small molecular dianions would be unstable against spontaneous ejection of an electron in the gas phase,[17] but the usual computational methods are unable to describe this fact and, therefore, fortunately describe the system as it could be in solution. Both anionic systems **8** and **7** adopt high symmetry (D_{3h} and D_{4h}) structures, respectively, and this indicates that they have significant stability, as discussed below. As a consequence the electronic net charges carried by the carbonyl oxygen atoms adopt maximum values in the corresponding series of systems. The calculated δ(^{17}O) NMR chemical shifts are lower by 300 (**1**) and 160 (**2**) ppm compared with the respective chlorine-substituted compounds. Calculated ^{17}O chemical shifts for carbonyl groups differ in some cases from experimental values (Table 1) by up to 50 ppm, but the values in Tables 2 and 3 exhibit correct trends. Among the neutral systems **1** and **2** the squaric

---

[11] Boykin, D. W.; Ed. *O-17 NMR Spectroscopy in Organic Chemistry* CRC Press: Boca Raton, FL, 1991.

[12] Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1, Wisconsin, 1988.

[13] GAUSSIAN 94, Revision B.3, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc, Pittsburgh, PA, 1995.

[14] MacDonald, D. J. *J. Org: Chem.* **1968**, *33*, 4559.

[15] Darken, L. S. *J. Am. Chem. Soc.* **1941**, *63*, 1007.

[16] Pinching, G. D.; Bates, R. G. *J. Res. Nat. Bur. Stand., A* **1948**, *40*, 405.

[17] Janoschek, R. *Z. Anorg. Allg. Chem.* **1992**, *616*, 101.

Table 2. MP2/6-31G(d,p) Optimized Geometry Data (Å, deg) of Cyclobutene-1,2-diones 1, RHF/6-311G(d) Calculated Natural Net Atomic Charges *q*, and GIAO/6-311++G(2d,2p) NMR Chemical Shifts $\delta(^{17}O)$ (ppm), Referenced to $H_2O(l)$

	R = R′					
	O^- D_{4h}	H C_{2v}	OH C_{2v}	F C_{2v}	Cl C_{2v}	Me C_{2v}
C1−O, Å	1.268	1.209	1.219	1.211	1.209	1.214
C1−C2, Å	1.493	1.582	1.552	1.568	1.570	1.571
C1−C3, Å	1.493	1.512	1.486	1.496	1.506	1.505
C3−C4, Å	1.493	1.359	1.380	1.367	1.369	1.370
O−C1−C2, deg	135.0	137.6	139.7	137.4	138.0	138.4
O, *q*	−0.881	−0.584	-0.629^{a}	−0.565	−0.567	−0.610
C1, *q*	0.381	0.565	0.532	0.529	0.574	0.577
C3, *q*	0.381	−0.195	0.292	0.373	−0.100	−0.024
R, *q*	−0.881	0.214	−0.194	−0.338	0.093	0.056
$\delta(^{17}O)$	251 $(265)^{b}$	562	475^{a} $(254)^{b}$	551	550 $(499)^{b}$	528 $(477)^{b}$

[a] Average values, according to $^1/_2$O(H) + $^1/_2$O(C), for *q*(O) and $\delta(^{17}O)$ are −0.656 and 266 ppm, respectively. [b] Observed.

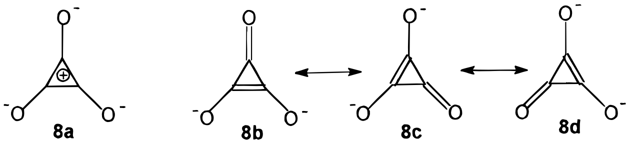
Table 3. MP2/6-31G(d,p) Optimized Geometry Data (Å, deg) of Cyclopropenones 2, RHF/6-311G(d) Calculated Natural Net Atomic Charges *q*, and GIAO/6-311++G(2d,2p) NMR Chemical Shifts $\delta(^{17}O)$ (ppm), Referenced to $H_2O(l)$

	R = R′				
	O^- D_{3h}	OH C_{2v}	F C_{2v}	Cl C_{2v}	MeC_{2v}
C1−O, Å	1.291	1.217	1.204	1.205	1.219
C1−C2, Å	1.455	1.451	1.468	1.458	1.439
C2−C3, Å	1.455	1.355	1.347	1.351	1.361
O, *q*	−0.969	-0.718^{a}	−0.656	−0.655	−0.716
C1, *q*	0.302	0.559	0.579	0.650	0.623
C2, *q*	0.302	0.284	0.375	−0.075	−0.002
R, *q*	−0.969	−0.204	−0.336	0.077	0.049
$\delta(^{17}O)$	75	173^{a}	215	235	222 $(233)^{b}$

[a] Average values, according to $^2/_3$O(H) + $^1/_3$O(C), for *q*(O) and $\delta(^{17}O)$ are −0.698 and 91 ppm, respectively. [b] Observed.

1a and deltic acid (**2**, R = OH) molecules show more or less maximum C=O and C=C bond lengths, maximum electronic charges at the carbonyl oxygen atoms, and minimum ^{17}O chemical shifts for the respective series. For comparison with experimental values in solution, calculated atomic charges and chemical shifts for carbonyl and hydroxyl oxygens should be properly averaged due to the rapid chemical exchange. These values appear in the footnotes to Tables 2 and 3. The significantly long CC distance in **1** which connects the two carbonyl groups is already described in the literature,[9] where the negative hyperconjugative interaction between the oxygen lone pairs and the adjacent C−C σ^* orbital is suggested to be the principal reason for the relatively long C_1-C_2 bond on diketones. We found that the parent compound of **1** exhibits the maximum C_1-C_2 bond length (1.582 Å) in our series of cyclobutene-1,2-diones (Table 2). According to the NBO analysis, either of the oxygen n(p) lone-pairs donates 0.11e into the adjacent antibonding C−O π^* orbital; and the C_3-C_4 π orbital is delocalized to the C_1-C_2 σ^* orbital and donates 0.12e. Thus, the parent compound of **1** should have a distinct diradical character.

The question of the stability of the dianions of deltic and squaric acids may be answered by the calculated π-electron resonance structures. The structure with the three-center π-bond orbital of the deltic acid anion turned out not to be a good Lewis structure according to localization criteria. A more complete description of the electronic structure is based on mixing the resonance structures **8** where hybrids **8b**−**d** are degenerate. The number of π-electrons in the carbon ring is calculated, by summing over all natural atomic orbital occupancies which contribute to the π-orbitals and summing over all carbon atoms, to be 2.6 electrons. In contrast, the charges q in the Tables 2 and 3 are natural net atomic total charges. Thus, the "real" structure may be assumed between the three-center-two-electron formula **8a** and the triply degenerate set with a neutral carbon ring.



8a **8b** **8c** **8d**

The π-system of the four-membered carbon ring has the quadruply degenerate set of resonance structures **7a**−**d** shown above and is calculated as above to be occupied by 3.3 electrons which confirms the relevance of these resonance structures. The lifting of the degeneracy of resonance structures for the neutral system, due to symmetry reduction, leads to better Lewis structures which resemble the usual formulae **1** and **2**.

Harmonic vibrational frequencies confirm planar backbone moieties for compounds **1** and **2** in their minima. The lowest out-of-plane vibrational wave number of the oxygens in $C_3O_3^{2-}$ is found to be 313 cm^{-1} (A2″), but in $C_4O_4^{2-}$ the corresponding wave number is as low as 65 cm^{-1} (B_{2u}). Thus, the stabilizing character of π-electron delocalization in the carbon four-membered ring, which usually stiffens the planarity of the ring, is either insignificantly low or is compensated by other effects. The corresponding out-of-plane wave numbers of the neutral C_4O_4RR' systems are roughly 100 cm^{-1}.

Equivalence between the two oxygen atoms of a carboxylic group has been consistently observed[18a,b] and has been ascribed[18a] to a fast, by the timescale of ^{17}O NMR spectroscopy, exchange of the proton between the two oxygens of the carboxylic acid group, in dimeric or higher aggregates. That the ^{17}O NMR shifts in carboxylic acids have roughly an intermediate value between those of the ester carbonyls and alkoxy groups corroborate this fact.[18b] However monocarboxylic acids differ from squaric acid and oxalic acid in the difference between the ^{17}O chemical shifts in the acids and in their salts. For both pairs, squarates **1a** and **1b** and oxalates **5a** and **5b**, there is a relatively smaller difference in shift (10 ppm) compared to the larger difference ($\Delta\delta$ = *ca.* 25 ppm) observed[19] in a large series of carboxylic acids and their anions. It has been noted[19] that increasing acid strength diminishes this difference, e.g. for chloroacetic acid $\Delta\delta$ = 18.4 ppm. It is

---

(18) (a) Boykin, D. W.; Baumstark, A. L. in ref 11, Chap. 8, p 217 and references therein. (b) Delseth, C.; Nguyen, T. T.-T.; Kintzinger, J.-P. *Helv. Chim. Acta* **1980**, *63*, 498. (c) Boykin, D. W. *Spectrochim. Acta* **1991**, *47A*, 323.

(19) Gerothanassis, I. P.; Hunston, R.; Lauterwein, J. *Helv. Chim. Acta* **1982**, *65*, 1764 and ref 39 therein (Carrupt, P.-A.; Gerothanassis, I. P.; Lauterwein, J. Unpublished results).

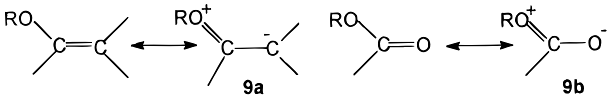
known, from X-ray crystallography,[20] that the dianion of squaric acid is, true to its name, a square with four identical C−C and four identical C−O bond lengths, and four identical internal angles close to 90°. The small difference in ^{17}O chemical shifts between the free acid and its dipotassium salt indicates that **1a** and **1b** have a close structural similarity. Our own ^{13}C NMR measurements give analogous results, only one signal being observed for **1a** and for **1b**, at 195.1 and 203.9 ppm, respectively. A similar difference (10.7 ppm) is observed in the ^{17}O NMR spectrum between oxalic acid and its diammonium salt. Again, as a strong acid, oxalic acid should be completely ionized in aqueous solution.

Solvation has an important effect on the ^{17}O NMR shift and comparisons should be made in the same or very similar solvents. Thus benzoic acid shows a remarkably constant shift (250−250.5 ppm) in DMSO,[21] acetone,[22] or acetonitrile[23] while its lithium salt shift[24] varies over 19 ppm (262−281 ppm) in DMSO and methanol solutions.

The carbonyl oxygens of the dimethoxy- and diethoxycyclobutenediones **1c** and **1d** are deshielded by *ca.* 76 and 71 ppm, respectively, compared to those of normal carboxylic esters $CH_3CO_2CH_3$ and $CH_3CO_2C_2H_5$, respectively,[18] and likewise the bis(NMe$_2$)cyclobutenedione **1f** is deshielded by *ca.* 40 ppm compared with carboxylic amides.[18] On the other hand, a remarkable shielding (*ca.* 80 ppm) is observed when comparing **1f** with some enamine ketones.[25]

The lower field shift of the carbonyl oxygens and the higher field shifts of the ether oxygens of the 3,4-(OR)$_2$ substituted cyclobutenediones **1c** and **1d** compared to carboxylic esters CH_3CO_2R is consistent with a smaller degree of conjugation between these oxygens in the cyclobutenediones, and this may be attributed to the high degree of negative charge already present on the carbonyl oxygens in the cyclobutenediones.

The ether oxygens of the cyclobutenediones **1c** and **1d** are deshielded by *ca.* 30 ppm in comparison to α,*β*-unsaturated ethers,[26] and this is consistent with greater electron donation according to the strucure **9a** in the former case. The ether oxygens of both α,*β*-unsaturated ethers and esters appear downfield compared to ethers,[27] and this is a consequence of the importance of resonance structures **9a** and **9b**, respectively.

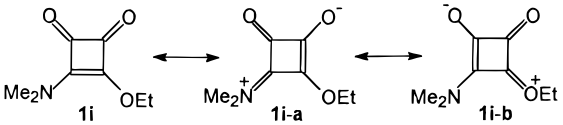


9a **9b**

The 3,4-(OSiMe$_3$)$_2$ substituted cyclobutenedione **1j** shows an even greater deshielding for the carbonyl oxygens of 23.1 and 26.3 ppm, respectively, compared to the 3,4-(OMe)$_2$ and 3,4-(OEt)$_2$ derivatives **1c** and **1d**, respectively. There are, to the best of our knowledge, no comparable published data for Me$_3$Si esters of carboxylic acids, and so for the sake of comparison we have measured the ^{17}O shifts of $CH_3CO_2SiMe_3$, observing δ(C=O) = 376.8 ppm ($\nu_{1/2}$ = 290 Hz) and δ(OSi) = 177.3 ppm ($\nu_{1/2}$ = 205 Hz). The carbonyl oxygens in $CH_3CO_2SiMe_3$ and $CH_3CO_2CH_3$ are thus found to be shifted upfield by 80 and 76 ppm, respectively, compared to the 3,4-(OSiMe$_3$)$_2$ and 3,4-(OMe)$_2$ cyclobutenediones, whereas the corresponding OSiMe$_3$ and OCH$_3$ are shifted downfield by 54 and 44 ppm, respectively, compared to the cyclobutene-1,2-diones, showing a strong consistency in behavior.

Similar considerations can also apply for the di(NMe$_2$) derivative **1f**. Since this is an amide analog we cannot, in this case, observe by ^{17}O NMR the atoms which participate in resonance structures type **9b**. We note, however, that the difference observed between **1f** and an average *N*,*N*-dimethylamino amidic shift[18a] of *ca.* 330 ppm is much smaller than that observed in the case of esters, as it could be forecast by the greater ability of nitrogen, compared to oxygen, to donate an electron pair and to bear a positive charge.

The shift difference between ester and amidic carbonyls allows an easy assignment of the two signals of the mixed derivative **1i**, the more deshielded carbonyl group being that conjugated to the OEt group. Both the two carbonyls are, however, slightly shielded when compared to those of unmixed derivatives, i.e. **1c**, **1d**, and **1f**. Thus it appears that conjugation is mostly localized between one carbonyl group and its farthest substituent. It has been observed[28] that the unsymmetrical **1i** has a rotational barrier around its amidic bond with a $\Delta G^{\ddagger}$ value of 17.3 kcal/mol. However, **1f** and some analogous diamides showed no observed coalescence and did not give any measurable rotational barrier even when the solution was cooled to −60 °C.[28]



1i **1i-a** **1i-b**

Dimethyl- and diphenylcyclobutenediones **1g** and **1l** show shifts of 477.1 and 479.8 ppm, respectively, upfield from the usually observed range (530−565 ppm) of α,*β*-unsaturated ketones.[29]

By comparison, the ^{17}O NMR chemical shifts of dimethylcyclopropenone **2b**, and tropone **6**,[10a] are at 234 and 502 ppm, respectively (Table 1). Thus the ^{17}O NMR shifts of the cyclobutenediones **1g** and **1l** are only about 20−25 ppm upfield from tropone **6**, which is 269 ppm downfield from dimethylcyclopropenone **2b**. This high upfield shift of cyclopropenone is consistent with the importance of the aromatic structure **2a**, but the aromatic character of the cyclobutenediones is not great and is only comparable to that of tropone **6**. Thus the electronic structure of the cyclobutenedione is best described by the structures **10a** and **10b**, so that on average the oxygens have a negative charge near 0.6, and there is a net positive charge near 1.0 in the ring. As noted above this is consistent with the results of the theoretical calculation.

In the case of squaric acid **1a** and the dipotassium salt **1b** (Table 1) where the negative charges are delocalized

---

(20) Macintyre, W. M.; Werkema, M. S. *J. Chem. Phys.* **1964**, *42*, 3563.

(21) Monti, D.; Orsini, F.; Ricca, G. S. *Spectrosc. Lett.* **1986**, *19*, 91.

(22) Balakrishnan, P.; Baumstark, A. L.; Boykin, D. W. *Org. Magn. Reson.* **1984**, *22*, 753.

(23) Baumstark, A. L.; Balakrishnan, P.; Dotrong, M.; McCloskey, C. J.; Oakley, M. G.; Boykin, D. W. *J. Am. Chem. Soc.* **1987**, *109*, 1059.

(24) Baltzer, L.; Becker, E. D. *J. Am. Chem. Soc.* **1983**, *105*, 5730.

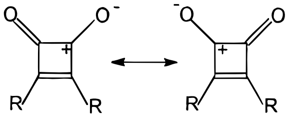
(25) Boykin, W. D.; Kumar, A.; Shevchenko, S. M. *Magn. Reson. Chem.* **1992**, *30*, 16.

(26) (a) Kintzinger, J.-P.; Delseth, C.; Nguyen, T. T.-T. *Tetrahedron* **1980**, *36*, 3431. (b) Kalabin, G. A.; Kushnarev, D. F.; Valeyev, R. B.; Trofimov, B. A.; Fedotov, M. A. *Org. Magn Reson.* **1982**, *18*, 1.

(27) Chandrasekaran, S. in ref 11, Chap. 7.

(28) Thorpe, J. E. *J. Chem. Soc. (B)* **1968**, 435.

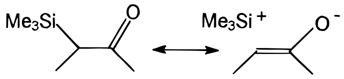
(29) Boykin, D. W.; Baumstark, A. L. in ref 11, Chap. 8, pp 208 −11 and references therein.



10a **10b**

over all the four oxygen atoms, aromaticity is greater as shown by the ^{17}O and ^{13}C NMR spectra of **1a** and **1b** and by the X-ray study[20] of **1b**. It can also be observed that on going from the dimethyl derivative **1g** to the diphenyl compound **1l** a very slight deshielding (2.7 ppm) is observed. The same observation applies also to the dimethyl- and diphenylcyclopropenones **2b** and **2c**, but with a somewhat greater extent (12 ppm). This behavior resembles that observed by ^{13}C NMR spectroscopy, with a shielding instead of a deshielding, for the carbonyl carbons of these four compounds. For compounds **2b** and **2c** carbonyl ^{13}C shifts have been determined[30] as 159.6 and 155.8 ppm, respectively, and for compounds **1g** and **1l** as 199.8 from our laboratories, and 196.1[30] ppm, respectively. These shift differences between the cyclopropenones and the cyclobutene-1,2-diones parallel the difference in ^{13}C shifts of the sp^2 carbons in cyclopropene (108.7 ppm) and cyclobutene (137.2 ppm).[31]

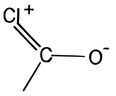
Bis(SiMe$_3$) cyclobutenedione **1e** is 22 ppm downfield compared to the Me,Me derivative **1g**, and this is opposite to our recent observation[32] for substrates where the Me$_3$-Si−C bond is coplanar with the carbonyl π-system that substitution of a γ (with respect to oxygen) alkyl group by trimethylsilyl causes upfield shifts at the carbonyl oxygens both in saturated ketones (*e.g.* $\Delta\delta = 28.6$ ppm for *tert*-butylacetone and 1-(trimethylsilyl)propan-2-one) and in ketenes (*e.g.* $\Delta\delta = 74.0$ ppm for dimethylketene and trimethylsilylketene). This latter effect has been attributed[32] to "neutral hyperconjugation"[33] involving the coplanar C−Si bond and the carbonyl π orbitals, as shown in **11b**. In the case of the cyclobutenedione system such "neutral hyperconjugation" is not possible, as the C−Si bond and the carbonyl π orbitals are orthogonal. Similarly the ^{29}Si NMR shift of bis(trimethylsilyl)cyclobutenedione[32] **1e** (−8.4 ppm) is comparable to those[34] of Me$_3$SiPh (−4.5 ppm) and Me$_3$SiCH=CH$_2$ (−6.6 ppm), so there is also no evidence of a significant transfer of charge between the Si and the ring by this criterion. The upfield ^{17}O shift of the dimethyl derivative **1g** may be attributed to the greater electron-donating power of the methyl groups compared to Me$_3$Si when such neutral conjugation is not possible, as indicated by the respective σ values.[35]



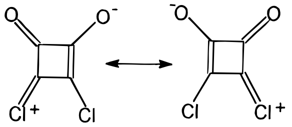
11a **11b**

Substitution of one or two carbon atoms directly bound to a carbonyl group by a silicon atom causes very large deshielding.[36] In such a case, Dahn and co-workers[36c] have convincingly established that this deshielding is due to a change in the electron excitation energy, represented by the ΔE term in the Karplus−Pople equation.[37] This term is empirically approximated by the longest wave (symmetry forbidden) absorption in the UV-vis spectrum. As we have observed (*vide supra*), a certain similarity (although reduced) of the effects of 3,4 substitutions on the carbonyl shifts in comparison with analogous effects observed in acids, esters, and amides with respect to ketones, we may compare the UV-vis absorptions of **1e** and **1g**. We note that these two spectra are very similar, particularly in the longest wave absorption (**1e**[38] $\lambda = 354$, $\epsilon = 37$, **1g**[39] $\lambda = 355$, $\epsilon = 23$), and this is consistent with the rather small difference (22 ppm) in the ^{17}O shifts.

Dichlorocyclobutenedione **1h** shows a ^{17}O NMR chemical shift (499.3 ppm) very similar to those of aliphatic acyl chlorides[18b] (493.5−504.5 ppm) and 4-substituted benzoyl chlorides (469−502 ppm).[18c] This finding seems in agreement with the similarities described above between squaric acid derivatives and typical carboxylic acids derivatives. A possible explanation of the closer similarity could be that the importance of resonance structures type **12** is already small for acyl chlorides and thus their effects became comparable with those of **1h-a**,**b**.



12



1h-a **1h-b**

A comparison for the bis(SPh) cyclobutenedione **1k** is possible with thiol esters.[40] Also with this compound we observe both a similarity and a difference with analogous carboxylic acid derivatives. Thiol esters have an ^{17}O chemical shift[40] (*ca.* 500 ppm) different from that of esters[40] (*ca.* 350 ppm) and more similar[40a] to that of analogous ketones (*ca.* 550 ppm).[11] In the case of cyclobutenedione derivative **1k**, too, there is a deshielding ($\Delta\delta = ca.$ 26 ppm) in comparison with esters **1c** and **1d** but to quite a minor extent. A shielding of similar value ($\Delta\delta = ca.$ 20 ppm) is observed in comparison with "ketones" **1g** and **1l**.

Benzocyclobutenedione **4** is the most deshielded of the studied compounds, although it is still some 50 ppm more shielded than aromatic diketones,[41] and is only 29 ppm upfield from diphenylcyclobutenedione **1l**. A proper comparison is with 9,10-phenantrenequinone[41] (555 ppm), to model the influence of the torsional angle between the carbonyl groups. The influence of the ring size should be roughly 13 ppm,[42] as observed from cyclobutanone to cyclohexanone. The observed shielding may be attributed to the possibility to delocalize the partial positive

---

(30) Dehmlow, E. V.; Zeisberg, R.; Dehmlow, S. S. *Org. Magn Reson.* **1975**, *7*, 418.

(31) Orendt, A. M.; Facelli, J. C.; Beeler, A. J.; Reuter, K.; Horton, W. J.; Cutts, P.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 3386.

(32) Allen, A. D.; Egle, I.; Janoschek, R.; Liu, H. W.; Ma, J.; Marra, R. M.; Tidwell, T. T. *Chem. Lett.* **1996**, 45 and references therein.

(33) Lambert, J. B.; Singer, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 10246. *J. Am. Chem. Soc.* **1995**, *117*, 2122.

(34) Sakurai, H.; Kamiyama, Y.; Mikoda, A.; Kobayashi, T.; Sasaki, K.; Nakadaira, Y. *J. Organomet. Chem.* **1980**, *201*, C14.

(35) Bassindale, A. R.; Taylor, P. G. in *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds. Wiley: New York, 1989; Part 2, Chap. 14, p 902.

(36) (a) Dahn, H.; Péchy, P.; Toan, V. V. *Magn. Reson. Chem.* **1990**, *28*, 883. (b) Chimichi, S.; Mealli, C. *J. Mol. Struct.* **1992**, *271*, 133. (c) Dahn, H.; Péchy, P.; Bestmann, H. J. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1497.

(37) Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803.

(38) Zhao, D.-C.; Tidwell, T. T. *J. Am. Chem. Soc.* **1992**, *114*, 10980.

(39) Blomquist, A. T.; Vierling, R. A. *Tetrahedron Lett.* **1961**, 655.

(40) (a) Boykin, D. W. *Spectrosc. Lett.* **1990**, *23*, 1133. (b) Dahn, H.; Péchy, P.; Toan, V. V. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 647. (c) Dahn, H.; Péchy, P. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1721. (d) Dahn, H.; Péchy, P *J. Chim. Phys.* **1992**, *89*, 1683.

(41) Cerioni, G.; Plumitallo, A.; Frey, J.; Rappoport, Z. *Magn. Reson. Chem.* **1995**, *33*, 874.

(42) Delseth, C.; Kintzinger, J.-P. *Helv. Chim. Acta* **1976**, *59*, 466.

charges on C1 and C2 in the condensed aromatic ring, with subsequent increase of the importance of the keto group resonance structure $C^{+}-O^{-}$.

More insight into the stability of the cyclic compounds **1** and **2** can be achieved by means of homodesmic eqs 1 and 2. The reaction energies of homodesmic equations have been used successfully in the past for the estimation of electronic delocalization and ring strain energies of cyclic compounds. For the present cyclic species the calculated values are the sum of these two effects. The negative ΔE values of the neutral OH and CH_3 substituted systems indicate that ring strain energy predominates over delocalization stabilization, by some 25 to 35 kcal/mol more in the three-membered ring system (**2**) compared to the four-membered ring system (**1**). In the doubly charged anions, however, delocalization of two extra electrons among three (**8**) or four (**7**) oxygen centers overwhelms the effect of delocalization in the carbon rings and of ring strain dramatically. Thus, it is the relief of Coulomb repulsion between the pair of extra electrons upon delocalization which makes the anions remarkably stable, for the squaric acid dianion by 60 kcal/mol more than for the deltic acid dianion. This leads to an understanding of calculated properties in Tables 2 and 3.

Summary

In summary cyclobutene-1,2-diones **1** are indicated by theoretical studies to be best represented as hybrids of the structures **10a**,**b**, with a net negative charge near 1 delocalized on the oxygens, and with a positive charge near 1 in the ring. In cyclopropenones a comparable charge is delocalized to the single oxygen. ^{17}O NMR chemical shifts are consistent with this conclusion and provide evidence for electron delocalization from donor substituents on the ring to oxygen. The dianions of squaric acid and deltic acid are represented by the resonance structures **7** and **8**, respectively, and show a high stabilization and major ^{17}O NMR shielding due to electron delocalization to oxygen.

Experimental Section

Materials. Compounds **1a**, **1c**, **1d**, **5a**, and **5b** are commercially available and were used without any further purification. All the other compounds had been previously reported, **1b**,[1b] **1e**,[38] **1g**,[43] **1h**,[44] **1i**,[28] **1k**,[45] and **1l**,[46] and were prepared according to their respective reference. Compounds **1f** and **4** are gifts from Professor H. Dahn.

NMR Spectroscopy. O-17 NMR spectra were recorded in the Fourier transform mode, mostly on a Varian VXR 300 spectrometer equipped with a Sun 3/60 computer and with a 10 mm broad band probe at room temperature (probe temperature = 294 K) and natural isotopic abundance. The instrumental settings were: 40.662 MHz frequency, spectral width 36 KHz, acquisition time 10 ms, preacquisition delay 100 μs, pulse angle 90° (pulse width 28 μs), number of scans 100000−200000; the spectra were recorded with sample spinning and without lock. The signal to noise ratio was improved by applying a 30 Hz exponential broadening factor to the FID prior to Fourier transformation. The data point resolution was improved by zero filling to 16K data points. A Varian VXR 400S spectrometer was used for some of the measurements, with analogous settings. The reproducibility of the chemical shift data is estimated to be ±1 ppm.

The C-13 shifts have been obtained with the VXR 300 instrument at 75.429 MHz under routine conditions using 10 mm tubes. C-13 shifts were referred to $CDCl_3$ ($\delta = 77.0$).

Acknowledgment. One of us (G.C.) is indebted to Prof. H. Dahn for a gift of compounds **1f** and **4** and for helpful discussions. We thank K. Sung, J. D. Colomovakos, and I. Egle for preparing some of the substrates and M.U.R.S.T. (60% fund) and the Natural Science and Engineering Research Council of Canada for financial support.

Supporting Information Available: Z-matrices and total energies of calculated compounds (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm and CD-ROM versions of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO960484A

---

(43) Blomquist, A. T.; LaLancette, J. *Tetrahedron Lett.* **1961**, 655.

(44) DeSelms, R. C.; Fox, C. J.; Riordan, R. C. *Tetrahedron Lett.* **1970**, 781.

(45) Schmidt, A. H.; Kunz, C.; Debo, M.; Mora-Ferrer, J. *Synthesis* **1990**, 819.

(46) Green, B. R.; Neuse, E. W. *Synthesis* **1974**, 46.