The Squaric Acid Molecule: a Hydrogen Bond Study of Dimethylammonium Hydrobis(hydrogen squarate) $(H_2NMe_2)^+[H_3(C_4O_4)_2]^-$

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The title compound has been synthesized and studied by *X*-ray diffraction methods. Crystals are orthorhombic, space group *Pccn*, with $Z = 4$ in a unit cell of dimensions: $a = 6{\cdot}080(3)$, $b = 15{\cdot}739(14)$, $c = 11{\cdot}883(9)$ Å. The structure was solved by direct methods and the final weighted discrepancy factor was 0·050, after anisotropic full-matrix least-squares refinement on 2369 unique reflections measured on a diffractometer. Strong intermolecular hydrogen bonding interactions, both symmetric [O · · · O 2·435(2) Å] and asymmetric [O · · · O 2·582(2) Å] exist between squaric acid molecules, two of which are linked *via* one hydrogen atom, with a dihedral angle 26·5° between two C_4O_4 planes.

A NEUTRON and *X*-ray diffraction study of the structure of squaric acid, $H_2C_4O_4$, was recently reported,[1] and strong asymmetric hydrogen bonds were found between the molecules. Furthermore, in contrast to the dianion, $C_4O_4^{2-}$,[2-4] which is considered to be an aromatic anion with an unusual amount of resonance energy, $H_2C_4O_4$ was found to contain partially localized double bonds in the four-membered ring, a result which is consistent with a recent interpretation of the single-crystal Raman study of squaric acid.[5] The strong hydrogen bonding in $H_2C_4O_4$ suggests that highly associated $[H_2C_4O_4]_n$ aggregates might exist in solution and that proton dissociation could proceed step-wise according to the equation: $[H_2C_4O_4]_n \longrightarrow mH^+ + H_{2n-m}(C_4O_4)_n^{-m}$. In order to investigate further the step-wise dissociation and the asymmetric double-minimum potential well between the oxygen atoms and the localized bonding in squaric acid, the hydrobis(hydrogen squarate) ion, $H_3(C_4O_4)_2^-$, was synthesized and studied by *X*-ray diffraction techniques.

EXPERIMENTAL

Synthesis and Characterization.—Excess of squaric acid was added to *NN*-dimethylacetamide and the solution heated until the squaric acid had completely dissolved. The salt was obtained as *crystals* by diffusing benzene into the solution (Found: C, 44·0; H, 3·9; N, 5·25. $C_{10}H_{11}NO_8$ requires C, 43·95; H, 3·65; N, 5·15%).

The i.r. spectrum (KBr pressed disk) can be compared with that of squaric acid.[5] Two strong peaks at 2770 and 2975 cm^{-1}, not observed in the squaric acid, are assigned to the C–H and N^+–H stretching frequencies of the dimethylammonium ion.[6] The small peak at 2430 cm^{-1} is assigned as an $N^+\text{–}H \cdots O^-$ symmetric stretching frequency and indicated that the compound did contain the dimethylammonium ion as well as a squaric acid unit. A mass spectrometric study gave a spectrum similar to that of squaric acid,[7] except for some extra peaks around *m/e* 46, which is the mass of the dimethylammonium ion.

X-*Ray Intensity Measurements*.—A rectangular crystal with dimensions of 0·3 × 0·3 × 0·35 mm was mounted on a glass fibre with the [032] direction parallel to the axis for diffractometer data collection. A computer-controlled four-circle Picker diffractometer equipped with a highly oriented graphite monochromator (Mo-K_α radiation) was used for data measurements. Integrated intensities were collected, by the θ—2θ scan technique at a scan rate of 1° min^{-1}. Each reflection was measured by using a dispersion corrected 1·6° scan on 2θ with 10 s background counts taken at both sides of the peak. The take-off angle was 1·6°. 2369 Unique reflections were collected to a maximum 2θ angle of 70°. Intensities were corrected for background, Lorentz, and polarization effects. Scattering factors for all atoms were taken from ref. 8.

Crystal Data.—$C_{10}H_{11}NO_8$, $M = 273{\cdot}11$. Orthorhombic, $a = 6{\cdot}080(3)$, $b = 15{\cdot}739(14)$, $c = 11{\cdot}883(9)$ Å, $U = 1137{\cdot}12$ Å^3, $D_c = 1{\cdot}595$, $Z = 4$, $D_o = 1{\cdot}582(5)$ (flotation in benzene–1,3-dibromobenzene); $F(000) = 568$. Space group *Pccn* (D_{2h}): Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, $\mu(\text{Mo-}K_\alpha) = 1{\cdot}51$ cm^{-1}.

Solution and Refinement.—The structure was solved by the application of direct methods, by use of the FAME–MAGIC–LINK–SYMPL[9] programs. These results led to a three-dimensional *E* map calculated with 208 data and a satisfactory trial structure. All six hydrogen atoms were located in the difference Fourier synthesis after several cycles of least-square refinement.[10] The weighted factor $R' [= (\Sigma w|F_o - F_c|^2/\Sigma wF_o^2)^{1/2}]$ was 0·131 after isotropic thermal parameter factor refinement without hydrogen atoms, and 0·117 with six hydrogen atoms refined isotropically with positional parameters. The weight w was taken as $1/\sigma^2(F)$ where $\sigma(F) = \frac{F}{2I}[CN + 0{\cdot}25(T_C/T_B)^2(B_1 + B_2) + p^2I^2]$, where CN = total integrated peak counts, B_1,B_2 = background counts at both sides of the peak, T_B = background scan time (= 10 s), T_C total scan time (s), I = net peak count, p = constant = 0·02. The inclusion of anisotropic thermal parameters for all non-hydrogen atoms gave final discrepancy factors of R' 0·050 (all data), and R 0·054 (observed data only). Observed reflections had $I > 3\sigma(I)$ where $\sigma(I) = [CN + (T_C/T_B)^2(B_1 + B_2)]^{1/2}$. A final difference Fourier map showed no peaks $> 0{\cdot}46$ eÅ^{-3}.

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TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) and thermal parameters *

	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
C(2)	2081(2)	−1197(1)	3415(1)	80(3)	17(5)	46(1)	−1(1)	−1(2)	2(1)
C(3)	1217(2)	−397(1)	3678(1)	94(3)	17(1)	42(1)	2(1)	−1(2)	−1(1)
C(4)	3405(2)	−11(1)	3781(1)	102(3)	21(1)	42(1)	2(1)	−1(2)	−0(1)
C(1)	4323(2)	−866(1)	3505(1)	96(4)	18(1)	46(1)	1(1)	1(2)	0(1)
O(2)	1197(2)	−1912(1)	3169(1)	99(3)	17(0)	87(1)	−4(1)	−5(1)	−4(1)
O(3)	−751(2)	−69(1)	3777(1)	88(3)	23(1)	66(1)	12(1)	−1(1)	−6(1)
O(4)	4166(2)	691(1)	3956(1)	149(3)	21(0)	88(1)	−8(1)	−11(2)	−10(1)
O(1)	6198(2)	−1163(1)	3363(1)	82(3)	25(0)	76(1)	5(1)	5(1)	−5(1)
N	2500	2500	3476(2)	204(6)	37(1)	60(2)	−6(2)		
C(5)	611(4)	2215(1	4162(2)	208(6)	34(1)	84(2)	7(2)	25(3)	4(1)
				B ($\times 10^2$)					
H(4)	−468(34)	1980(13)	3657(18)	3·00(55)					
H(5)	1095(36)	1789(16)	4730(21)	4·80(64)					
H(6)	117(30)	2707(13)	4552(16)	1·88(48)					
H(3)	2923(43)	2082(13)	3000(18)	4·61(68)					
H(2)	25	−25	3142(28)	5·33(86)					
H(1)	8176(37)	−535(14)	3669(20)	4·89(67)					

* β values are in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

The intensities of all unobserved reflections were taken to be $\sigma(I)$ with an estimated standard deviation of $2I_{\text{min.}}/\sqrt{45}$, where $I_{\text{min.}} = 3\sigma(I)$.[11] During refinement, all unobserved reflections with $F_o > F_c$ were given zero weight. The estimated standard deviation of an observation of unit weight $S = (\Sigma w|F_o - F_c|^2/N_o - N_v)^{1/2} = 1{\cdot}47$ with $N_o = 2369$ and $N_v = 109$. Positional and thermal parameters from the last cycle of least-squares refinement are in Table 1, and bond distances and angles, with their errors,[10] in Table 2. Structure factors of observed and unobserved reflections are listed in Supplementary Publication No. SUP 20942 (2 pp.).*

TABLE 2

Bond distances and angles

a) Distances (Å)

C(4)–C(3)	1·467(2)	N–C(5)	1·478(2)
C(3)–C(2)	1·400(2)	N–H(3)	0·907(20)
C(2)–C(1)	1·462(2)	C(5)–H(4)	0·963(21)
C(1)–C(4)	1·494(2)	C(5)–H(5)	0·995(25)
C(4)–O(4)	1·215(2)	C(5)–H(6)	0·951(20)
C(3)–O(3)	1·308(2)	O(2)–H(2)	1·218(1)
C(2)–O(2)	1·282(2)	O(3)–H(1)	0·989(23)
C(1)–O(1)	1·238(2)	H(1)–O(1)	1·603(23)

(*b*) Non-bonded contacts (Å)

O(2) ··· O(2^{I})	2·435(2)	H(3^{I}) ··· O(1^{II})	2·411(23)
O(1) ··· O(3)	2·582(2)	H(3) ··· O(4)	2·582(21)
H(3^{I}) ··· O(2^{II})	2·439(25)		

(*c*) Angles (deg.)

C(1)–C(2)–C(3)	90·8(1)	O(1)–C(1)–C(2)	135·2(1)
C(2)–C(3)–C(4)	92·9(1)	H(2)–C(2)–C(2)	113·6(4)
C(3)–C(4)–C(1)	87·0(1)	H(1)–O(3)–C(3)	107·4(13)
C(4)–C(1)–C(2)	89·3(1)	H(3)–N–H(3^{I})	102·2(29)
O(2)–C(2)–C(3)	133·2(1)	H(3)–N–C(5)	110·3(16)
O(2)–C(2)–C(1)	136·0(1)	C(5)–N–C(5^{I})	113·0(3)
O(3)–C(3)–C(2)	135·8(1)	H(6)–C(5)–H(4)	113·6(16)
O(3)–C(3)–C(4)	131·2(1)	H(5)–C(5)–N	110·4(13)
O(4)–C(4)–C(3)	137·3(1)	O(4^{I})–H(2)–O(2)	177·0(31)
O(4)–C(4)–C(1)	135·6(1)	O(1)–H(1)–O(3)	169·4(21)
O(1)–C(1)–C(4)	135·4(1)		

Roman numeral superscripts denote the following equivalent positions: I $\frac{1}{2} - x, \frac{1}{2} - y, z$; II $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$.

DISCUSSION

Both the i.r. and mass spectrum of this compound indicated that the structure of the $H_3(C_4O_4)_2^-$ fragment was similar to that of squaric acid. This is confirmed by the crystallographic results (Figure 1). The corresponding carbon–carbon distances in the ring are essentially the same for the two structures (see Figure 2), with C(3)–C(2) [1·400(2) Å] being the shortest and C(1)–C(4) [1·494(2) Å] the longest. Both C(2)–C(1) [1·462(2) Å] and C(4)–C(3) [1·467(2) Å] are a little longer than the corresponding distances in the acid. However, some of the corresponding carbon–oxygen distances

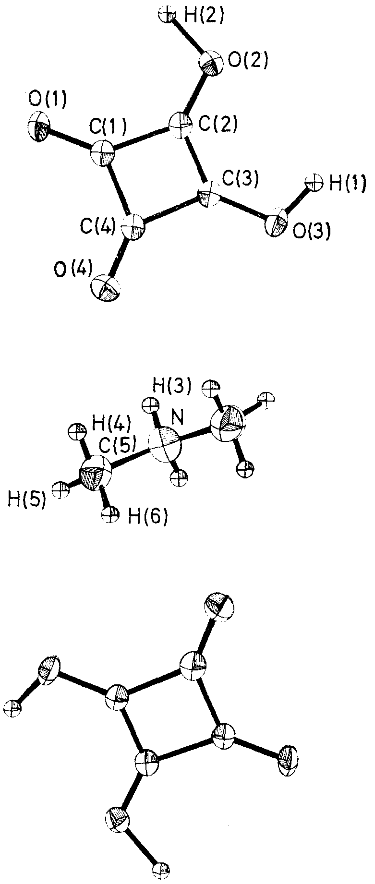

FIGURE 1 The molecular structure

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

[11] W. Hamilton, *Acta Cryst.*, 1955, **8**, 185.

are obviously different (*X*-ray parameters): C(4)–O(4) is shortened from 1·232(2) to 1·215(2) in the anion, and C(1)–O(1) from 1·257(2) to 1·238(2), whereas C(3)–O(3) is lengthened from 1·259(2) to 1·308(2) Å; C(2)–O(2) [1·285(2) Å] stays the same [1·282(2) Å]. Figure 2 shows that the anion has a configuration closer to that of a 1,2-dione than does the squaric acid molecule. The structural data for squaric acid[1] suggests that O(4) ··· O(2) forms a weaker hydrogen bond than does O(3) ··· O(1) (Figure 2). The breaking of a hydrogen bond by the ammonium ion would therefore be expected to occur between O(4) and O(2). The dimethylammonium ions are, in fact, inserted between atoms O(4) and O(2) in the squaric acid structure (see Figure 3). This insertion shortens O(4) ··· O(2) so as to form a single minimum potential well, and the hydrogen atom is bonded symmetrically between O(4) and O(2) {O(4) ··· O(2′) * in $(H_2NMe_2)^+[H_3(C_4O_4)_2]^-$}. Further, one of the squaric acid molecules changes into its tautomeric isomer because of the shift of hydrogen atoms. The shortening of C(4)–O(4) is expected as a result of the insertion of the ammonium ion between O(4) ··· O(4′). The blue shift of carbonyl stretching frequency in the i.r. absorption (from 1643 to 1720 cm^{-1}) is in agreement with this shortening. The negative charge is believed to be delocalized between two bonded squaric acid molecules. However, the distances C(1)–O(1), C(4)–O(4), and C(2)–C(3) are close to those expected for a double bond while the remaining distances correspond reasonably well to single bonds as previously noted for the squaric acid structure.[12]

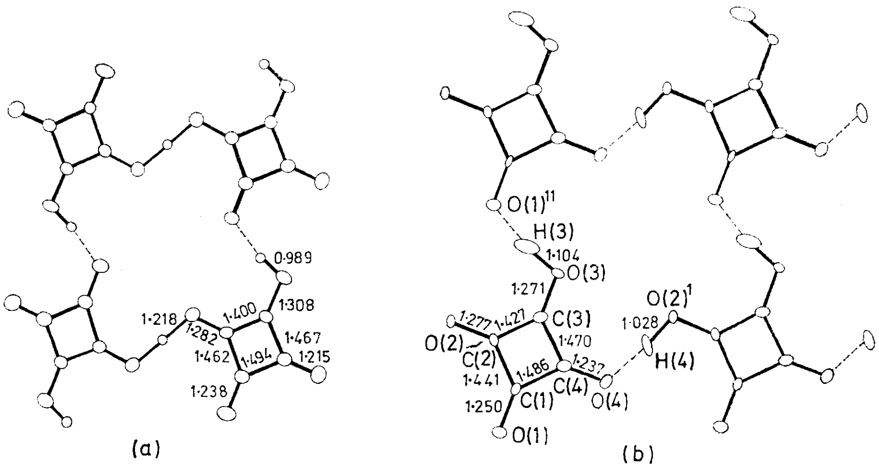

FIGURE 2 (a) $[H_3(C_4O_4)_2]_n$ in $(Me_2NH_2)[H_3(C_4O_4)_2]$, and (b) $[H_2C_4O_4]_n$ in squaric acid

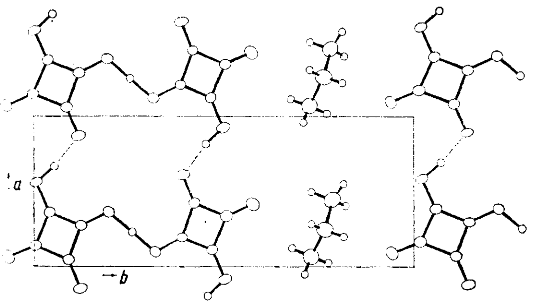

FIGURE 3 Crystal packing along one of the *ab* planes in the unit cell

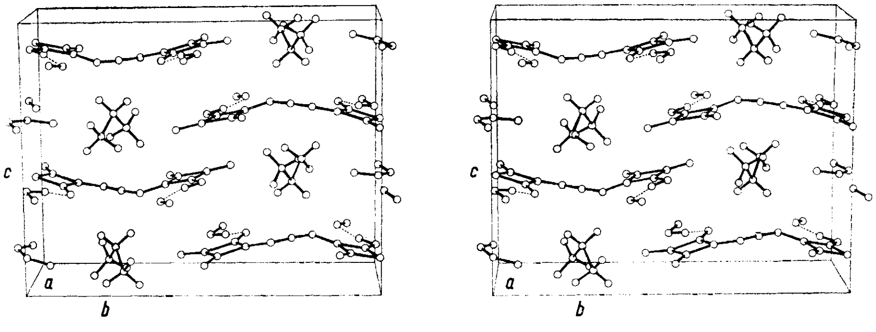

FIGURE 4 A stereo-view showing the molecular packing

A two-fold symmetry axis parallel to the *c* axis passes through the nitrogen atom in the dimethylammonium ion, as well as through the symmetrically bonded hydrogen atom in the anion. The nitrogen atom is in a tetrahedral environment with H–N–H 102·2(3)°, less than the tetrahedral value. From Figure 3, it is

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* A primed atom A(*n′*) represents the atom generated by the two-fold axis, parallel to *c* axis through atom N.

[12] S. Cohen, J. R. Lacker, and J. D. Park, *J. Amer. Chem. Soc.*, 1959, **81**, 3480.

obvious that the repeat unit is one dimethylammonium ion and two squaric acid molecules linked by one hydrogen atom. As in the infinite planar structure of squaric acid, the C_4O_4 unit is still planar, but the dihedral angle between two C_4O_4 planes in $H_3[C_4O_4]_n$ is 26·5°. O(2), H(2), and O(2′) are on a line parallel to the *b* axis with O(2)–H(2)–O(2′) 177·0(3)°. A stereo-view of the molecular packing in the unit cell is shown in Figure 4. Ionic forces apparently predominate between the cation and the anion; the closest distance between ions is >2·4 Å for O–H, which would represent an extremely weak hydrogen bond.

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