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Planar and Puckered Cyclobutanes. The Structure of a Sodium Salt of *trans*-1,3-Cyclobutanedicarboxylic Acid

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Abstract: The disodium salt of *trans*-1,3-cyclobutanedicarboxylic acid has the formula $Na^+{}_2C_4H_6(COO^-)_2\cdot 2C_4H_6(COOH)_2$. The crystals are triclinic, space group $P\bar{1}$, with $a = 10.006$, $b = 9.728$, $c = 5.360$ Å; $\alpha = 97.77°$, $\beta = 103.85°$, $\gamma = 91.38°$. There is one formula weight per unit cell. The dianion contains a planar cyclobutane ring, while the neutral diacid molecule contains a puckered cyclobutane ring. The C–C single bonds in the dianion average 1.563 Å in length; those of the diacid average 1.552 Å.

Planar cyclobutane rings in the solid state have been found in a number of simple derivatives in which the cyclobutane ring is neither conjugated nor fused to another ring. These include tetraphenylcyclobutane,[2,3] tetracyanocyclobutane,[4] octahydroxycyclobutane,[5] and *trans*-1,3-cyclobutanedicarboxylic acid.[6] All of these molecules are centrosymmetric and crystallize in space group $P2_1/c$ with the molecular center of symmetry coinciding with the crystallographic center of symmetry. The carbon–carbon single-bond lengths within the ring range from 1.547 to 1.57 Å in these compounds, somewhat longer than the ordinary C–C single bond length[7] of 1.537 Å. There has been only slight evidence for the existence of planar rings in gas phase[8] or in solution.

Puckered rings are also known in the solid state. These include *cis*-1,3-cyclobutanedicarboxylic acid,[9] *trans*-1,2-cyclobutanedicarboxylic acid,[10] and many other molecules.[11–13] In the puckered conformation, positions analogous to the equatorial and axial positions of cyclohexane occur; in the planar conformation all positions are equivalent. Precise gas-phase work[14–16] indicates C–C single-bond lengths somewhat longer than normal; the longest is 1.550 ± 0.005 Å found[16] in C_4H_7Cl. The X-ray work on puckered rings also supports long C–C bonds. For example, in *cis*-1,3-cyclobutanedicarboxylic acid the average bond length is 1.554 ± 0.01 Å. The dihedral angles range from 145 to 160°.

We have prepared the disodium salt of *trans*-1,3-cyclobutanedicarboxylic acid which crystallizes with two neutral acid molecules of crystallization, $Na^+{}_2C_4H_6(COO^-)_2\cdot 2C_4H_6(COOH)_2$. The surprising result of our X-ray study described in this paper is that the neutral acid molecule, which has a planar cyclobutane ring when crystallized by itself,[6] has a puckered ring in this

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(2) T. N. Margulis, *Acta Cryst.*, **19**, 857 (1965).

(3) J. D. Dunitz, *ibid.*, **2**, 1 (1949).

(4) B. Greenberg and B. Post, Abstracts, Annual Meeting of the American Crystallographic Association, Austin, Texas, 1966.

(5) C. M. Bock, Abstracts, Annual Meeting of the American Crystallographic Association, Atlanta, Ga., 1967.

(6) T. N. Margulis and M. Fischer, *J. Am. Chem. Soc.*, **89**, 223 (1967).

(7) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956–1959," The Chemical Society, London, 1965.

(8) R. West, H. Y. Niu, and M. Ito, *J. Am. Chem. Soc.*, **85**, 2580 (1963).

(9) E. Adman and T. N. Margulis, *Chem. Commun.*, 1967, 641.

(10) D. van der Helm, J. J. Sims, and D. S. Seigler, Abstracts, Summer Meeting of the American Crystallographic Association, Minneapolis, Minn., 1967.

(11) I. L. Karle and J. Karle, *Acta Cryst.*, 20, 555 (1966).

(12) T. B. Owen and J. L. Hoard, *ibid.*, **4**, 172 (1951).

(13) I. L. Karle, J. Karle, and K. Britts, *J. Am. Chem. Soc.*, **88**, 2918 (1966).

(14) A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961).

(15) W. G. Rothchild and B. P. Dailey, *J. Chem. Phys.*, **36**, 2931 (1962).

(16) H. Kim and W. D. Gwinn, *ibid.*, **44**, 865 (1966).

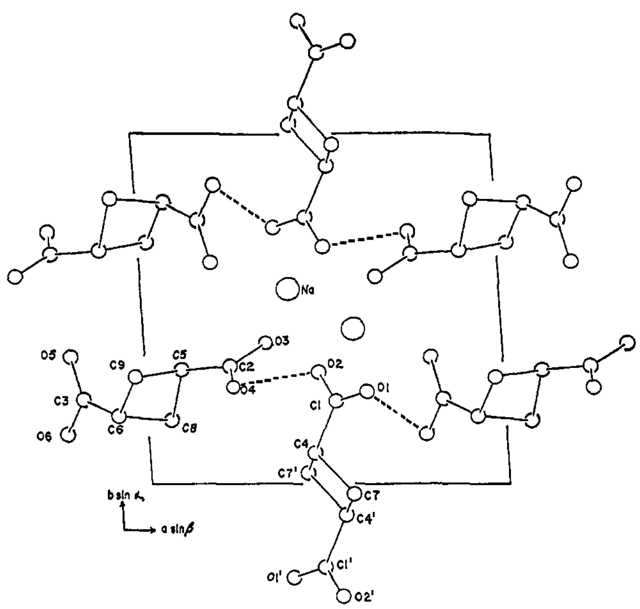

Figure 1. The crystal structure viewed along *c*. Hydrogen-bonded chains run in the [101] direction.

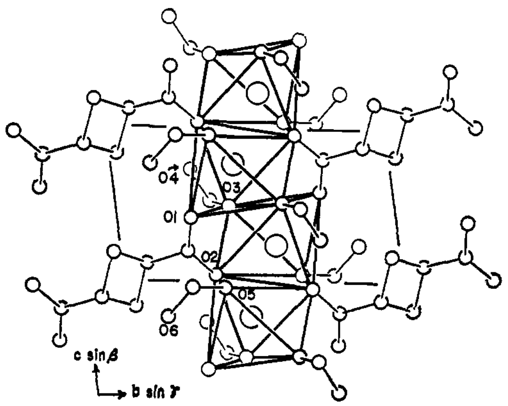

Figure 2. The crystal structure viewed along *a* showing sodium–oxygen octahedra. For the sake of clarity, the puckered cyclobutane groups are omitted.

salt. The dianion of this acid is found to have a planar ring.

Experimental Section

In an attempt to prepare the monosodium salt of *trans*-1,3-cyclobutanedicarboxylic acid, 10 mg of the acid was mixed with 1 ml of 0.1 *N* NaOH. At least two new compounds were found when the solution had evaporated to dryness. One of these materials was hygroscopic and was not identified. The other material was used in the X-ray diffraction study. The melting point and density of all the material was measured before it was realized that there was more than one substance present and so will not be reported.

A Picker full-circle diffractometer with scintillation counter and pulse-height analyzer was used for the determination of cell dimensions and measurement of intensities. All X-ray measurements were made with Cu Kα radiation (λ 1.5418 Å). A crystal of dimension 0.12 × 0.13 × 0.22 mm was mounted on the *c* axis of the triclinic unit cell, as indicated by a plot of the reciprocal lattice made from both diffractometer and Weissenberg film measurements. Reciprocal cell translations were measured directly on the diffractometer; reciprocal angles were measured directly by realigning the crystal and were also calculated from 2θ measurements of three additional reflections.

Intensities were measured by the stationary crystal–stationary counter technique. Background corrections were plotted as a function of the setting angles and applied accordingly. An additional correction due to daily fluctuations in the intensities was applied based on measurements of a few standard reflections at the beginning and end of each work day. A total of 1680 reflections were measured ($2\theta_{max} = 130°$), of which 1289 were judged observable. The intensities were converted to structure factors in the usual way without correction for absorption. Wilson's method was used to put the data on an absolute scale, and normalized structure factors[17] (*E*'s) were calculated assuming that the unit cell contained two formula weights of the monosodium salt and eight water molecules. The statistical distribution of the *E*'s agreed with expected values for a centrosymmetric structure. Thus $P\bar{1}$ was chosen as the probable space group. The successful determination of the structure confirms this choice.

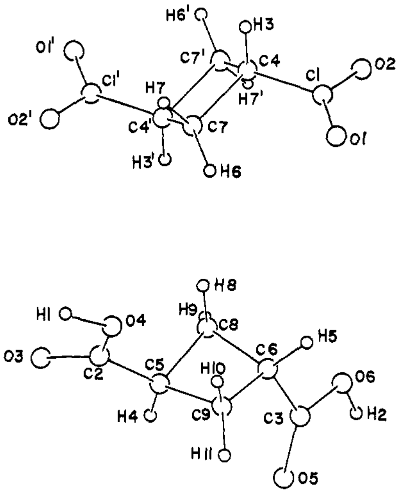

Figure 3. (a) The dianion viewed along *c*. (b) The diacid viewed along *c*.

Results

Crystal Data. Crystals of $Na^{+}{}_{2}C_4H_6(COO^{-})_2 \cdot 2C_4H_6(COOH)_2$ are triclinic, space group $P\bar{1}$, with one formula weight per unit cell. The dimensions of the Delauney reduced cell are: $a = 10.006 \pm 0.003$, $b = 9.728 \pm 0.003$, $c = 5.360 \pm 0.003$ Å; $\alpha = 97.77 \pm 0.30°$, $\beta = 103.85 \pm 0.30°$, $\gamma = 91.38 \pm 0.30°$. The calculated density is 1.58 g/cm^3.

Determination of the Structure. The structure was solved directly from the normalized structure factors using the computer program of Long.[18] This program provides solutions to the Σ_2 relationship.[17] Three *E*'s with large magnitudes were arbitrarily assigned positive signs to specify the origin. Four more large *E*'s were then used as a starting set. The program then generated signs for large *E*'s for all 16 possible combinations of the signs of the starting set. An *E* map[17] using 246 terms from the most consistent solution revealed the positions of the nonhydrogen atoms and thus the correct formulation of the salt.

Refinement was accomplished by full-matrix least-squares calculations[19] minimizing the function $\Sigma w(F_o - F_c)^2$, with w assigned unity for all reflections. Atomic scattering factors for neutral atoms were taken from the "International Tables for X-ray Crystallography."[20]

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(17) J. Karle and I. L. Karle, *Acta Cryst.*, **21**, 849 (1966).

(18) R. E. Long, Ph.D. Dissertation, University of California at Los Angeles, 1965.

(19) The bulk of the computations were done using the programs described by J. M. Stewart, Technical Report TR-64-6 "Crystal Structure Calculations System for the IBM 709/7090/7094," Computer Science Center, University of Maryland, and Research Computer Laboratory, University of Washington, 1964.

(20) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

Table I. Positional and Isotropic Thermal Parameters[a]

Atom	x	y	z	B, Å^2
Na	0.4157 (3)	0.5543 (3)	0.2417 (5)	
O(1)	0.6127 (5)	0.2658 (5)	0.4069 (9)	
O(2)	0.4818 (4)	0.3285 (4)	0.0477 (8)	
O(3)	0.3442 (5)	0.4035 (5)	0.4942 (9)	
O(4)	0.2460 (5)	0.2788 (6)	0.7286 (10)	
O(5)	−0.2032 (5)	0.3664 (5)	−0.0406 (9)	
O(6)	−0.2280 (5)	0.1461 (5)	−0.2312 (11)	
C(1)	0.5260 (6)	0.2370 (6)	0.1937 (12)	
C(2)	0.2428 (6)	0.3422 (6)	0.5251 (13)	
C(3)	−0.1765 (6)	0.2465 (7)	−0.0368 (13)	
C(4)	0.4641 (7)	0.0902 (6)	0.1057 (13)	
C(5)	0.1058 (7)	0.3258 (7)	0.3306 (13)	
C(6)	−0.0816 (7)	0.1931 (8)	0.1885 (14)	
C(7)	0.5569 (8)	−0.0301 (7)	0.1868 (13)	
C(8)	0.0682 (7)	0.1826 (8)	0.1576 (15)	
C(9)	−0.0272 (7)	0.3064 (9)	0.4238 (14)	
H(1)	0.331 (9)	0.305 (8)	0.849 (16)	2.6 (18)
H(2)	−0.277 (9)	0.179 (8)	−0.359 (17)	2.2 (19)
H(3)	0.373 (7)	0.084 (7)	0.158 (13)	1.4 (15)
H(4)	0.095 (8)	0.388 (8)	0.210 (15)	2.2 (17)
H(5)	−0.127 (7)	0.112 (7)	0.233 (13)	1.6 (15)
H(6)	0.654 (8)	0.009 (8)	0.280 (15)	2.0 (17)
H(7)	0.511 (8)	−0.091 (8)	0.295 (15)	2.0 (16)
H(8)	0.114 (8)	0.107 (8)	0.261 (16)	2.8 (18)
H(9)	0.074 (9)	0.167 (9)	−0.047 (19)	4.6 (23)
H(10)	0.003 (9)	0.261 (9)	0.617 (19)	4.4 (22)
H(11)	−0.083 (9)	0.390 (9)	0.436 (16)	2.8 (19)

[a] Standard deviations are given in parentheses as deviations in the last significant figure.

Table II. Anisotropic Thermal Parameters[a] in the Form $\mathrm{Exp}[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	0.0073 (3)	0.0078 (3)	0.0254 (11)	0.0007 (2)	0.0014 (4)	0.0037 (4)
O(1)	0.0102 (6)	0.0080 (6)	0.0241 (20)	0.0008 (5)	−0.0041 (9)	0.0015 (8)
O(2)	0.0078 (5)	0.0064 (5)	0.0220 (18)	0.0006 (4)	−0.0008 (8)	0.0039 (8)
O(3)	0.0073 (5)	0.0101 (6)	0.0327 (21)	−0.0010 (5)	0.0012 (9)	0.0056 (9)
O(4)	0.0067 (6)	0.0145 (7)	0.0335 (23)	−0.0015 (5)	−0.0018 (9)	0.0129 (11)
O(5)	0.0098 (6)	0.0090 (6)	0.0328 (22)	0.0019 (5)	−0.0023 (9)	0.0013 (9)
O(6)	0.0110 (7)	0.0087 (6)	0.0346 (24)	0.0005 (5)	−0.0055 (11)	0.0032 (10)
C(1)	0.0065 (7)	0.0069 (7)	0.0209 (26)	0.0004 (6)	0.0021 (11)	0.0006 (11)
C(2)	0.0064 (7)	0.0068 (7)	0.0288 (29)	0.0010 (6)	0.0010 (12)	0.0031 (12)
C(3)	0.0056 (7)	0.0100 (9)	0.0260 (29)	−0.0004 (6)	0.0018 (11)	0.0039 (13)
C(4)	0.0065 (7)	0.0060 (7)	0.0248 (27)	0.0007 (6)	0.0012 (11)	0.0026 (11)
C(5)	0.0062 (7)	0.0088 (8)	0.0248 (29)	0.0010 (6)	−0.0001 (12)	0.0037 (13)
C(6)	0.0065 (7)	0.0106 (9)	0.0292 (31)	0.0006 (7)	0.0002 (12)	0.0072 (14)
C(7)	0.0097 (9)	0.0063 (7)	0.0237 (28)	0.0002 (6)	−0.0015 (13)	0.0010 (12)
C(8)	0.0060 (7)	0.0099 (9)	0.0309 (32)	0.0017 (6)	−0.0000 (12)	0.0029 (14)
C(9)	0.0052 (7)	0.0152 (12)	0.0268 (32)	0.0011 (7)	0.0007 (12)	0.0014 (15)

[a] Standard deviations are given in parentheses as deviations in the last significant figure.

Using anisotropic thermal parameters, the R factor, $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, dropped to 0.091 when only carbon, oxygen, and sodium atoms were refined. A difference map revealed the positions of all 11 hydrogen atoms without ambiguity. The hydrogen atoms were included in the final cycles of least squares with isotropic temperature factors. Five reflections, believed to suffer from systematic errors and one obvious blunder, were omitted from the last cycle of refinement. The final value of R is 0.063 for 1283 independent nonzero reflections.[21] A difference map calculated from the final structure showed no peaks greater then 0.25 e/Å^3. Atomic positions and thermal parameters are shown in Tables I and II; interatomic distances and angles are listed in Tables III and IV.

The standard deviations given in these tables and in the text are based on the least-squares calculations and should be considered lower limits to the real uncertainties.

The structure is illustrated in Figures 1–3.

Crystal Structure. The center of the dianion, $C_4H_6(COO^-)_2$, coincides with a center of symmetry of the unit cell which means that the cyclobutane ring is planar. The diacid, $C_4H_6(COOH)_2$, is in a general position and has a puckered cyclobutane ring. The sodium ion is surrounded by oxygen atoms in a distorted octahedral arrangement. These octahedra share edges to form chains running parallel to the c axis. The chains are cross-linked by dianions and by diacid molecules. There are asymmetric hydrogen bonds between diacid and dianion.

Dianion. The carbon–carbon bond lengths[22] within the planar cyclobutane ring of the dianion average 1.563 Å, each ±0.01 Å. This value is comparable to the values found in other planar cyclobutanes as shown in Table V. The bond lengths and angles in the carboxylate ion groups are in agreement with expected values.[7] The near-equality of the C–O bond lengths[22] (1.267 and 1.287 Å, each ±0.008 Å) and of the C–C–O bond angles (117.4 and 119.7°, each ±0.6°) are evidence that this moiety is indeed an ion. The conformation of the COO$^-$ groups is such that the dianion has nearly C_{2h}-2/m symmetry. A least-squares plane through C(1), C(4), O(1), and O(2) makes an angle of 94.1° with the plane through C(1), C(4), C(1′), and C(4′).

Diacid. The average carbon–carbon bond length in the puckered cyclobutane ring of the diacid is 1.552 Å. This is a typical value for puckered rings as shown in Table VI. Although this value is not significantly lower than the values for the planar ring in the dianion, it is interesting that no bond in the puckered ring is found to be as long as the shortest bond of the planar ring. The dihedral angle of the puckered ring is 155°, well within the range of the dihedral angles of other compounds (Table VI). If a *trans*-1,3-substituted cy-

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[21] A table of observed and calculated structure factors has been deposited as Document No. 9942 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by an advance remittance ($1.25 for photoprints or $1.25 for 35-mm microfilm) payable to: Chief, Photoduplication Service, Library of Congress.

[22] Corrected for thermal motion assuming one atom to ride on another; see W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

Table III. Interatomic Distances

Atoms	Bond length, Å Obsd	Bond length, Å Temp cor	Atoms	Bond length, Å Obsd	Bond length, Å Temp cor
		Dianion			
C(1)-O(1)	1.251 ± 0.007	1.267	C(4)-C(7′)	1.560 ± 0.009	1.567
C(1)-O(2)	1.280 ± 0.008	1.287	C(4)-H(3)	1.02 ± 0.08	
C(1)-C(4)	1.511 ± 0.009	1.512	C(7)-H(6)	1.02 ± 0.07	
C(4)-C(7)	1.555 ± 0.010	1.559	C(7)-H(7)	1.06 ± 0.09	
		Diacid			
C(2)-O(3)	1.222 ± 0.008	1.233	C(6)-C(9)	1.539 ± 0.011	1.546
C(2)-O(4)	1.318 ± 0.009	1.338	C(5)-H(4)	0.94 ± 0.09	
C(3)-O(5)	1.205 ± 0.009	1.222	C(6)-H(5)	0.99 ± 0.08	
C(3)-O(6)	1.321 ± 0.008	1.339	C(8)-H(8)	1.03 ± 0.09	
C(2)-C(5)	1.500 ± 0.009	1.503	C(8)-H(9)	1.12 ± 0.12	
C(3)-C(6)	1.508 ± 0.010	1.515	C(9)-H(10)	1.16 ± 0.10	
C(5)-C(8)	1.550 ± 0.009	1.553	C(9)-H(11)	1.01 ± 0.10	
C(6)-C(8)	1.551 ± 0.010	1.552	O(4)-H(1)	0.94 ± 0.07	
C(5)-C(9)	1.546 ± 0.011	1.556	O(6)-H(2)	0.85 ± 0.09	
		Sodium-Oxygen Octahedron			
Na-O(2)	2.475 ± 0.005		Na-O(2′)	2.438 ± 0.006	
Na-O(3)	2.333 ± 0.006		Na-O(3″)	2.472 ± 0.005	
Na-O(1′)	2.466 ± 0.005		Na-O(5″)	2.342 ± 0.005	
		Hydrogen Bond			
O(1)-O(6)	2.623 ± 0.007		O(2)-O(4)	2.552 ± 0.006	

Table IV. Interatomic Angles

Atoms	Angle, deg	Atoms	Angle, deg
	Dianion		
O(1)-C(1)-O(2)	122.9 ± 0.5	C(1)-C(4)-H(3)	108 ± 4
C(4)-C(1)-O(1)	119.7 ± 0.6	C(4)-C(7)-H(6)	110 ± 4
C(4)-C(1)-O(2)	117.4 ± 0.5	C(4)-C(7)-H(7)	110 ± 4
C(1)-C(4)-C(7)	117.5 ± 0.5	C(4′)-C(7)-H(6)	115 ± 5
C(1)-C(4)-C(7′)	117.6 ± 0.6	C(4′)-C(7)-H(7)	115 ± 4
C(7)-C(4)-C(7′)	90.7 ± 0.5	H(6)-C(7)-H(7)	114 ± 4
C(4)-C(7)-C(4′)	89.3 ± 0.5		
	Diacid		
O(3)-C(2)-O(4)	122.6 ± 0.5	C(5)-C(9)-C(6)	89.3 ± 0.5
O(5)-C(3)-O(6)	123.6 ± 0.6	C(2)-C(5)-H(4)	114 ± 5
C(5)-C(2)-O(3)	123.5 ± 0.6	C(3)-C(6)-H(5)	110 ± 4
C(6)-C(3)-O(5)	124.3 ± 0.8	C(5)-C(8)-H(8)	109 ± 4
C(5)-C(2)-O(4)	113.9 ± 0.6	C(5)-C(8)-H(9)	122 ± 5
C(6)-C(3)-O(6)	112.2 ± 0.6	C(6)-C(8)-H(8)	108 ± 5
C(2)-C(5)-C(8)	116.6 ± 0.6	C(6)-C(8)-H(9)	112 ± 5
C(2)-C(5)-C(9)	119.4 ± 0.6	H(8)-C(8)-H(9)	114 ± 8
C(3)-C(6)-C(8)	112.8 ± 0.4	C(5)-C(9)-H(10)	107 ± 5
C(3)-C(6)-C(9)	113.2 ± 0.6	C(5)-C(9)-H(11)	116 ± 6
C(8)-C(5)-C(9)	88.2 ± 0.5	C(6)-C(9)-H(10)	113 ± 4
C(8)-C(6)-C(9)	88.4 ± 0.5	C(6)-C(9)-H(11)	117 ± 5
C(5)-C(8)-C(6)	88.7 ± 0.5	H(10)-C(9)-H(11)	112 ± 7
	Sodium-Oxygen Octahedron		
O(2)-Na-O(3)	78.7 ± 0.2	O(3)-Na-O(2′)	168.0 ± 0.2
O(2)-Na-O(2′)	89.8 ± 0.2	O(1′)-Na-O(2′)	106.9 ± 0.2
O(2)-Na-O(3″)	88.2 ± 0.2	O(1′)-Na-O(3″)	78.9 ± 0.2
O(2)-Na-O(5″)	117.5 ± 0.2	O(1′)-Na-O(5″)	80.4 ± 0.2
O(2)-Na-O(1′)	156.5 ± 0.2	O(2′)-Na-O(3″)	79.8 ± 0.2
O(3)-Na-O(1′)	83.3 ± 0.2	O(2′)-Na-O(5″)	87.8 ± 0.2
O(3)-Na-O(3′)	96.4 ± 0.2	O(3″)-Na-O(5″)	151.5 ± 0.2
O(3)-Na-O(5″)	100.4 ± 0.2		

clobutane is puckered, one of the substituents must be axial while the other is equatorial. In this case C(3), O(5), and O(6) form the axial carboxyl group. The acid hydrogen atoms are found localized on O(6) and O(4) which provides further evidence for the distinction between ion and molecule. Hydrogen bonding occurs from O(6) to O(1) and from O(4) to O(2) with O–O distances of 2.62 and 2.55 Å, respectively. The carboxyl groups are rotated such that a plane through C(2), C(5), C(6), and C(3) makes an angle of 23° with the plane through O(3), O(4), C(2), and C(5) and an angle of 46° with the plane through O(5), O(6), C(3), and C(6).

Sodium Coordination. The various oxygen atoms participate in octahedral coordination of the sodium ion to a different extent. There are two close approaches each from O(3) and O(2), and one each from O(5) and O(1). The C–OH oxygen atoms are not

Table V. Carbon–Carbon Bond Lengths (by X-Ray Diffraction) in Planar Cyclobutane Rings[a]

Compound	Bond length, Å	Ref
1,2,3,4-Tetraphenylcyclobutane	1.566 ± 0.015 1.573 ± 0.015	2, 3
1,2,3,4-Tetracyanocyclobutane	1.547 ± 0.002 1.561 ± 0.002	4
Octahydroxycyclobutane	1.562 (av)	5
trans-1,3-Cyclobutanedicarboxylic acid	1.552 ± 0.006 1.567 ± 0.006	6
trans-1,3-Cyclobutanedicarboxylic acid dianion	1.559 ± 0.01 1.567 ± 0.01	This work

[a] Only compounds in which the ring is not part of a condensed polycyclic system and is not involved with endo- or exocyclic unsaturation are listed. All compounds listed are the centrosymmetric isomers.

coordinated to the sodium ion. The distortion from octahedral symmetry may be seen from the bond distances and angles given in Tables III and IV. The Na–O distances vary from 2.33 to 2.48 Å. Distances of 2.404 to 2.445 Å have been found[23] in $NaH(H_3C_2O_2)_2$, and a short distance of 2.31 Å has been reported.[24] The Na–Na distances are 3.21 and 3.48 Å in this salt, while in $NaH(H_3C_2O_2)_2$ this distance is 3.297 Å.

Discussion

Our results show that crystalline forces can have an important influence on the conformation of a cyclobutane ring. A molecule, *trans*-1,3-cyclobutanedicarboxylic acid, which by itself crystallizes with a planar ring, has a puckered ring when crystallized in this salt. Furthermore, the dianion of this same molecule is found to contain a planar ring in this salt. These results are in accord with the fairly low barrier of about 1 kcal/mole between puckered and planar conformations estimated[25] for C_4H_8 in the gas phase.[26] It is also clear from this work that it is not possible to extrapolate solid-state results on cyclobutane conformation to the gas, liquid, or solution phases.

This study adds to the evidence that C–C bonds in cyclobutane rings are longer than C–C bonds in less strained molecules. A summary of the available X-ray results on some simple planar cyclobutane derivatives is presented in Table V. No bond is shorter than the normal[7] bond length of 1.537 Å, the range being 1.547–1.57 Å. In puckered rings (Table VI) the situation is less obvious since the X-ray work is less precise than for the planar rings and because of the inherent difficulties in comparing microwave, electron diffraction, and X-ray diffraction results. Still the weight of the evidence is toward longer than normal carbon–carbon single bonds in puckered rings.

Table VI. Dimensions of Puckered Cyclobutane Rings

Compound	C–C bond length, Å	Dihedral angle[a]	Technique[b] (ref)
cis-1,3-Cyclobutanedicarboxylic acid	1.554 (av) ± 0.01	149°	XRD (9)
Anemonin	1.537 (av) ± 0.014	152°	XRD (11)
Octachlorocyclobutane	1.575 (av) ± 0.03	153°	XRD (2, 12)
trans-1,2-Dibromo-1,2-dicarbomethoxycyclobutane	1.55 (av) ± 0.027	153°	XRD (13)
cis-1,2-Dibromo-1,2-dicarbomethoxycyclobutane	1.56 (av) ± 0.027	150°	XRD (13)
Cyclobutane	1.548 ± 0.003		ED (14)
Cyclobutane		145°	NMR[c]
Bromocyclobutane	1.540 ± 0.003 1.548 ± 0.003	151° 38′	MWS (15)
Chlorocyclobutane	1.525 ± 0.005 1.550 ± 0.005	160°	MWS (16)
trans-1,3-Cyclobutanedicarboxylic acid	1.552 (av) ± 0.01	155°	XRD (this work)

[a] Defined as the angle between normals to two three-carbon planes with the transannular distance common to both planes. [b] Abbreviations: XRD, X-ray diffraction; ED, electron diffraction; NMR, nuclear magnetic resonance; and MWS, microwave spectroscopy. [c] S. Meiboom and L. C. Snyder, *J. Am. Chem. Soc.*, **89**, 1038 (1967).

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(23) J. C. Speakman and H. H. Mills, *J. Chem. Soc.*, 1164 (1961).

(24) S. S. Tavale, L. M. Pant, and A. B. Biswas, *Acta Cryst.*, **16**, 566 (1963).

(25) G. W. Rathjens, N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5634 (1953).

(26) In the structure of the 1,1′-dicarboxylic acid of cyclobutane, which we have nearly completed, the carbon atom opposite the substituted one is disordered giving considerable electron density in both puckered conformations and in the planar conformation.