

Structure of a Planar Cyclobutane.

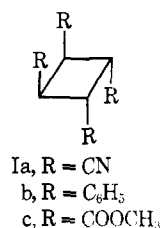
cis,trans,cis-1,2,3,4-Cyclobutanetetracarboxylic Acid Tetramethyl Ester

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Abstract: A single-crystal X-ray diffraction study of *cis,trans,cis*-1,2,3,4-cyclobutanetetracarboxylic acid tetramethyl ester, $C_8H_{16}(COOCH_3)_4$, shows the cyclobutane ring to be planar with C-C bond lengths of 1.572 ± 0.005 and 1.541 ± 0.004 Å. The crystals are triclinic, space group $P\bar{1}$, with $a = 8.939$, $b = 5.963$, and $c = 6.454$ Å; $\alpha = 95.17^\circ$, $\beta = 81.43^\circ$, $\gamma = 78.74^\circ$. There is one molecule per cell. The calculated density is 1.45 g/cm^3 . The structure was refined to an R value of 0.035 for 833 independent reflections.

Planar cyclobutane rings¹ have been found only in the solid state. It is not clear whether planarity is an intrinsic characteristic of a molecule or a function of intermolecular forces. Indeed at least one molecule, *trans*-1,3-cyclobutanedicarboxylic acid,^{2,3} has been shown to exist in both the planar and the puckered forms depending upon crystalline environment. Cyclobutanes with four substituents arranged *cis,trans,cis* (I) are promising candidates for being intrinsically planar because all cases investigated have shown a planar ring. These include tetraphenylcyclobutane^{4,5} and tetracyanocyclobutane⁶ as well as several structures in which the substituents are part of fused rings.^{7,8} Continuing a study of planar cyclobutanes we now report the structure of *cis,trans,cis*-1,2,3,4-cyclobutanetetracarboxylic acid tetramethyl ester (Ic).



Experimental Section

Colorless single crystals were kindly provided by Dr. G. W. Griffin. A crystal of dimensions $0.02 \times 0.01 \times 0.006$ cm was mounted so that c^* of the triclinic unit cell coincided with the ϕ axis of the diffractometer. All X-ray work was done with this crystal on a Picker full-circle manual diffractometer using $Cu K\alpha$ ($\lambda = 1.54178$) radiation. Cell dimensions were obtained from 2θ , χ , and ϕ values of carefully centered reflections. Intensities were measured with the moving-crystal moving-counter (2θ scan) method. Background was measured by stationary counts on either side of the reflection. A total of 1203 reflections were measured of which 835 were considered to be observable. These intensities were converted to structure factors without correction for absorption, scaled by

- (1) We exclude from consideration molecules in which the cyclobutane ring is fused to another ring or involved with double bonds.
- (2) T. N. Margulis and M. Fischer, *J. Amer. Chem. Soc.*, **89**, 223 (1967).
- (3) E. Adman and T. N. Margulis, *ibid.*, **90**, 4517 (1968).
- (4) J. D. Dunitz, *Acta Crystallogr.*, **2**, 1 (1949).
- (5) T. N. Margulis, *ibid.*, **19**, 857 (1965).
- (6) B. Greenberg and B. Post, *ibid.*, *Sect. B*, **24**, 918 (1968).
- (7) N. Camerman, S. C. Nyburg, and D. Weinblum, *Tetrahedron Lett.*, 4127 (1967).
- (8) J. R. Einstein, J. L. Hosszu, J. W. Longworth, R. O. Rahn, and C. H. Wei, *Chem. Commun.*, 1063 (1967).

Wilson's method, and converted to normalized structure amplitudes for use in phase determination. The Laue symmetry and the statistical distribution of the normalized structure amplitudes indicated $P\bar{1}$ as the probable space group. The successful determination of the structure confirms this choice.

Crystal Data. Crystals of *cis,trans,cis*-1,2,3,4-tetracarboxylic acid tetramethyl ester (Ic), $C_8H_{16}(COOCH_3)_4$, are triclinic, space group $P\bar{1}$ with one molecule per unit cell. The cell dimensions

Table I. Observed (F_o) and Calculated (F_c) Structure Amplitudes $\times 10$

M	N	PO	FC	M	N	PO	FC	M	N	PO	FC	M	N	PO	FC	M	N	PO	FC
3	0	00	65	-1	3	1	21	21	-4	-4	-4	-4	-4	-4	-4	-4	-4	-4	-4
3	0	00	52	-1	3	1	22	22	-3	-3	-3	-3	-3	-3	-3	-3	-3	-3	-3
4	0	00	51	1	3	1	19	18	0	0	0	0	0	0	0	0	0	0	0
4	0	00	53	2	3	1	20	20	1	1	1	1	1	1	1	1	1	1	1
4	0	00	54	3	3	1	21	21	2	2	2	2	2	2	2	2	2	2	2
3	0	00	55	-2	3	1	22	22	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
3	0	00	56	-3	3	1	23	23	-2	-2	-2	-2	-2	-2	-2	-2	-2	-2	-2
3	0	00	57	-4	3	1	24	24	-3	-3	-3	-3	-3	-3	-3	-3	-3	-3	-3
3	0	00	58	-5	3	1	25	25	-4	-4	-4	-4	-4	-4	-4	-4	-4	-4	-4
3	0	00	59	-6	3	1	26	26	-5	-5	-5	-5	-5	-5	-5	-5	-5	-5	-5
3	0	00	60	-7	3	1	27	27	-6	-6	-6	-6	-6	-6	-6	-6	-6	-6	-6
3	0	00	61	-8	3	1	28	28	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7
3	0	00	62	-9	3	1	29	29	-8	-8	-8	-8	-8	-8	-8	-8	-8	-8	-8
3	0	00	63	-10	3	1	30	30	-9	-9	-9	-9	-9	-9	-9	-9	-9	-9	-9
3	0	00	64	-11	3	1	31	31	-10	-10	-10	-10	-10	-10	-10	-10	-10	-10	-10
3	0	00	65	-12	3	1	32	32	-11	-11	-11	-11	-11	-11	-11	-11	-11	-11	-11
3	0	00	66	-13	3	1	33	33	-12	-12	-12	-12	-12	-12	-12	-12	-12	-12	-12
3	0	00	67	-14	3	1	34	34	-13	-13	-13	-13	-13	-13	-13	-13	-13	-13	-13
3	0	00	68	-15	3	1	35	35	-14	-14	-14	-14	-14	-14	-14	-14	-14	-14	-14
3	0	00	69	-16	3	1	36	36	-15	-15	-15	-15	-15	-15	-15	-15	-15	-15	-15
3	0	00	70	-17	3	1	37	37	-16	-16	-16	-16	-16	-16	-16	-16	-16	-16	-16
3	0	00	71	-18	3	1	38	38	-17	-17	-17	-17	-17	-17	-17	-17	-17	-17	-17
3	0	00	72	-19	3	1	39	39	-18	-18	-18	-18	-18	-18	-18	-18	-18	-18	-18
3	0	00	73	-20	3	1	40	40	-19	-19	-19	-19	-19	-19	-19	-19	-19	-19	-19
3	0	00	74	-21	3	1	41	41	-20	-20	-20	-20	-20	-20	-20	-20	-20	-20	-20
3	0	00	75	-22	3	1	42	42	-21	-21	-21	-21	-21	-21	-21	-21	-21	-21	-21
3	0	00	76	-23	3	1	43	43	-22	-22	-22	-22	-22	-22	-22	-22	-22	-22	-22
3	0	00	77	-24	3	1	44	44	-23	-23	-23	-23	-23	-23	-23	-23	-23	-23	-23
3	0	00	78	-25	3	1	45	45	-24	-24	-24	-24	-24	-24	-24	-24	-24	-24	-24
3	0	00	79	-26	3	1	46	46	-25	-25	-25	-25	-25	-25	-25	-25	-25	-25	-25
3	0	00	80	-27	3	1	47	47	-26	-26	-26	-26	-26	-26	-26	-26	-26	-26	-26
3	0	00	81	-28	3	1	48	48	-27	-27	-27	-27	-27	-27	-27	-27	-27	-27	-27
3	0	00	82	-29	3	1	49	49	-28	-28	-28	-28	-28	-28	-28	-28	-28	-28	-28
3	0	00	83	-30	3	1	50	50	-29	-29	-29	-29	-29	-29	-29	-29	-29	-29	-29
3	0	00	84	-31	3	1	51	51	-30	-30	-30	-30	-30	-30	-30	-30	-30	-30	-30
3	0	00	85	-32	3	1	52	52	-31	-31	-31	-31	-31	-31	-31	-31	-31	-31	-31
3	0	00	86	-33	3	1	53	53	-32	-32	-32	-32	-32	-32	-32	-32	-32	-32	-32
3	0	00	87	-34	3	1	54	54	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33
3	0	00	88	-35	3	1	55	55	-34	-34	-34	-34	-34	-34	-34	-34	-34	-34	-34
3	0	00	89	-36	3	1	56	56	-35	-35	-35	-35	-35	-35	-35	-35	-35	-35	-35
3	0	00	90	-37	3	1	57	57	-36	-36	-36	-36	-36	-36	-36	-36	-36	-36	-36
3	0	00	91	-38	3	1	58	58	-37	-37	-37	-37	-37	-37	-37	-37	-37	-37	-37
3	0	00	92	-39	3	1	59	59	-38	-38	-38	-38	-38	-38	-38	-38	-38	-38	-38
3	0	00	93	-40	3	1	60	60	-39	-39	-39	-39	-39	-39	-39	-39	-39	-39	-39
3	0	00	94	-41	3	1	61	61	-40	-40	-40	-40	-40	-40	-40	-40	-40	-40	-40
3	0	00	95	-42	3	1	62	62	-41	-41	-41	-41	-41	-41	-41	-41	-41	-41	-41
3	0	00	96	-43	3	1	63	63	-42	-42	-42	-42	-42	-42	-42	-42	-42	-42	-42
3	0	00	97	-44	3	1	64	64	-43	-43	-43	-43	-43	-43	-43	-43	-43	-43	-43
3	0	00	98	-45	3	1	65	65	-44	-44	-44	-44	-44	-44	-44	-44	-44	-44	-44
3	0	00	99	-46	3	1	66	66	-45	-45	-45	-45	-45	-45	-45	-45	-45	-45	-45
3	0	00	100	-47	3	1	67	67	-46	-46	-46	-46	-46	-46	-46	-46	-46	-46	-46
3	0	00	101	-48	3	1	68	68	-47	-47	-47	-47	-47	-47	-47	-47	-47	-47	-47
3	0	00	102	-49	3	1	69	69	-48	-48	-48	-48	-48	-48	-48	-48	-48	-48	-48
3	0	00	103	-50	3	1	70	70	-49	-49	-49	-49	-49	-49	-49	-49	-49	-49	-49
3	0	00	104	-51	3	1	71	71	-50	-50	-50	-50	-50	-50	-50	-50	-50	-50	-50
3	0	00	105	-52	3	1	72	72	-51	-51	-51	-51	-51	-51	-51	-51	-51	-51	-51
3	0	00	106	-53	3	1	73	73	-52	-52	-52	-52	-52	-52	-52	-52	-52	-52	-52
3	0	00	107	-54	3	1	74	74	-53	-53	-53	-53	-53	-53	-53	-53	-53	-53	-53
3	0	00	108	-55	3	1	75	75	-54	-54	-54	-54	-54	-54	-54	-54	-54	-54	-54
3	0	00	109	-56	3	1	76	76	-55	-55	-55	-55	-55	-55	-55	-55	-55	-55	-55
3	0	00	110	-57	3	1	77	77	-56	-56	-56	-56	-56	-56	-56	-56	-56	-56	-56
3	0	00	111	-58	3	1	78	78	-57	-57	-57	-57	-57	-57	-57	-57	-57	-57	-57
3	0	00	112	-59	3	1	79	79	-58	-58	-58	-58	-58	-58	-58	-58	-58	-58	-58
3	0	00	113	-60	3	1	80	80	-59	-59	-59	-59	-59	-59	-59	-59	-59	-59	-59
3	0	00	114	-61	3	1	81	81	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60
3	0	00	115	-62	3	1	82	82	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61
3	0	00	116	-63	3	1	83	83	-62	-62	-62	-62	-62	-62	-62	-62	-62	-62	-62
3	0	00	117	-64	3	1	84	84	-63	-63	-63	-63	-63	-63	-63	-63	-63	-63	-63
3	0	00	118	-65	3	1	85	85	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64
3	0	00	119	-66	3	1	86	86	-65	-65	-65	-65	-65	-65	-65	-65	-65	-65	-65
3	0	00	120	-67	3	1	87	87	-66	-66	-66	-66	-66	-66	-66	-66	-66	-66	-66
3	0	00	121	-68	3	1	88	88	-67	-67	-67	-67	-67	-67	-67	-67	-67	-67	-67
3	0	00	122	-69	3	1	89	89	-68	-68	-68	-68	-68	-68	-68	-68	-68	-68	-68
3	0	00	123	-70	3	1	90												

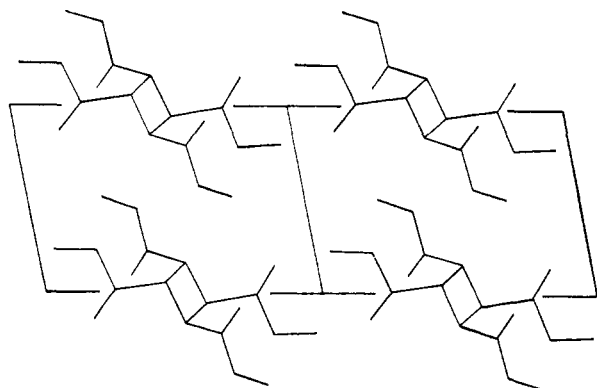


Figure 1. Two unit cells viewed along [001]. Origin at upper left-hand corner with $a \sin \beta$ horizontal and $b \sin \alpha$ vertical.

are $a = 8.939 \pm 0.004$, $b = 5.963 \pm 0.003$, $c = 6.454 \pm 0.003$ Å; $\alpha = 95.17 \pm 0.3^\circ$, $\beta = 81.43 \pm 0.3^\circ$, $\gamma = 78.74 \pm 0.3^\circ$. The calculated density is 1.45 g/cm^3 .

Table II. Positional and Isotropic Thermal Parameters^a

Atom	x	y	z	$B, \text{Å}^2$
C1	0.4920 (2)	0.1686 (4)	0.0937 (3)	
C2	0.2539 (2)	-0.0124 (4)	0.1852 (3)	
C3	0.6013 (2)	0.2193 (4)	0.2381 (3)	
C4	0.5734 (2)	0.0477 (4)	-0.1325 (3)	
C5	0.7279 (3)	0.4972 (5)	0.3730 (5)	
C6	0.0510 (3)	-0.2194 (7)	0.2232 (6)	
O1	0.6100 (2)	0.4402 (2)	0.2577 (3)	
O2	0.6778 (2)	0.0765 (3)	0.3221 (3)	
O3	0.7864 (2)	0.2163 (3)	-0.1740 (3)	
O4	0.1645 (2)	0.1679 (3)	0.2333 (3)	
H1	0.416 (2)	0.301 (4)	0.092 (3)	2.5 (4)
H2	0.535 (2)	0.129 (4)	0.760 (3)	3.2 (5)
H3	0.699 (3)	0.457 (4)	0.531 (5)	6.4 (7)
H4	0.830 (4)	0.414 (5)	0.300 (5)	6.0 (7)
H5	0.720 (3)	0.663 (5)	0.369 (5)	6.3 (8)
H6	0.007 (5)	0.149 (7)	0.864 (7)	10.1 (13)
H7	0.961 (4)	0.368 (7)	0.785 (6)	9.7 (12)
H8	-0.008 (4)	0.138 (7)	0.638 (7)	10.5 (12)

^a Standard deviations are given in parentheses as deviations in the last significant figures.

Table III. Anisotropic Thermal Parameters^a $\times 10^8$ in the Form $\text{Exp}[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C1	7.5 (3)	17.0 (6)	19.1 (6)	-5.8 (7)	-4.2 (6)	6.4 (10)
C2	8.7 (3)	25.1 (8)	17.7 (6)	-11.3 (8)	-2.9 (7)	4.6 (10)
C3	8.5 (3)	18.6 (6)	18.2 (6)	-7.2 (7)	-2.7 (6)	4.0 (10)
C4	8.1 (3)	19.8 (7)	17.4 (6)	-9.3 (7)	-5.4 (6)	8.1 (10)
C5	13.4 (4)	25.4 (9)	32.1 (10)	-17.3 (9)	-15.6 (10)	1.0 (14)
C6	9.5 (4)	43.2 (13)	39.5 (12)	-23.1 (11)	-2.6 (11)	9.6 (20)
O1	11.9 (2)	18.1 (5)	26.0 (5)	-11.2 (5)	-12.6 (5)	4.1 (7)
O2	15.5 (3)	23.3 (6)	35.8 (6)	-12.9 (6)	-26.3 (7)	16.0 (9)
O3	8.8 (2)	27.7 (6)	29.7 (6)	-16.2 (5)	-0.8 (5)	4.6 (8)
O4	10.1 (2)	27.7 (6)	44.2 (7)	-6.0 (6)	2.0 (7)	-2.8 (10)

^a Standard deviations are given in parentheses as deviations in the last significant figures.

Structure Determination. A trial structure was easily obtained by direct methods as described by Karle and Karle.⁹ The structure was refined by full-matrix least-squares calculations minimizing the function $\sum w(|F_o| - |F_c|)^2$. The weight w is equal to $1/\sigma^2$ where σ is the standard deviation of the structure factor, estimated from counting statistics, and machine instability.¹⁰ The least-squares

(9) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

(10) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination: A Practical Guide," Macmillan, New York, N. Y., 1968, pp 454-458.

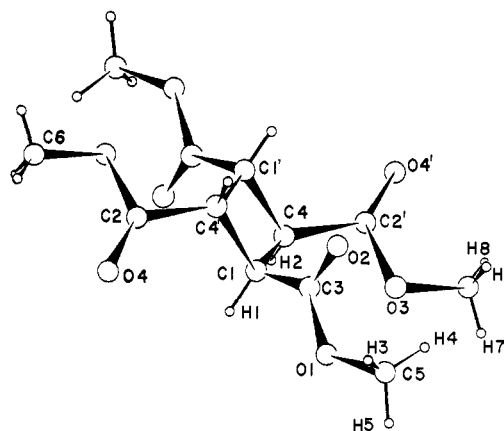


Figure 2. One molecule viewed along [001].

program used was that of Gantzel-Sparks and Trueblood modified to operate on a time-shared CDC 3600 computer.¹¹ Hydrogen atoms were located from a difference map and refined with isotropic temperature factors. All other atoms were refined anisotropically. Atomic scattering factors for hydrogen were those of Stewart, *et al.*,¹² while all others were obtained from the "International Tables for X-Ray Crystallography."¹³ Two reflections, 002 and 111, were omitted from the final cycles of refinement because they seemed to suffer from extinction. The final value of $R = \sum |F_o| - |F_c| / \sum |F_o|$ is 0.035. A difference map calculated after the final least-squares cycle showed no unusual features. Table I lists observed and calculated structure amplitudes. Positional and thermal parameters are listed in Tables II and III. Bond distances and angles are given in Tables IV and V. Standard deviations given in the tables are based on the least-squares calculation. The crystal structure is illustrated in Figures 1 and 2.

Discussion

The cyclobutane ring is planar but not square. The two independent C-C bond lengths differ by 0.03 Å, about six standard deviations. The longer bond of 1.572 ± 0.005 Å is longer than any reported in a simple planar cyclobutane. Long C-C bonds and a rectangular shape are not unusual in cyclobutanes. For example, 1,2,3,4-tetracyanocyclobutane (Ia) has C-C bonds of 1.547 and 1.561 ± 0.003 Å each, and

the C-C bonds in Ib average 1.570 ± 0.015 Å. In both Ia and Ic the longer C-C bond is between the cis groups indicating steric interference.

(11) All computations were carried out from a teletype terminal using the UMASS time-sharing system. The details of using time sharing for crystallographic calculations will be described elsewhere.

(12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

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

Table IV. Observed Interatomic Distances^a

Atoms	Distance, Å	Atoms	Distance, Å
C1-C1'	2.220 (6)	C4-C4'	2.183 (6)
C1-C4	1.572 (5)	C4-H2	0.95 (2)
C1-C4'	1.541 (4)	C5-O1	1.452 (4)
C1-C3	1.500 (4)	C5-H3	1.07 (3)
C1-H1	0.93 (2)	C5-H4	0.97 (3)
C2-C4'	1.499 (3)	C5-H5	0.98 (3)
C2-O3'	1.333 (3)	C6-O3'	1.445 (4)
C2-O4	1.193 (4)	C6-H6	0.90 (4)
C3-O1	1.331 (3)	C6-H7	0.91 (4)
C3-O2	1.206 (4)	C6-H8	0.97 (4)

^a Standard deviations are given in parentheses as deviations in the last significant figures.

The center of each molecule coincides with a crystallographic center of symmetry which is generally true for simple, planar cyclobutanes. The general rules for predicting the conformation of a cyclobutane^{14,15} in the solid state apply here: (1) if the ring is not centrosymmetrically substituted the ring will be puckered, and (2) if the ring is centrosymmetrically substituted it *may* be planar.

Other bond lengths are typical.¹⁶ The C=O bonds average 1.200 ± 0.004 Å, somewhat shorter than the expected value¹⁶ of 1.233 ± 0.005 Å. When these two bond lengths are corrected for thermal motion according to the Busing and Levy¹⁷ "riding" model, they average 1.227 Å. The C-H bonds average 0.96 Å, somewhat shorter than the spectroscopic value¹⁶ of 1.09 Å, as is often the case in X-ray diffraction. The plane of the carboxyl group C1-C3-O2-O1 makes a

(14) T. N. Margulis, *Chem. Commun.*, 9215 (1969).

(15) E. Adman and T. N. Margulis, *J. Phys. Chem.*, **73**, 1480 (1969).

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

(17) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

Table V. Observed Bond Angles^a

Atoms	Angle, deg	Atoms	Angle, deg
C3-C1-C4	114.4	C2'-C4-C1	117.9
C3-C1-C4'	114.3	C2'-C4-C1'	116.4
C3-C1-H1	110.1	C2'-C4-H2	105.5
C4-C1-C4'	89.0	C1-C4-C1'	91.0
C4-C1-H1	113.8	C1-C4-H2	111.6
C4'-C1-H1	113.9	C1'-C4-H2	114.5
C4-C2'-O3	109.4	C1-C3-O1	112.5
C4-C2'-O4'	126.3	C1-C3-O2	124.5
O3-C2'-O4'	124.3	O1-C3-O2	122.9
O1-C5-H3	107.2	O3-C6'-H6	114.5
O1-C5-H1	109.4	O3-C6'-H7	109.5
O1-C5-H5	104.8	O3-C6'-H8	110.0
H3-C5-H4	113.9	H6-C6'-H7	106.8
H3-C5-H5	111.7	H6-C6'-H8	105.1
H4-C5-H5	109.4	H7-C6'-H8	110.9
C3-O1-C5	115.6	C2'-O3-C6'	118.0

^a Standard deviations are about 0.3° for angles not involving hydrogen atoms.

dihedral angle of 25.5° with the plane of C3-C1-C4' and a dihedral angle of 26.3° with the diagonal plane of the cyclobutane ring defined by C1-C1'-C3-C3'. This is to be compared with expectations of 0° for the former angle as predicted by Dunitz and Strickler.¹⁸ The other carboxyl group C4-C2'-O3-O4 makes an angle of 10.4° with C2'-C4-C1', closer to the expected value.

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(18) J. D. Dunitz and P. Strickler in "Structural Chemistry and Molecular Biology," A. Reil and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, p 595.