

Table 4 (cont.)

C(5)-C(4), C(6)	118.4	-C(13), O(20)	102.3
-C(4), C(10)	112.3	C(13)-C(12), C(14)	98.7
-C(4), O(5)	118.3	-C(12), C(16)	111.0
-C(6), C(10)	122.1	-C(14), C(16)	104.6
-C(6), O(5)	61.3	C(14)-C(8), C(13)	101.6
-C(10), C(5)	115.3	-C(8), C(20)	108.8
C(6)-C(5), C(7)	117.9	-C(13), C(20)	102.2
-C(5), O(5)	58.8	C(15)-C(8), C(16)	104.8
-C(7), O(5)	118.1	C(16)-C(13), C(15)	108.9
C(7)-C(6), C(8)	112.3	-C(13), C(17)	122.4
C(8)-C(7), C(9)	109.9	-C(14), C(17)	128.6
-C(7), C(14)	116.8	C(19)-C(4), N(1)	114.0
-C(7), C(15)	108.7	C(20)-C(10), C(14)	102.6
-C(9), C(14)	99.1	-C(10), O(20)	108.2
-C(9), C(15)	116.0	-C(10), N(1)	113.1
-C(14), C(15)	106.3	-C(14), O(20)	106.1
C(9)-C(8), C(10)	99.7	-C(14), N(1)	121.8
-C(8), C(11)	105.2	-O(20), N(1)	104.4
-C(10), C(11)	113.3	O(5)-C(5), C(6)	59.9
		O(20)-C(12), C(20)	103.6
		N(1)-C(19), C(20)	114.1
		-C(19), C(21)	108.9
		-C(20), C(21)	113.3

Table 5. Intramolecular hydrogen-bond contacts  $\leq 3.30 \text{ \AA}$ 

	H...X	A-H...X
O(2)-H(O2)...N(1)	1.94 $\text{\AA}$	136°
O(2)-H(O2)...O(20)	2.57	128
O(11)-H(O11)...O(5)	2.90	80

Molecular packing in the crystal appears to be governed by van der Waals interactions. The relevant contact distances and angles for the two H atoms capable of acting as hydrogen-bond donors are listed in Table 5. There is a weak intramolecular hydrogen bond between H(O2) and N(1). The H(O11) atom does not bond at all as the only contact within 3.3  $\text{\AA}$  which is suitable as an acceptor is poorly placed with respect to angle.

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### 1-Phthalimido-1-deoxy-2,3:4,6-di-O-isopropylidene- $\alpha$ -L-sorbofuranose

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**Abstract.**  $C_{20}H_{23}NO_7$ , orthorhombic,  $P2_12_12_1$ ;  $a = 11.776$  (1),  $b = 18.162$  (2),  $c = 9.143$  (1)  $\text{\AA}$ ;  $Z = 4$ ,  $D_c = 1.32$ ,  $D_m = 1.33$  g cm $^{-3}$ . Full-matrix least-squares refinement led to an  $R$  of 0.051. The molecular conformation in the crystal is the same as the preferred conformation in solution. Potential-energy calculations show that attractive London dispersion forces favor this conformation.

**Introduction.** NMR studies (Glass & Williams, 1972) of the title compound (I) demonstrated the importance of the conformation illustrated in Fig. 1. Especially revealing was the intramolecular shielding of the hydrogens of the methyl group placed above the phthalimide

ring. It was suggested that the preference for this conformation may be due to a stabilizing interaction between the O atoms of the 1,3-dioxane ring and the carbonyl carbons of the phthalimide moiety. Analogous interactions are the subject of considerable interest. Furthermore, such interactions may be of biological significance, for example in the binding of barbiturates (Voet, 1972) and the teratogenic properties of thalidomide (Jönsson, 1972). Thus an X-ray crystallographic structural analysis was performed on (I) to determine the significance of the interaction.

Preliminary X-ray photographs showed orthorhombic symmetry and the following systematic absences were observed:  $h00$  when  $h = 2n + 1$ ,  $0k0$  when  $k = 2n + 1$ , and  $00l$  when  $l = 2n + 1$ . The space group is thus determined to be  $P2_12_12_1$ . Twelve reflections were centered on a Picker four-angle diffractometer and a least-

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molecule (3.7 Å) (Pauling, 1960). The bond lengths and bond angles are very similar for the phthalimide ring in (I) and that in *N*-( $\alpha$ -glutarimido)phthalimide (thalidomide) (Allen & Trotter, 1971). The N atom in (I) is not quite planar, being 0.059 Å out of the plane of the three atoms [C(7), C(14), C(1)] attached to it, but the sum of the angles C(7)–N–C(14), C(7)–N–C(1)

is 359°. The N atom of the phthalimide ring in 4-bromothalidomide is planar (Peterson, 1969), but that in thalidomide itself is pyramidal (Allen & Trotter, 1971).

The tetrahydrofuran ring approximates an envelope conformation; starting at O(5)  $q=0.324$  Å and  $\varphi=138.06^\circ$  (Cremer & Pople, 1975). The r.m.s. deviation of the least-squares plane of O(5), C(2), C(3) and C(4) is 0.015 Å and C(5) is displaced from this plane by 0.499 Å. The conformation of furanose rings usually involves puckering of C(2') or C(3') (Spencer, 1959; Sundaralingam, 1965, 1969; Sundaralingam & Jensen, 1965) [although sometimes both C(2') and C(3') (Sundaralingam, 1965, 1969; Sundaralingam & Jensen, 1965)]. However, if the furanose is fused to a six-membered ring, as in cyclic adenosine-3',5'-phosphate (Watenpaugh, Dow, Jensen & Furberg, 1968) or cyclic uridine-3',5'-phosphate (Coulter, 1969), then C(4') is displaced from the plane of the other four atoms of the ribose ring. Such a conformation is analogous to the conformation of the furanose ring in (I). For the 1,3-dioxolane ring in (I) starting at O(5)  $q$  is 0.310 Å and  $\varphi$  is 46.56°. Displaced by 0.356 Å from the plane of C(2), C(3) and O(2) is C(15), and O(3) is removed by 0.140 Å from this plane on the opposite side.

The 1,3-dioxane ring is in a chair conformation;  $q=0.493$  Å,  $\varphi=356.72^\circ$ ,  $\theta=11.14^\circ$ . Substantial puckering occurs in the O(6)–C(18)–O(4) moiety as expected (de Kok & Romers, 1970; Nader, 1975), whereas the C(4)–C(5)–C(6) portion is flattened relative to cyclohexane, undoubtedly because of its fusion with the five-membered tetrahydrofuran ring. This is best seen by consideration of the torsional angles O(6)–C(18)–O(4)–C(4) (58.9), O(4)–C(18)–O(6)–C(6) (–60.1), C(18)–O(6)–C(6)–C(5) (51.9), C(5)–C(4)–O(4)–C(18) (–50.5), O(6)–C(6)–C(5)–C(4) (–42.5) and C(6)–C(5)–C(4)–O(4) (41.7°).

A major objective of this structural study was to determine whether there is an intramolecular stabilizing electrostatic interaction between the O atoms of the 1,3-dioxane ring and the carbonyl C atoms of the phthalimide ring. The results proffer no evidence for a strong interaction of this type. The relevant nonbonded distances are C(7)···O(6) 4.758, C(7)···O(4) 3.350, C(14)···O(6) 4.136, and C(14)···O(4) 3.940 Å. The sum of the van der Waals radii for O and C is 3.1 Å (Pauling, 1960). Thus, there is no evidence for substantial electrostatic attraction.

To gain more insight into the relative potential energies for the conformers of (I) obtained by rotation about the C(1)–C(2) bond, calculations were made with the Lennard–Jones 6–12 potential function and the constants listed by Hopfinger (1973). The calculations show that the preferred conformation is near the lowest potential-energy minimum. Further analysis reveals that the preferred conformer is favored over the other minimum-energy conformations (by 3.0–3.6 kcal mol<sup>-1</sup>) principally due to favorable London dispersion forces in the preferred conformer. This result is reminiscent of the greater thermodynamic stability

Table 1. Atomic positional parameters

The parameters and standard deviations (in parentheses) for the least significant digit of the non-hydrogen atoms are  $\times 10^4$ .

	x	y	z
N	–779 (4)	4519 (2)	5133 (4)
O(2)	–3545 (3)	4281 (2)	3275 (4)
O(3)	–3366 (3)	3052 (2)	3166 (5)
O(4)	–323 (3)	3113 (2)	2820 (4)
O(5)	–1759 (3)	4399 (2)	2205 (4)
O(6)	412 (4)	3827 (2)	964 (4)
O(7)	–960 (4)	3507 (2)	6587 (4)
O(14)	–69 (4)	5573 (2)	4072 (5)
C(1)	–1957 (5)	4621 (3)	4728 (6)
C(2)	–2348 (4)	4154 (3)	3463 (6)
C(3)	–2224 (4)	3316 (3)	3495 (6)
C(4)	–1484 (5)	3135 (3)	2234 (6)
C(5)	–1616 (5)	3775 (3)	1238 (6)
C(6)	–631 (5)	3911 (3)	229 (6)
C(7)	–385 (5)	3977 (3)	6057 (6)
C(8)	846 (5)	4129 (3)	6284 (6)
C(9)	1665 (5)	3740 (4)	7047 (7)
C(10)	2711 (7)	4022 (4)	7112 (8)
C(11)	3016 (6)	4664 (4)	6344 (8)
C(12)	2207 (5)	5055 (3)	5572 (7)
C(13)	1107 (5)	4757 (3)	5515 (6)
C(14)	88 (5)	5024 (3)	4790 (6)
C(15)	–4114 (5)	3605 (3)	3588 (6)
C(16)	–4340 (6)	3548 (4)	5244 (8)
C(17)	–5181 (6)	3574 (4)	2712 (9)
C(18)	545 (5)	3167 (3)	1732 (6)
C(19)	1644 (6)	3233 (5)	2608 (9)
C(20)	534 (6)	2500 (3)	734 (8)

Table 2. Idealized hydrogen-atom positional ( $\times 10^3$ ) and thermal parameters

	x	y	z	Atomic B
H(1)	147	324	756	10.0
H(2)	333	376	776	12.1
H(3)	386	485	635	6.2
H(4)	241	555	505	4.8
H(5)	–207	518	444	4.8
H(6)	–246	449	564	10.0
H(7)	–493	395	556	10.6
H(8)	–358	363	582	5.5
H(9)	–467	302	549	4.5
H(10)	–499	366	160	9.2
H(11)	–556	305	284	9.8
H(12)	–574	398	308	6.1
H(13)	–191	311	448	2.4
H(14)	–170	264	172	6.1
H(15)	–234	370	59	5.9
H(16)	–67	353	–64	6.1
H(17)	–69	445	–18	7.5
H(18)	180	274	317	7.9
H(19)	157	367	336	4.7
H(20)	232	334	189	7.9
H(21)	72	203	134	5.8
H(22)	–27	245	25	9.7
H(23)	115	257	–9	7.2

of the axial over the equatorial isomer of thiacyclohexane 1-oxide (Johnson & McCants, 1964; Martin & Uebel, 1964; Lambert & Keske, 1966) because of attractive van der Waals interaction between the axial O atom and the *syn*-axial hydrogens (Johnson & McCants, 1964; Allinger, Hirsch, Miller & Tyminski, 1969). Although it is reasonable to ascribe the conformational preference in (I) to attractive van der Waals interactions it should be emphasized that the calculations for (I) did not include energy minimization, e.g. by rotation about bonds other than C(1)–C(2), or entropy considerations. Furthermore, no attempt was made to calculate electrostatic interactions.

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### *S*-Carboxymethyl-L-cysteine Sulfoxide (Configuration 2*R*:4*R*)

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**Abstract.** C<sub>5</sub>H<sub>9</sub>SO<sub>5</sub>N, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>; *a* = 4·786 (2), *b* = 8·312 (1), *c* = 18·914 (5) Å; *Z* = 4, *D*<sub>x</sub> = 1·723, *D*<sub>m</sub> = 1·732 (5) g cm<sup>-3</sup> (floatation at 21°C). The structure has been determined by standard Fourier techniques from X-ray diffractometer data and refined by least-squares methods to *R* = 0·035 for 924 independent reflections. As found by X-ray analysis, the title compound exists as an 'apparent' zwitterion. The cysteine carboxyl and the methyl carboxyl groups of adjacent molecules are involved in a very strong hydrogen bond [O···O 2·449 (3) Å].

**Introduction.** The title compound and an epimeric sulfide were prepared by oxidation of *S*-carboxymethyl-L-cysteine (SCMC). Fractional crystallization from water was used to separate and purify the two epimers. The title compound was the first epimer to crystallize from solution (analysis, calculated for C<sub>5</sub>H<sub>9</sub>SO<sub>5</sub>N: 30·77% C, 7·17% N, 4·64% H; composition found: 30·96% C, 6·37% N, 4·78% H). Precession photographs showed *mmm* symmetry. Systematic absences (*h*00, *h* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1; 00*l*, *l* = 2*n* + 1) observed on the films and verified on the diffractometer