

Absorption correction: $k = 0 \rightarrow 8$
 refined from ΔF $l = -23 \rightarrow 23$
 3532 measured reflections 3 standard reflections
 2204 independent reflections intensity decay: 15%

Refinement

Refinement on F $(\Delta/\sigma)_{\max} = 0.08$
 $R = 0.074$ $\Delta\rho_{\max} = 0.64 \text{ e } \text{\AA}^{-3}$
 $wR = 0.081$ $\Delta\rho_{\min} = 0.0 \text{ e } \text{\AA}^{-3}$
 $S = 3.89$ Extinction correction: none
 1517 reflections Atomic scattering factors
 283 parameters from *International Tables*
 H-atom parameters not for *X-ray Crystallography*
 refined (1974, Vol. IV)
 $w = 1/\sigma^2(F)$

C14—C2—C31 122 (1) N2—C44—C43 106 (1)
 C14—C2—C41 123 (1) C1'—C44—C43 126 (1)
 C31—C2—C41 114 (1) C12—C11—N1 109 (1)
 Symmetry code: (i) $-x, -y, -z$.

Data collection was performed using *CAD-4 Software* (Enraf-Nonius, 1989). All calculations were performed on a PDP11/44 computer with *SDP* (Enraf-Nonius, 1985) programs. The structure was solved by direct methods and difference Fourier syntheses; refinement was by the full-matrix least-squares method. The coordinates of the H atoms were calculated according to theoretical methods.

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Br1	0.3823 (1)	0.4604 (3)	0.0159 (1)	5.07 (4)
Br2	0.2451 (1)	0.7266 (2)	0.10589 (8)	3.72 (3)
C12	0.2054 (9)	0.479 (2)	0.0658 (7)	2.6 (3)
C13	0.2557 (9)	0.385 (2)	0.0241 (7)	2.4 (3)
C11	0.117 (1)	0.368 (2)	0.0668 (7)	2.6 (3)
C14	0.1984 (9)	0.211 (2)	-0.0047 (7)	2.02 (2)
N1	0.1145 (7)	0.207 (2)	0.0230 (5)	2.3 (2)
N2	0.0778 (7)	-0.153 (1)	-0.0622 (6)	2.0 (2)
C1	0.0491 (9)	0.405 (2)	0.1083 (7)	2.5 (3)
C2	0.2222 (9)	0.078 (2)	-0.0532 (7)	2.4 (3)
C21	0.0691 (9)	0.555 (2)	0.1648 (7)	2.5 (3)
C22	0.136 (1)	0.514 (2)	0.2272 (7)	3.4 (3)
C23	0.152 (1)	0.651 (2)	0.2808 (7)	3.3 (3)
C24	0.104 (1)	0.827 (2)	0.2732 (9)	4.6 (4)
C25	0.040 (1)	0.873 (2)	0.2133 (9)	4.3 (4)
C26	0.020 (1)	0.737 (2)	0.1597 (7)	3.3 (3)
C31	0.3055 (9)	0.110 (2)	-0.0875 (7)	2.7 (3)
C32	0.295 (1)	0.259 (3)	-0.1409 (9)	4.9 (4)
C33	0.460 (1)	0.185 (3)	-0.1560 (9)	5.7 (5)
C34	0.381 (1)	0.299 (3)	-0.170 (1)	5.7 (5)
C35	0.469 (1)	0.034 (4)	-0.106 (1)	6.0 (5)
C36	0.388 (1)	0.001 (2)	-0.0732 (8)	4.0 (3)
C41	0.165 (1)	-0.089 (2)	-0.0778 (7)	2.6 (3)
C42	0.1831 (9)	-0.219 (2)	-0.1345 (6)	2.6 (3)
C43	0.105 (1)	-0.344 (2)	-0.1504 (7)	3.2 (3)
C44	0.0397 (9)	-0.310 (2)	-0.1052 (7)	2.2 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Br1—C13	1.86 (1)	C1—C11	1.38 (2)
Br2—C12	1.88 (1)	C1—C21	1.47 (2)
C12—C13	1.33 (2)	C1—C44'	1.39 (2)
C12—C11	1.45 (2)	C2—C14	1.38 (2)
C13—C14	1.47 (2)	C2—C31	1.46 (2)
N1—C11	1.38 (2)	C2—C41	1.41 (2)
N1—C14	1.38 (2)	C41—C42	1.47 (2)
N2—C41	1.38 (2)	C42—C43	1.36 (2)
N2—C44	1.38 (2)	C43—C44	1.40 (2)
Br2—C12—C13	122 (1)	C12—C11—C1	127 (1)
Br2—C12—C11	130 (1)	N1—C11—C1	124 (1)
C13—C12—C11	108 (1)	C13—C14—N1	108 (1)
Br1—C13—C12	123 (1)	C13—C14—C2	126 (1)
Br1—C13—C14	129 (1)	N1—C14—C2	126 (1)
C12—C13—C14	108 (1)	N2—C41—C2	130 (1)
C11—N1—C14	108 (1)	N2—C41—C42	105 (1)
C41—N2—C44	111 (1)	C2—C41—C42	124 (1)
C11—C1—C21	120 (1)	C41—C42—C43	107 (1)
C11—C1—C44'	127 (1)	C42—C43—C44	110 (1)
C21—C1—C44'	113 (1)	N2—C44—C1'	128 (1)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Homogentisic Acid

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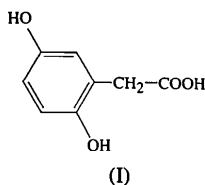
Abstract

The plane of the acetic acid side chain of the title compound (2,5-dihydroxybenzeneacetic acid, $\text{C}_8\text{H}_8\text{O}_4$) is nearly perpendicular to that of the benzene ring. Molecules are linked through hydrogen bonds of the $\text{O—H} \cdots \text{O}$ type.

Comment

Homogentisic acid, (I), is a famous intermediate of phenylalanine and tyrosine metabolism (Martin, Mayes & Rodwell, 1983). It is found in the urine of patients with alkaptonurea. It is produced by oxidation of *p*-

hydroxyphenylpyruvic acid and is further converted to maleoylacetoacetate. The latter step is catalyzed by homogentisate oxygenase (EC 1.13.11.5) which patients with alkaptonurea lack genetically. For a detailed understanding of the mechanism of oxidation by the oxygenase, it is important to know the precise structure of the starting compound. Homogentisic acid has also been tested as one of the biological markers of the neuronal differentiation of the human neuroblastoma cell induced by treatment with biological agents such γ -interferon and tumor necrosis factor (Ponzoni, Casaloro, Lanciotti, Montaldo & Cornaglia-Ferraris, 1992). In horticultural research, homogentisic acid has been identified as the cause of the disagreeable pungent taste of bamboo shoots called 'egumi' in Japan (Kozukue & Mizuno, 1989).



Molecules are held together by intermolecular hydrogen bonds of the O—H...O type: O(8A)—H(8)...O(8B)(-x, -y, -z) 2.775 (3), O(2)—H(2)...O(8B)($\frac{1}{2} + x, -\frac{1}{2} - y, z$) 2.685 (3) and O(5)—H(5)...O(5)($\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$) 2.781 (2) Å.

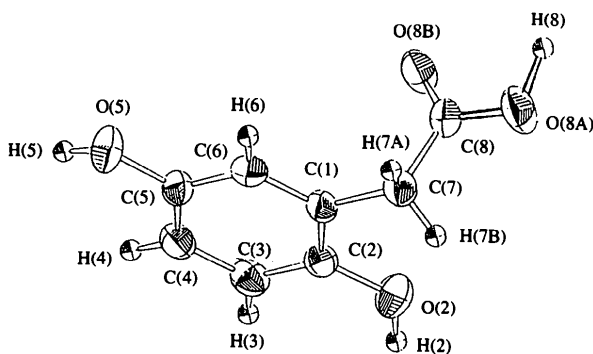


Fig. 1. Perspective view of the title compound with the atomic numbering. Ellipsoids for non-H atoms correspond to 50% probability.

Experimental

Crystal data

C₈H₈O₄
M_r = 168.15
 Monoclinic
*P*2₁/*a*
a = 10.127 (2) Å
b = 4.870 (2) Å
c = 15.811 (2) Å
 β = 106.61 (1)°
V = 747.2 (4) Å³
Z = 4
D_x = 1.495 Mg m⁻³

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 20 reflections
 θ = 9.3–10.6°
 μ = 0.114 mm⁻¹
T = 296 K
 Plate
 0.4 × 0.3 × 0.1 mm
 Brown
 Crystal source: evaporation from 50% ethanol

Data collection

Rigaku AFC-5R diffractometer
 ω -2 θ scans
 Absorption correction: none
 2043 measured reflections
 1938 independent reflections
 899 observed reflections [*I* > 2 σ (*I*)]

*R*_{int} = 0.043
 θ_{\max} = 27.55°
h = 0 → 12
k = 0 → 6
l = -20 → 17
 3 standard reflections monitored every 150 reflections
 intensity decay: 0.5%

Refinement

Refinement on *F*²
R = 0.051
wR = 0.049
S = 1.47
 899 reflections
 109 parameters
 H-atom parameters not refined

$w = 4F_o^2/\sigma^2(F_o^2)$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
O(2)	0.4736 (2)	-0.0927 (5)	0.1840 (1)	4.0 (1)
O(5)	0.2462 (3)	0.0858 (5)	0.4569 (1)	3.7 (1)
O(8A)	0.1277 (2)	0.2922 (6)	0.0150 (1)	4.4 (1)
O(8B)	0.0898 (3)	-0.0284 (5)	0.1046 (1)	3.9 (1)
C(1)	0.3183 (3)	0.1401 (7)	0.2441 (2)	2.4 (1)
C(2)	0.4200 (3)	-0.0583 (7)	0.2539 (2)	2.7 (1)
C(3)	0.4644 (3)	-0.2090 (8)	0.3303 (2)	3.1 (1)
C(4)	0.4072 (3)	-0.1637 (7)	0.3989 (2)	3.0 (1)
C(5)	0.3077 (3)	0.0314 (7)	0.3904 (2)	2.7 (1)
C(6)	0.2629 (3)	0.1816 (7)	0.3133 (2)	2.7 (1)
C(7)	0.2709 (3)	0.3010 (7)	0.1601 (2)	3.0 (1)
C(8)	0.1545 (3)	0.1680 (7)	0.0918 (2)	2.8 (1)

Table 2. Selected geometric parameters (Å, °)

O(2)—C(2)	1.374 (3)	C(1)—C(7)	1.498 (4)
O(5)—C(5)	1.391 (3)	C(2)—C(3)	1.376 (5)
O(8A)—C(8)	1.313 (4)	C(3)—C(4)	1.385 (4)
O(8B)—C(8)	1.209 (4)	C(4)—C(5)	1.363 (5)
C(1)—C(2)	1.388 (4)	C(5)—C(6)	1.382 (4)
C(1)—C(6)	1.381 (4)	C(7)—C(8)	1.500 (4)
C(2)—C(1)—C(6)	118.1 (3)	O(5)—C(5)—C(4)	122.4 (3)
C(2)—C(1)—C(7)	120.2 (3)	O(5)—C(5)—C(6)	117.4 (3)
C(6)—C(1)—C(7)	121.8 (3)	C(4)—C(5)—C(6)	120.2 (3)
O(2)—C(2)—C(1)	116.5 (3)	C(1)—C(6)—C(5)	121.1 (3)
O(2)—C(2)—C(3)	122.5 (3)	C(1)—C(7)—C(8)	113.6 (3)
C(1)—C(2)—C(3)	121.0 (3)	O(8A)—C(8)—O(8B)	122.7 (3)
C(2)—C(3)—C(4)	119.8 (3)	O(8A)—C(8)—C(7)	112.3 (3)
C(3)—C(4)—C(5)	119.8 (3)	O(8B)—C(8)—C(7)	125.0 (3)

Programs used for data collection and cell refinement: *MSC/AFC Data Collection and Refinement Software* (Rigaku Corporation, 1988). Programs used to solve structure: *SHELX86* (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). All calculations including data reduction: *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including bond distances and angles involving H atoms, and torsion angles have been deposited with the IUCr (Reference: AS1128). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,3'-(1,1,3,3-Tetramethyldisiloxane-1,3-diyl)bis(*N*-ethyl-*N,N*-dimethyl-1-propanaminium) Diperchlorate at 163 K and Room Temperature

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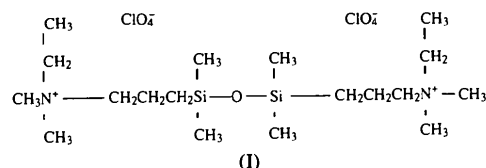
Abstract

In the title compound, $C_{18}H_{46}N_2OSi_2^{2+} \cdot 2ClO_4^-$, the cations lie in special positions on the crystallographic twofold axis. The contacts between N^+ and ClO_4^- build up a three-dimensional net. The Si—O—Si angle is relatively small [between 141.8 (3) and 144.4 (5)°] and depends on the measuring temperature.

Comment

This article is part of an ongoing series of crystal structure investigations of siloxane amphiphilic compounds (Ramm, Schulz, Sonnek & Schmaucks, 1990; Ramm, Schmaucks, Rudert & Schulz, 1993; Rudert & Schmaucks, 1994*a,b*). The comparison of crystal structure data of siloxane surfactants with data determined from the adsorption isotherm at

interfaces should give information about the possible arrangement of molecules at the interface. Recently published results show good agreement of the surface area per molecule of *N*-alkyl-*N,N*-dimethyl-3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-1-propanaminium bromides determined from their X-ray crystal structures with those calculated from the Frumkin adsorption isotherm (Schmaucks, Sonnek, Wüstneck, Herbst & Ramm, 1992). The investigation of additional siloxane surfactants with different structures should reveal possible principle connections. Here we report the crystal structure of the title compound, (I), at 163 K and room temperature.



The atomic numbering scheme is shown in Fig. 1. Fig. 2 shows a perspective projection of the crystal structure. The cation has C_2 symmetry with a twofold axis through O1. One interesting feature is the Si—O—Si angle. In other crystal structures, in which this angle is not part of a ring, it ranges from 137 to 180° [for a theoretical discussion, see Newton (1981) and Gibbs (1982)]. The Si—O—Si angle of the title compound, being 141.8 (3)° at low temperature, is one of the lowest ever found in this class of compounds. As predicted by Gibbs (1982) and confirmed by X-ray crystal structure determination by Rudert & Schmaucks (1994*a*), the temperature may have a rather large effect on the Si—O—Si angle. In this study, this angle is only 2.6° larger at room temperature than at 163 K, but nevertheless concurs with the prediction of Gibbs (1982).

The displacement parameters of the ethyl group are remarkably high. This leads to an apparent shortening of the C5—C6 bond, especially at room temperature. The ethyl group may be disordered at room temperature, but it was impossible to resolve separate positions for C6. The position of C6 is different from the corresponding positions of this atom in dialkyldimethylammonium bromides (Taga, Machida, Kimura, Hayashi, Umemura & Takenaka, 1986, 1987; Taga, Miwa, Machida, Kimura, Hayashi, Umemura & Takenaka, 1990), in *N*-alkyl-*N,N*-dimethyl-3-(heptamethyltrisiloxan-3-yl)-1-propanaminium bromide (Ramm, Schulz, Sonnek & Schmaucks, 1990) and in *N*-butyl-*N,N*-dimethyl-3-(1,1,3,3,5,5,5-heptamethyltrisiloxan-1-yl)-1-propanaminium bromide (Rudert & Schmaucks, 1994*a*). The title compound has a C3—N4—C5—C6 torsion angle of 178.0 (4)°, whereas the above cited compounds have corresponding torsion angles between 50.2 and 57.3° (absolute values). The Si—C—C—N chains have *trans*-planar conformations. The maximum deviation from the least-squares plane is 0.04 (2) Å. The