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2,2′-Dithiodisalicyclic Acid Tetrahydrofuran Solvate

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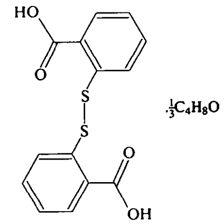
Abstract

The title structure (2,2′-disulfanediyldibenzoic acid tetrahydrofuran solvate, $C_{14}H_{10}O_4S_2.\frac{1}{3}C_4H_8O$) contains two crystallographically distinct $[C_6H_4(2\text{-COOH})S]_2$ molecules, one of which consists of symmetry-related halves. The molecules form extended chains in the crystal by means of hydrogen bonding, but each $[C_6H_4(2\text{-COOH})S]_2$ unit bonds only to units equivalent to itself resulting in two crystallographically inequivalent chains aligned along the *c* axis. There is also a tetrahydrofuran molecule present, disordered over two sites.

Comment

In the title compound (I), the geometrical parameters of the three $[C_6H_4(2\text{-COOH})S]$ sub-units are similar. The angle between the best plane through the phenyl ring containing C(1) and that related by $(-x, y, \frac{1}{2}-z)$ is 80.4 (6)°, while the corresponding angle between the rings containing atoms C(8) and C(15) is 73.8 (4)°. The hydrogen bonds, likewise, are all of a similar length, the $O(2)\cdots O(1^{i})$ distance being 2.641 (12), $O(4)\cdots O(5^{ii})$ being 2.651 (11) and $O(6)\cdots O(3^{iii})$ being 2.658 (12) Å [symmetry codes: (i) $-x, -y, 1-z$; (ii) $x, -y, z+\frac{1}{2}$; (iii) $x, -y, z-\frac{1}{2}$]. There appears to be a slight torsional strain in the latter two bonds, since the angle between the planes defined by O(5)—C(21)—O(6) and $O(3^{iii})$—$C(14^{iii})$—$O(4^{iii})$ is 9.3 (6)°. The O(1)—C(7)—O(2) and $O(1^{i})$—$C(7^{i})$—$O(2^{i})$ groups are essentially coplanar.



(I)

The tetrahydrofuran molecule, which refined poorly as an unconstrained group, was known to be present from the observation of characteristic signals in the NMR spectrum of (I). Also, it should be mentioned that there is some ambiguity as to the correct space group for this structure. A possible alternative is *Cc*, although attempts at refinement in this space group were severely hampered by a low data-to-parameter ratio and poor convergence.

A large number of other dithiodiaryl compounds have been structurally characterized and by comparison of the structure of (I) with these, its features can be seen to be broadly typical of the class. Comparable structures are those of $[C_6H_4(4\text{-Cl})S]_2$ (Spirlet, van den Bossche, Dideberg & Dupont, 1979) and especially $[C_6H_4(2\text{-COCl})S]_2$, for which the attributed space group is also *C*2/*c* ($Z = 12$) (Parkanyi, Kálmán, Kucsman & Kapovits, 1989).

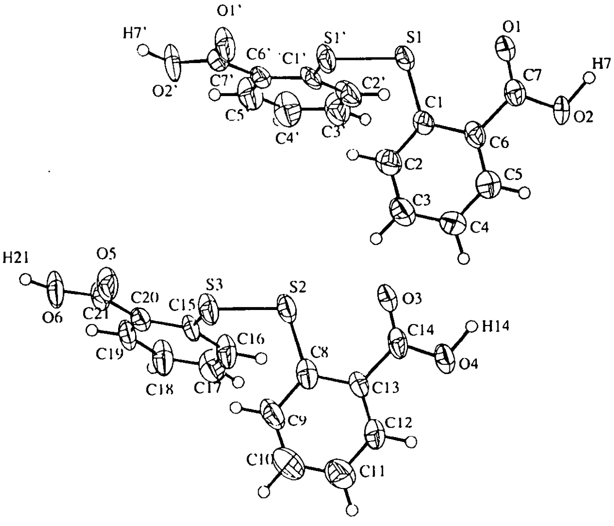


Fig. 1. Molecular diagram (*SNOOPI*; Davies, 1982) of the title compound with displacement ellipsoids depicted at the 50% probability level. Unlabelled H atoms possess the same numerical label as do their parent C atoms. [Symmetry code: (′) $-x, y, \frac{1}{2}-z$.]

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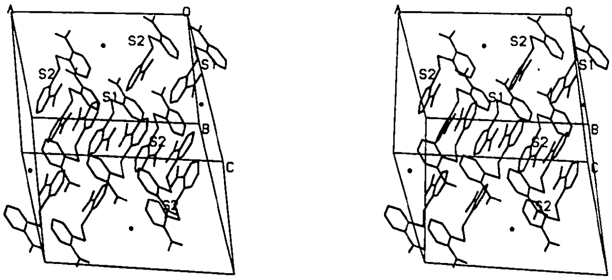

Fig. 2. A stereoview (*PLUTO*; Motherwell & Clegg, 1983) of the extended structure of the title compound showing the unit-cell contents. The small spheres indicate the special position ($\frac{1}{2}$,0,$\frac{1}{4}$) and its equivalents which are the approximate locations of the disordered tetrahydrofuran molecules.

Experimental

Crystal data

$C_{14}H_{10}O_4S_2.\frac{1}{3}C_4H_8O$
$M_r = 330.40$
Monoclinic
$C2/c$
$a = 17.223$ (6) Å
$b = 12.904$ (6) Å
$c = 21.073$ (4) Å
$\beta = 107.44$ (2)°
$V = 4468$ (2) Å^3
$Z = 12$
$D_x = 1.473$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–12°
$\mu = 0.357$ mm^{-1}
$T = 293$ K
Lozenge
0.6 × 0.2 × 0.2 mm
Pale straw
Crystal source: tetrahydrofuran

Data collection

Nicolet *R*3*m*/*E* diffractometer
Wyckoff scans
Absorption correction: empirical
$T_{\min} = 0.952$, $T_{\max} = 1.000$
3786 measured reflections
2935 independent reflections
1209 observed reflections $[|F_o|^2 > 3\sigma|F_o|^2]$

$R_{\rm int} = 0.0255$
$\theta_{\max} = 22.5°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 13$
$l = -22 \rightarrow 21$
3 standard reflections monitored every 97 reflections intensity variation: <5%

Refinement

Refinement on F
$R = 0.0500$
$wR = 0.0505$
$S = 1.413$
1209 reflections
291 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + |g|(F_o)^2]$
$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S(1)	−0.0016 (2)	0.0443 (2)	0.2983 (1)	0.048
S(2)	0.7628 (2)	0.0578 (2)	0.3827 (1)	0.052
S(3)	0.7726 (2)	0.0530 (2)	0.2884 (1)	0.053
O(1)	0.0030 (4)	0.0175 (6)	0.4248 (3)	0.059
O(2)	0.0699 (4)	0.1101 (5)	0.5121 (3)	0.066
O(3)	0.7576 (4)	0.0355 (5)	0.5070 (3)	0.063
O(4)	0.8237 (4)	0.1264 (5)	0.5957 (3)	0.065
O(5)	0.7586 (4)	0.0071 (6)	0.1604 (3)	0.058
O(6)	0.6774 (4)	0.0816 (5)	0.0695 (3)	0.068
C(1)	0.0686 (5)	0.1422 (7)	0.3405 (4)	0.036
C(2)	0.1066 (6)	0.2070 (8)	0.3073 (5)	0.050
C(3)	0.1606 (7)	0.2830 (8)	0.3389 (5)	0.065
C(4)	0.1774 (7)	0.2970 (8)	0.4064 (5)	0.064
C(5)	0.1401 (7)	0.2335 (9)	0.4401 (5)	0.062
C(6)	0.0872 (6)	0.1552 (8)	0.4096 (5)	0.039
C(7)	0.0485 (6)	0.0862 (8)	0.4488 (5)	0.042
C(8)	0.8285 (6)	0.1608 (8)	0.4252 (4)	0.049
C(9)	0.8653 (7)	0.2286 (9)	0.3918 (5)	0.063
C(10)	0.9138 (7)	0.3079 (10)	0.4247 (5)	0.072
C(11)	0.9249 (7)	0.3224 (9)	0.4920 (6)	0.071
C(12)	0.8899 (6)	0.2567 (9)	0.5258 (5)	0.057
C(13)	0.8414 (6)	0.1751 (8)	0.4937 (4)	0.041
C(14)	0.8029 (6)	0.1065 (8)	0.5319 (4)	0.045
C(15)	0.7019 (5)	0.1498 (7)	0.2434 (4)	0.040
C(16)	0.6733 (7)	0.2262 (8)	0.2765 (4)	0.058
C(17)	0.6194 (7)	0.3000 (8)	0.2415 (6)	0.063
C(18)	0.5937 (7)	0.3003 (8)	0.1718 (5)	0.065
C(19)	0.6241 (7)	0.2255 (8)	0.1392 (5)	0.056
C(20)	0.6771 (6)	0.1487 (7)	0.1734 (4)	0.040
C(21)	0.7078 (7)	0.0727 (8)	0.1347 (4)	0.049
O(7)	0.5074 (11)	−0.0068 (13)	0.1616 (7)	0.137
C(22)	0.4674 (9)	0.0734 (12)	0.1859 (9)	0.121
C(23)	0.4655 (13)	0.0403 (18)	0.2545 (10)	0.177
C(24)	0.5417 (13)	−0.0284 (19)	0.2780 (7)	0.153
C(25)	0.5447 (10)	−0.0777 (12)	0.2134 (10)	0.105

Table 2. *Selected geometric parameters* (Å, °)

S(1)—S(1′)	2.051 (5)	O(3)—C(14)	1.216 (10)
S(1)—C(1)	1.791 (9)	O(4)—C(14)	1.309 (10)
S(2)—S(3)	2.046 (3)	O(5)—C(21)	1.221 (10)
S(2)—C(8)	1.800 (10)	O(6)—C(21)	1.321 (10)
S(3)—C(15)	1.802 (9)	C(6)—C(7)	1.500 (12)
O(1)—C(7)	1.191 (10)	C(13)—C(14)	1.481 (12)
O(2)—C(7)	1.310 (10)	C(20)—C(21)	1.471 (12)
S(3)—S(2)—C(8)	106.4 (4)	S(2)—S(3)—C(15)	104.5 (3)
O(3)—C(14)—O(4)	122.3 (9)	O(3)—C(14)—C(13)	123.3 (9)
O(4)—C(14)—C(13)	114.4 (9)	O(1)—C(7)—O(2)	123.7 (10)
O(1)—C(7)—C(6)	123.6 (9)	O(2)—C(7)—C(6)	112.7 (10)
O(5)—C(21)—O(6)	122.0 (9)	O(5)—C(21)—C(20)	123.0 (9)
O(6)—C(21)—C(20)	115.0 (10)	C(1)—S(1)—S(1′)	106.1 (6)

Symmetry code: (′) $-x, -y, \frac{1}{2} - z$.

The crystal symmetry and axial dimensions were confirmed using axial photographs. A total of 3786 data, including 739 systematic absences, were measured. The scan range was 1° and the rate variable from 2.9 to 29° min^{-1}. An empirical absorption correction was applied on the basis of azimuthal scans of five reflections with $5 < 2\theta < 45°$. The positions of all non-H atoms in the dithiodisalicylic acid units were estimated using direct methods (Sheldrick, 1985). The tetrahydrofuran O and C atoms were located using subsequent difference Fourier syntheses and assigned occupancies of 50%. The interatomic distances were constrained to their literature values (David & Ibberson, 1992). H atoms were placed in idealized positions (dithiodisalicylic acid groups: C—H = 0.98 Å, $U_{\rm iso}$ = 0.070 Å^2; tetrahydrofuran: C—H = 0.98 Å, $U_{\rm iso}$ = 0.180 Å^2; carboxylate groups: O—H = 1.10 Å, $U_{\rm iso}$ = 0.170 Å^2). Only non-H atoms of the dithiodisalicylic acid groups were refined anisotropically.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HH1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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L-Nitroarginine Monohydrochloride Monohydrate

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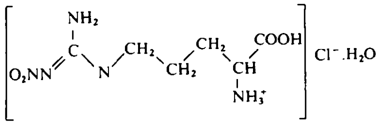
Abstract

Two conformers are present in the asymmetric unit of the title compound, $C_6H_{14}N_5O_4^+.Cl^-.H_2O$, whose conformational differences are characterized by rotations about the C^{α}—C^{β} and C^{δ}—N^{ϵ} bonds. The nitroguanidyl moieties of both conformers are nearly planar; each is involved in an intramolecular hydrogen bond between the N^{ϵ} atom and an O atom of the nitro group. Molecules are held together by a hydrogen-bond network involving the nitroguanidyl moieties, the protonated α-amino and carboxyl groups, two water molecules and two chloride ions.

Comment

L-Nitroarginine (1) is a specific and potent inhibitor of nitric oxide (NO) generation (Mülsch & Busse, 1990) which is formed by the enzymatic oxidation of L-arginine and plays a crucial role in non-adrenergic and non-cholinergic inhibitory neuromuscular transmission in certain smooth muscles (Moncada, Palmer & Higgs, 1991; Rand, 1992). For this reason, it is important to determine the precise structure of L-nitroarginine in order to clarify the relationship between its structure and function.



(1)

L-Nitroarginine crystallizes with two conformers per asymmetric unit [forms (I) and (II)]. Both conformers have extended conformations as shown in Fig. 1. The prominent conformational differences between forms (I) and (II) are characterized by two rotations; one is a rotation about the C^{α}—C^{β} bond [N(1)—C(2)—C(3)—C(4): −53 (2) for (I), 64 (1)° for (II)], and the other is about the C^{δ}—N^{ϵ} bond [C(4)—C(5)—N(2)—C(6): −91 (1) for (I), 94 (1)° for (II)]. The nitroguanidyl group adopts a nearly planar conformation [C(5)—N(2)—C(6)—N(3), N(2)—C(6)—N(4)—N(5), C(6)—N(4)—N(5)—O(4): 4 (2), −3 (1) and −5 (1)° for (I), −8 (1), 0 (1) and 7 (1)° for (II)]. The hydrocarbon part of the side chain has a *trans* conformation [C(2)—C(3)—C(4)—C(5): −171 (1) for (I), −171.1 (7)° for (II)] and is oriented almost perpendicular to the nitroguanidyl plane. Intramoleculear hydrogen bonds, N(2)—H(2)···O(4) [2.57 (1) Å] and N(2′)—H(2′)···O(4′) [2.58 (1) Å], are present in the nitroguanidyl plane. Two conformers are linked through an intermolecular hydrogen-bonding network in which the $—NH_3^+$, —COOH and $—NH_2$ groups and H_2O molecules act as proton donors, and the Cl^- ions, the O atoms of the $—NO_2$ and —COOH groups, H_2O molecules and the —N= atoms all function as proton acceptors. All H atoms of the above donor groups take part in hydrogen bonding to the proton acceptors. The details of the hydrogen-bond geometry are available as part of the supplementary material. The thermal motion of the atoms C(3) and C(4) of form (I) is quite high, resulting in the unusual C(3)—C(4) bond length and C(2)—C(3)—C(4) and C(3)—C(4)—C(5) angles as compared with the normal values of form (II).

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