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Acta Cryst. (1997). C**53**, 1975–1978

Bis(4-methoxyphenylsulfonyl)methane: a Three-Dimensional Network Generated by Short C—H···O Hydrogen Bonds

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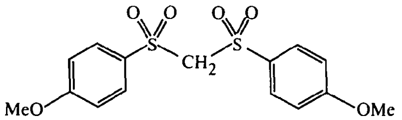
(*Received 19 May 1997; accepted 27 August 1997*)

Abstract

In the title compound, $C_{15}H_{16}O_6S_2$, each molecule utilizes CH_2, CH_3 and aromatic C—H bonds to form C—H···O hydrogen bonds to four other molecules, with C···O distances of 3.256 (4), 3.336 (4), 3.425 (3) and 3.431 (3) Å: the molecules are thereby linked into a continuous three-dimensional network.

Comment

In molecular solids which contain an excess of hard hydrogen-bond acceptors over hard hydrogen-bond donors (Braga *et al.*, 1995), it is to be expected that C—H bonds, particularly those in aromatic systems, will participate as donors in hydrogen bonds of C—H···O or C—H···N types (Hanton, Hunter & Purvis, 1992). Thus, in ferrocene-1,1′-diylbis(2-phenylethanedione), $[Fe(C_5H_4COCOPh)_2]$, which contains four carbonyl groups per molecule, but no hard hydrogen-bond donors, there is a three-dimensional network generated by short C—H···O hydrogen bonds in which C—H bonds from both the phenyl and the cyclopentadienyl groups participate (Ferguson, Glidewell, Royles & Smith, 1996): similarly, there is a two-dimensional network of C—H···N hydrogen-bonds in cyanoferrocene, $[(C_5H_5)Fe(C_5H_4CN)]$, where again there are no hard hydrogen-bond donors (Bell, Ferguson & Glidewell, 1996). We report here the structure of bis(4-methoxyphenylsulfonyl)methane, $(CH_3OC_6H_4SO_2)_2CH_2$, (I), which contains no hard hydrogen-bond donors, but even more hard hydrogen-bond acceptors per molecule than the ferrocenebisdione mentioned above: the crystal structure comprises a three-dimensional network of C—H···O hydrogen bonds, in which both methoxy and sulfonyl O atoms act as hydrogen-bond acceptors, while aromatic, methylene and methyl C atoms all act as hydrogen-bond donors.



(I)

The asymmetric unit (Fig. 1) consists of a single molecule and these molecules are connected into a continuous three-dimensional array by means of a variety of C—H···O hydrogen bonds. Both of the C—H bonds of the central methylene group act as donors, but to different types of O atom in different molecules as the corresponding acceptors. Atom C1 in the molecule at (x, y, z) acts as donor, *via* H1*A*, to the ether-type O23 atom in the molecule at $(x, 1-y, -\frac{1}{2}+z)$: the corresponding C—H bond at $(x, 1-y, \frac{1}{2}+z)$ acts as donor to O23 in the molecule at $(x, y, -1+z)$, thus giving a $C(8)$ chain (Bernstein *et al.*, 1995) running parallel to the [001] direction and generated by the action of the *c* glide plane (Fig. 2). These [001] chains are linked by a second type of C—H···O hydrogen bond into sheets parallel to the (100) plane: the methoxy carbon atom C17 at (x, y, z) acts as donor, H17*A*, to the sulfone oxygen O12 in the molecule at $(x, -y, -\frac{1}{2}+z)$, so linking two adjacent chains, and the carbon atom C17 in this latter molecule acts in turn as acceptor to O12 in the molecule at $(x, y, -1+z)$. Hence, between any pair of chains running along [001] and related by translation along [010], there are zigzag $C(9)$ cross-links generated by the methoxy···sulfone hydrogen bonds. These cross-links generate a continuous two-dimensional net built from a single type of $R^4_4(36)$ ring, which is propagated in the [010] direction by translation and in the [001] direction by the *c* glide plane (Fig. 2).

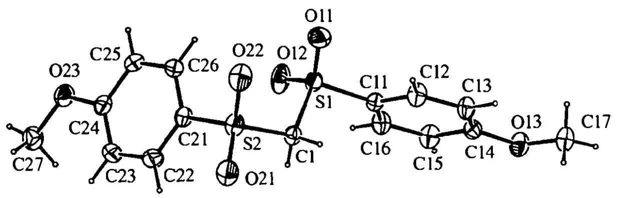


Fig. 1. A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

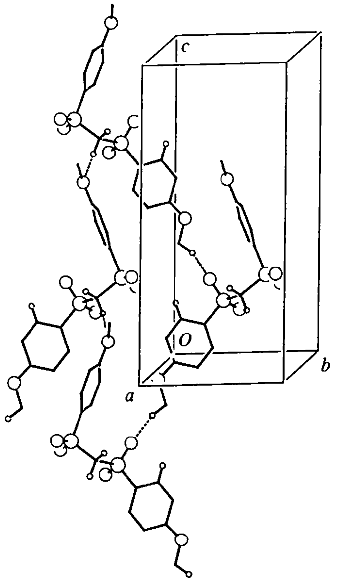


Fig. 2. A view of part of the crystal structure, showing one of the $R^4_4(36)$ rings generating the net parallel to (100).

This net utilizes just two of the eight molecules in the unit cell, so that there are four such nets in the structure. It is the linking of the two-dimensional nets by further types of C—H···O hydrogen bond which generates the three-dimensional network. The methylene carbon atom C1 in the molecule at (x, y, z) acts as donor, *via* H1*B* (*cf.* the involvement of H1*A* described above), to the sulfone oxygen atom O21 in the molecule at ($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$). This hydrogen bond and its symmetry-related equivalents link together pairs of [001] chains into ladders by means of centrosymmetric $R^4_4(20)$ motifs (Fig. 3), so utilizing four of the molecules in the unit cell: these ladders are then linked into a continuous two-dimensional network parallel to (010) and utilizing all the molecules in the cell, by means of further C—H···O hydrogen bonds formed by aromatic C—H bonds. Atom C25 in the molecule at (x, y, z) acts as donor to the sulfone oxygen atom O11 at ($-x$, y, $\frac{1}{2}-z$), so generating an $R^2_2(16)$ motif around the twofold axis at (0, y, $\frac{1}{4}$): the molecule at ($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$) is similarly linked to that at ($\frac{1}{2}+x$, $\frac{1}{2}+y$, z) forming another $R^2_2(16)$ motif around the twofold axis at ($\frac{1}{2}$, y, $\frac{1}{4}$) (Fig. 3). Thus, there are two-dimensional nets parallel to both (100) and (010) which together form a continuous three-dimensional array encompassing all the molecules in the structure. Repetition of the C1—H1*B*···O21^{ii} [symmetry code: (ii) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$] hydrogen bond generates a *C*(4) chain running parallel to the [010] direction, which also serves to tie the (010) nets together.

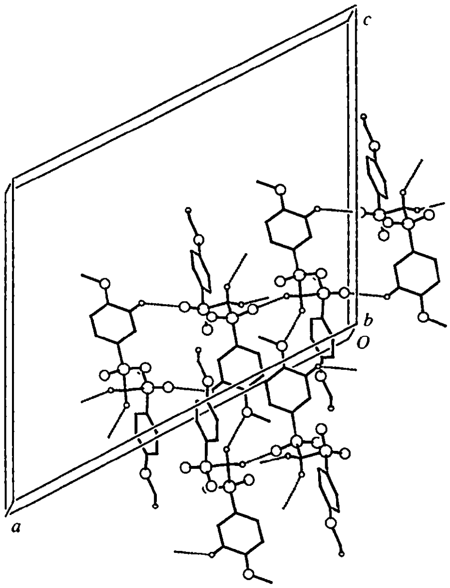


Fig. 3. A view of part of the crystal structure, showing the $R^4_4(20)$ and $R^2_2(16)$ rings forming the net parallel to (010).

It is appropriate to compare the three-dimensional intermolecular aggregation in (I) with the one-dimensional aggregation in the simpler analogue $(PhSO_2)_2CH_2$: this was not discussed in the original structure report (Glidewell, Lightfoot & Patterson, 1995), but it again depends solely upon C—H···O hydrogen bonds. In $(PhSO_2)_2CH_2$, one of the central C—H bonds and a neighbouring aromatic C—H bond in the molecule at (x, y, z) both act as donors to the same sulfone O atom in the molecule at ($-1+x$, y, z), forming *C*(4) and *C*(7) chains parallel to [100] as well as $R^1_2(7)$ rings, which combine to yield a $C(4)C(7)[R^1_2(7)]$ chain-of-rings (Bernstein *et al.*, 1995). The other central C—H bonds in the molecule at (x, y, z) acts as donor to a sulfone O atom at ($1-x$, $-y$, $1-z$), so forming a centrosymmetric $R^2_2(8)$ ring: the $R^2_2(8)$ rings act as the rungs of a ladder whose uprights are pairs of the [100] chains. There are two such ladders running through the unit cell, related by the *n* glide plane.

The conformation of compound (I), with S1 *trans* to O21 and S2 *trans* to C11 (Table 2) is very similar to the conformations observed previously in the related bis-sulfones $(PhSO_2)_2CH_2$, $(PhSO_2)_2CBr_2$ and $(PhSO_2)_2CI_2$ (Glidewell, Lightfoot & Patterson, 1995; Glidewell *et al.*, 1996). The central C—S distances in (I) are very similar to the value in $(PhSO_2)_2CH_2$, 1.786 Å: the corresponding distances in $(PhSO_2)_2CBr_2$ and $(PhSO_2)_2CI_2$ are much longer, mean values 1.863 and 1.854 Å, respectively. The C—O—C angles are both significantly greater than tetrahedral and the methyl C atoms lie almost in the plane of the adjacent ring, with the exocyclic O—C—C angles *cisoid* to the methoxy substituents much larger than 120° and those *transoid* much smaller: similar features were also observed in tris(4-methoxyphenyl)methanol (Ferguson, Glidewell & Patterson, 1996). The remaining bond lengths and angles are typical of those found previously in bis-sulfones of this type (Glidewell, Lightfoot & Patterson, 1995; Glidewell *et al.*, 1996).

Experimental

Compound (I) was prepared from 4-methoxybenzenethiol according to published procedures (Shriner, Struck & Jorison, 1930; Kohler & Tishler, 1935). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in methanol.

Crystal data

$C_{15}H_{16}O_6S_2$
$M_r = 356.40$
Monoclinic
$C2/c$
$a = 22.995\,(6)$ Å
$b = 8.0989\,(8)$ Å
$c = 19.225\,(4)$ Å
$\beta = 117.76\,(2)°$
$V = 3168.5\,(11)$ Å^3
$Z = 8$
$D_x = 1.494$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.90–17.43°$
$\mu = 0.364$ mm^{-1}
$T = 294\,(1)$ K
Plate
$0.42 \times 0.28 \times 0.19$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3957 measured reflections
3627 independent reflections
2267 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.007$

$\theta_{\rm max} = 27.39°$
$h = -29 \rightarrow 26$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity decay: no decay, variation 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0401$
$wR(F^2) = 0.0942$
$S = 1.170$
3627 reflections
208 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.000$
$\Delta\rho_{\rm max} = 0.272$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.238$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—O11	1.416 (2)	S2—C1	1.798 (2)
S1—O12	1.425 (2)	S2—C21	1.756 (2)
S1—C1	1.791 (2)	O13—C14	1.354 (3)
S1—C11	1.753 (2)	O13—C17	1.424 (3)
S2—O21	1.441 (2)	O23—C24	1.356 (3)
S2—O22	1.430 (2)	O23—C27	1.432 (3)
O11—S1—O12	119.81 (12)	O22—S2—C21	108.84 (11)
O11—S1—C11	108.76 (11)	C1—S2—C21	107.34 (10)
O11—S1—C1	107.46 (12)	C14—O13—C17	118.2 (2)
O12—S1—C1	107.44 (11)	C24—O23—C27	118.3 (2)
O12—S1—C11	108.83 (11)	S1—C1—S2	116.50 (12)
C11—S1—C1	103.30 (10)	O13—C14—C13	124.2 (2)
O21—S2—O22	118.96 (12)	O13—C14—C15	115.7 (2)
O21—S2—C21	108.90 (11)	O23—C24—C23	124.5 (2)
O21—S2—C1	103.74 (11)	O23—C24—C25	115.6 (2)
O22—S2—C1	108.44 (11)		
O11—S1—C1—S2	56.1 (2)	C21—S2—C1—S1	64.9 (2)
O12—S1—C1—S2	−74.1 (2)	O12—S1—C11—C16	−14.0 (2)
C11—S1—C1—S2	170.95 (13)	C17—O13—C14—C13	0.3 (3)
O22—S2—C1—S1	−52.5 (2)	O21—S2—C21—C22	−14.8 (2)
O21—S2—C1—S1	−179.88 (13)	C27—O23—C24—C23	−4.1 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···O23$^{\rm i}$	0.97	2.58	3.431 (3)	146
C1—H1B···O21$^{\rm ii}$	0.97	2.49	3.425 (3)	161
C17—H17A···O12$^{\rm iii}$	0.96	2.50	3.336 (4)	145
C25—H25···O11$^{\rm iv}$	0.93	2.55	3.256 (4)	133

Symmetry codes: (i) $x, 1-y, z-\frac{1}{2}$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x, -y, z-\frac{1}{2}$; (iv) $-x, y, \frac{1}{2}-z$.

Compound (I) crystallized in the monoclinic system, space group $C2/c$. H atoms were treated as riding atoms (C—H 0.93–0.97 Å) and methyl groups were permitted to rotate but not to tilt.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4 *Software* . Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*96. Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1996*a*) and *PLUTON* (Spek 1996*b*). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*93 and *WordPerfect* macro *PRPCIF*97 (Ferguson, 1997).

GF thanks NSERC (Canada) for Research Grants; RMG thanks EPSRC (UK) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1232). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1978–1980

Pairwise-Interwoven $R^6_6(48)$ Hexagonal Nets in the Hydrogen-Bonded Structure of Hexamethylenetetramine–1,1,1-Tris(4-hydroxyphenyl)ethane (1/1)

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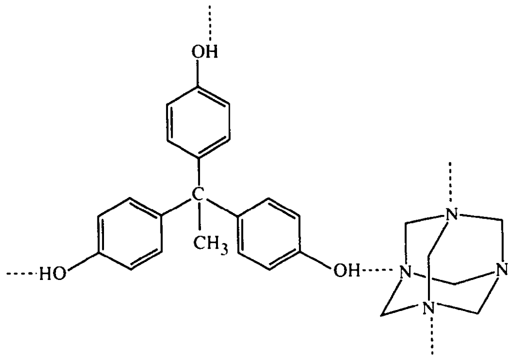
(Received 30 April 1997; accepted 5 August 1997)

Abstract

In the 1:1 adduct formed by hexamethylenetetramine (HMTA) and 1,1,1-tris(4-hydroxyphenyl)ethane, $C_6H_{12}N_4.C_{20}H_{18}O_3$, the tris-phenol acts as a triple donor of hydrogen bonds of type O—H···N and the HMTA as a triple acceptor of such hydrogen bonds, with O···N distances of 2.777 (4), 2.781 (4) and 2.795 (4) Å. The components are assembled into infinite nets comprising hexagonal rings, and pairs of such nets are interwoven; the pairs of interwoven nets are, in addition, connected by C—H···O hydrogen bonds with a C···O distance of 3.339 (5) Å.

Comment

In hydrogen-bonded adducts with aromatic hydroxy compounds, hexamethylenetetramine [HMTA, $(CH_2)_6N_4$] generally acts as a bis-acceptor of hydrogen bonds (Mak *et al.*, 1977; Mak, Yu & Lam, 1978; Mahmoud & Wallwork, 1979; Coupar, Glidewell & Ferguson, 1997). The only recorded example in which HMTA is observed to act as a tris-acceptor of hydrogen bonds is the complex with phenol, HMTA.(phenol)$_3$, where the ordered molecular aggregates lie on threefold rotation axes (Jordan & Mak, 1970). However, this precedent indicates that with an appropriate tris-phenol acting as a tris-donor of hydrogen bonds, it should be possible to design and construct a hydrogen-bonded system in which each component, HMTA and the tris-phenol, takes part in three hydrogen bonds, thereby generating a continuous molecular network. It can be estimated that a structure built from just one such network of hexagonal rings would have a density of around 0.35 Mg m^{-3}, so that based on the typical densities of adducts of this general type, the presence of four independent networks is to be expected, with the possibility of interweaving. The phase behaviour of the binary system HMTA/1,1,1-tris(4-hydroxyphenyl)ethane is complex, and homogeneous phases with HMTA to tris-phenol ratios of 2:1, 3:2 and 1:1 can all be crystallized from solutions in ethanol or propanol (Coupar, Glidewell & Ferguson, 1997). We report here the structure of the 1:1 adduct, (I), which indeed proves to contain HMTA acting as a tris-acceptor of hydrogen bonds in a continuous network structure.



(I)

The structure analysis (Figs. 1 and 2) confirms not only the 1:1 ratio of the two components deduced from microanalytical data (Coupar, Glidewell & Ferguson, 1997), but also the presence of four independent networks built from hexagonal rings. The two components are connected by O—H···N hydrogen bonds, with the tris-phenol acting as a triple donor of hydrogen bonds and the HMTA acting as a triple acceptor. There are no O—H···O hydrogen bonds, although such interactions are found in the adducts of 1,1,1-tris(4-hydroxyphenyl)ethane with both 1,4-diazabicyclo[2.2.2]octane

ISSN 0108-2701