Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry for (1) and (2), and least-squares-planes data for (1) have been deposited with the IUCr (Reference: CR1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Etension and Refinement of Difference Structure Factors.* Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6425 ED Nijmegen, The Netherlands.

Enas, J. D., Garcia, J. G., Mathis, C. A. & Gerdes, J. M. (1993). *J. Fluor. Chem.* **63**, 233–241.

Fair, C. K. (1990). *MolEN. An Interactive Structure Solution Procedure.* Enraf–Nonius, Delft, The Netherlands.

Garcia, J. G., Enas, J. D., Chang, E. & Fronczek, F. R. (1993). *Acta Cryst.* C**49**, 1401–1402.

Garcia, J. G., Enas, J. D. & Fronczek, F. R. (1993). *Acta Cryst.* C**49**, 1823–1824.

Garcia, J. G., Enas, J. D. & Fronczek, F. R. (1994). *Acta Cryst.* C**50**, 1141–1143.

Garcia, J. G., Enas, J. D. & Fronczek, F. R. (1995). *Acta Cryst.* In the press.

Garcia, J. G., Enas, J. D., VanBrocklin, H. F. & Fronczek, F. R. (1995). *Acta Cryst.* Submitted.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program from Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Quere, J.-P. & Marėchal, E. (1971). *Bull. Soc. Chim. Fr.* **8**, 2983–2989.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

VanBrocklin, H. F., Enas, J. D., Garcia, J. G. & Hanrahan, S. M. (1993). X^th International Symposium on Radiopharmaceutical Chemistry, Kyoto, Japan.

Yao, J.-X. (1981). *Acta Cryst.* A**37**, 642–644.

Acta Cryst. (1995). C**51**, 304–306

cis,trans-3,3′-Sulfinylbis(acrylic acid)

Thomas R. Webb, Zwei-Chang Ho and
Peter Livant

Department of Chemistry, Auburn University, Auburn, AL 36849-5312, USA

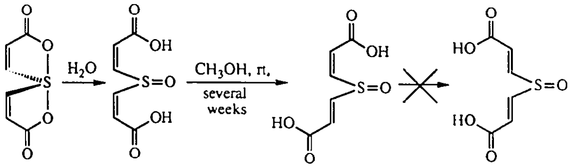
(*Received* 11 *January* 1994; *accepted* 19 *May* 1994)

Abstract

The title compound, (*E*,*Z*)-4-thia-2,5-heptadienedioic acid 4-oxide, ($C_6H_6O_5S$), exhibits an atypical hydrogen-bonding network in which normal carboxylic acid dimers are not observed; one carbonyl O atom is omitted from the scheme. The C—S—C angle [94.9 (1)°] is unusually compressed and the S—O bond [1.504 (2) Å] is somewhat lengthened.

Comment

In the course of the synthesis and study of the divinyl sulfurane (1), proof of the structure of its hydrolysis product (2) was sought. Much to our surprise, slow evaporation of a methanol solution of (2) afforded crystals of (3) rather than (2) (Ho, 1993). The product of isomerization of both *cis* double bonds of (2), namely (4), was not detected, even after prolonged reaction time. Thus (3) is thermodynamically more stable than (2) or (4). The structure of (3) is reported herein.



(1) (2) (3) (4)

The hydrogen-bonding network is interesting (Fig. 2). The sulfoxide diacid contains two hydrogen-bond donor sites (the OH's) but three hydrogen-bond acceptor sites (two carbonyl and one sulfinyl O atom). In this case, one hydrogen-bond acceptor, the carbonyl O atom of the *cis* acrylic acid moiety (O4), is simply excluded from the hydrogen-bonding scheme. The usual model of carboxylic acid dimerization is not in evidence nor is any intramolecular hydrogen bond. Instead, there is a centrosymmetric dimer formed by two hydrogen bonds (*a* in Fig. 2) between the *trans* acrylic acid carbonyl (O2) and the *cis* acrylic acid hydroxyl (O5). This dimer is in turn bound by hydrogen bonds (*b* in Fig. 2), involving the sulfinyl O atom (O1) and the *trans* acrylic acid hydroxyl (O3), to a dimer in the adjacent unit cell arrived at by a translation along *c*. The relevant intermolecular contacts are O2···O5($-x$, $1-y$, $1-z$) 2.683 (4) and O1···O3(x, y, $1+z$) 2.617 (4) Å. The length of the non-hydrogen-bonded carbonyl bond is 0.008 Å shorter than that of the hydrogen-bonded carbonyl. The presence of two non-equivalent carbonyls explains the IR spectrum of (3) (KBr) which shows a broad absorption of 1665 cm^{-1}, typical of α,β-unsaturated acids, and a sharp peak at 1709 cm^{-1} which may be assigned to the non-hydrogen-bonded carbonyl. This novel solution of the problem of one too many hydrogen-bond acceptors is reminiscent of the unusual hydrogen bonding observed in glycolic acid HOOC—CH_2OH, which forms a closed loop of six molecules (Ellison, Johnson & Levy, 1971; Pijper, 1971).

The S—O bond [1.504 (2) Å] is slightly longer than expected [*cf.* $(CH_3)_2SO$ 1.485 (6) Å (Typke, 1978), 1.471 Å (Viswamitra & Kannan, 1966) or 1.485 Å (Feder, Dreizler, Rudolph & Typke, 1969), and Ph_2SO 1.489 (5) Å (Rozsondai, Moore, Gregory & Hargittai, 1979)]. This is probably due to the involvement of the sulfinyl O atom in hydrogen bonding to the O3 hydroxyl. The S—O bond is, however, considerably shorter than both the O-bonded DMSO–metal complex S—O bonds (Kisenyi, Willey & Drew, 1985; Guy, Cooper, Gilardi, Flippen-Anderson & George, 1988; Alessio, Balducci, Calligaris, Costa, Attia & Mestroni, 1991) and the S—O bonds of the hydrogen-bonded cation $[(CH_3)_2SO\cdots H\cdots OS(CH_3)_2]^+$ [1.528 (4) and 1.536 (3) Å (Alessio, Balducci, Calligaris, Costa, Attia & Mestroni, 1991)].

Other structural features of (3) are normal except for C1—S—C4 which is smaller than usual [*cf.* 96.9 (3)° in *p*-bromobenzyl *o*-carbomethoxyphenyl sulfoxide (Koziol, Majewski, Janczewski, 1985) and 96.7 (3)° in 2-phenylsulfinyl-4-carbomethoxycyclohexanone 2,2-dimethylpropyl ketal (Soriano-Garcia, Toscano, García, Larvaza & Sánchez, 1984)].

The possibility of a higher-symmetry space group is suggested by the closeness of β [90.07 (2)°] to 90°. However, axial photographs showed mirror symmetry about one axis only, systematic absences were consistent with $P2_1/n$ but not with any orthorhombic space group and structure factors of reflections which would be equivalent in orthorhombic symmetry were not in fact equivalent.

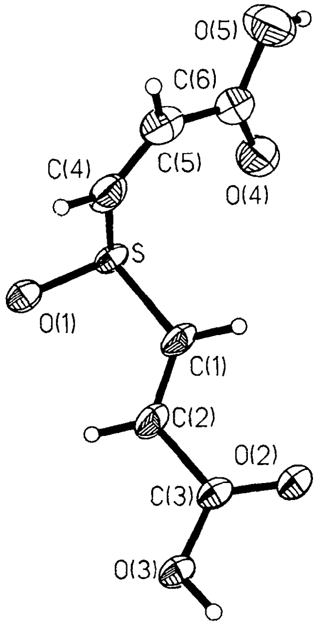


Fig. 1. *ORTEP* (Johnson, 1965) view of (3). Displacement ellipsoids are drawn at the 50% probability level.

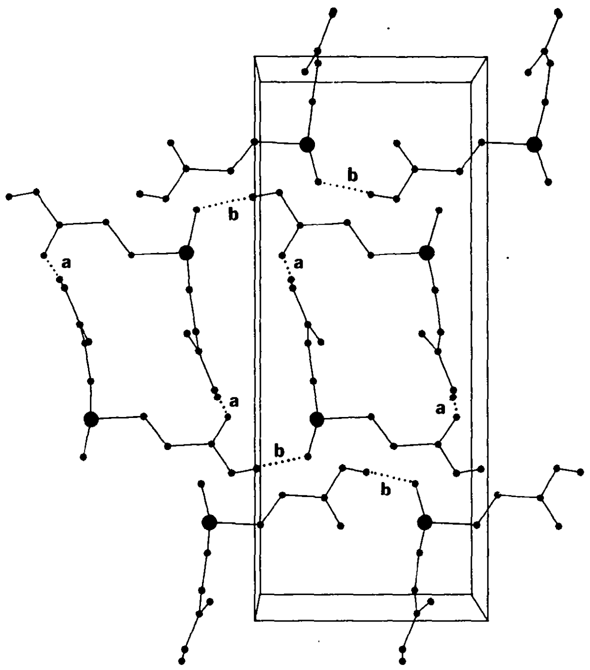


Fig. 2. View down the *a* axis, showing intermolecular hydrogen bonds (dotted lines). S atoms are represented by large filled circles. Only H atoms involved in hydrogen bonds are shown.

Experimental

Crystal data

$C_6H_6O_5S$
$M_r = 190.2$
Monoclinic
$P2_1/n$
$a = 5.782$ (2) Å
$b = 18.164$ (5) Å
$c = 7.531$ (2) Å
$\beta = 90.07$ (2)°
$V = 791.0$ (4) Å^3
$Z = 4$
$D_x = 1.597$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 4$–$10°$
$\mu = 0.370$ mm^{-1}
$T = 294$ K
Clear plate
0.20 × 0.10 × 0.01 mm
Colorless

Data collection

Nicolet Siemens *R3m/V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.595$, $T_{\max} = 1.000$
3099 measured reflections
1400 independent reflections
1192 observed reflections $[F_o > 4\sigma(F_o)]$

$R_{\rm int} = 0.0749$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 6$
$k = -21 \rightarrow 21$
$l = -8 \rightarrow 8$
2 standard reflections monitored every 100 reflections intensity decay: <2% from mean

Refinement

Refinement on F
$R = 0.0534$
$wR = 0.0649$

$(\Delta/\sigma)_{\max} = 0.044$
$\Delta\rho_{\max} = 0.62$ e Å^{-3}
$\Delta\rho_{\min} = -0.55$ e Å^{-3}

$S = 1.44$
1192 reflections
109 parameters
Riding model, fixed isotropic U for H atoms
$w = 1/[\sigma^2(F) + 0.0008F^2]$

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
S	0.2685 (1)	0.3526 (1)	0.7264 (1)	0.032 (1)
O1	0.3847 (4)	0.2809 (1)	0.7717 (3)	0.040 (1)
C1	0.2587 (5)	0.3571 (2)	0.4925 (4)	0.032 (1)
C2	0.3218 (5)	0.3016 (2)	0.3919 (4)	0.034 (1)
C3	0.2953 (5)	0.3064 (2)	0.1965 (4)	0.032 (1)
O2	0.1999 (4)	0.3570 (1)	0.1212 (3)	0.040 (1)
O3	0.3870 (4)	0.2510 (1)	0.1117 (3)	0.044 (1)
C4	0.4940 (5)	0.4193 (2)	0.7489 (4)	0.038 (1)
C5	0.4642 (5)	0.4900 (2)	0.7733 (4)	0.042 (1)
C6	0.2316 (5)	0.5234 (2)	0.7727 (4)	0.042 (1)
O4	0.0623 (4)	0.4927 (1)	0.7156 (4)	0.055 (1)
O5	0.2306 (4)	0.5904 (1)	0.8383 (5)	0.063 (1)

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

S—O1	1.504 (2)	C5—C6	1.475 (4)
S—C1	1.764 (3)	C3—O2	1.213 (3)
S—C4	1.788 (3)	C6—O4	1.205 (4)
C1—C2	1.312 (4)	C3—O3	1.304 (4)
C4—C5	1.309 (4)	C6—O5	1.315 (4)
C2—C3	1.482 (4)		
O1—S—C1	106.3 (1)	O1—S—C4	103.8 (1)
S—C1—C2	122.2 (2)	S—C4—C5	125.6 (2)
C1—C2—C3	120.0 (3)	C4—C5—C6	121.5 (3)
C2—C3—O2	123.7 (3)	C5—C6—O4	123.5 (3)
C2—C3—O3	113.6 (2)	C5—C6—O5	112.6 (3)
O2—C3—O3	122.7 (3)	O4—C6—O5	123.9 (3)
C1—S—C4	94.9 (1)		

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Alessio, E., Balducci, G., Calligaris, M., Costa, G., Attia, W. M. & Mestroni, G. (1991). *Inorg. Chem.* **30**, 609–618.
Ellison, R. D., Johnson, C. K. & Levy, H. A. (1971). *Acta Cryst.* B**27**, 333–344.
Feder, W., Dreizler, H., Rudolph, H. D. & Typke, V. (1969). *Z. Naturforsch. Teil A*, **24**, 266–278.
Guy, J. T. Jr, Cooper, J. C., Gilardi, R. D., Flippen-Anderson, J. L. & George, C. F. Jr (1988). *Inorg. Chem.* **27**, 635–638.
Ho, Z.-C. (1993). PhD thesis, Auburn Univ., Alabama, USA.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Kisenyi, J. M., Willey, G. R. & Drew, M. G. B. (1985). *Acta Cryst.* C**41**, 700–702.
Koziol, A. E., Majewski, W. & Janczewski, M. (1985). *Acta Cryst.* C**41**, 144–146.
Pijper, W. P. (1971). *Acta Cryst.* B**27**, 344–348.
Rozsondai, B., Moore, J. H., Gregory, D. C. & Hargittai, I. (1979). *J. Mol. Struct.* **51**, 69–76.
Soriano-Garcia, M., Toscano, R. A., García, G., Larvaza, M. I. & Sánchez, I. H. (1984). *Acta Cryst.* C**40**, 887–889.
Typke, V. (1978). *Z. Naturforsh. Teil A*, **33**, 842–847.
Viswamitra, M. A. & Kannan, K. K. (1966). *Nature (London)*, **209**, 1016–1017.

Acta Cryst. (1995). C**51**, 306–308

Decahydro-6,6-dimethoxy-1,2,2,4-tetramethylquinolinium Picrate

O. Kasemann and P. Stanetty

Institute for Organic Chemistry,
Technical University of Vienna, A-1060 Vienna, Austria

K. Mereiter*

Institute for Mineralogy,
Crystallography and Structural Chemistry,
Technical University of Vienna, A-1060 Vienna, Austria

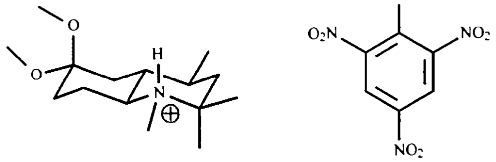
(*Received* 20 *May* 1993; *accepted* 17 *June* 1994)

Abstract

The crystal structure of the title compound, $C_{15}H_{30}NO_2^+.C_6H_2N_3O_7^-$, was determined in order to ascertain the stereochemistry of the decahydroquinoline moiety. It was found to show a normal chair–chair conformation with the 1- and 4-methyl groups in equatorial positions.

Comment

During the course of a project aimed at the development of new fungicidal compounds (Kasemann, 1993), the title compound (1) was synthesized by Birch reduction of 6-ethoxy-1,2,3,4-tetrahydro-1,2,2,4-tetramethylquinoline (Aldrich, Germany) followed by NaCNBH$_3$ reduction of the enamine moiety and subsequent conversion of the enol ether to the dimethyl ketal. As the quinoline base did not crystallize well, it was converted to the picrate, which crystallized from ethanol, after prolonged standing, as large yellow blocks.



(1)

Acta Crystallographica Section C
ISSN 0108-2701 ©1995