C13—C9—O10	107.0 (2)	107.6 (2)
C9—O10—N11	114.7 (2)	114.9 (1)
O10—N11—C12	118.0 (1)	117.7 (1)
N11—C12—N1	125.4 (2)	125.5 (2)
C12—N1—C13	114.7 (2)	115.5 (1)

Table 3. *Torsion angles (°) and distances (Å) to the plane fragments*

	(III)	(IV)
O5—N4—C3—N2	−2.9 (3)	−2.5 (2)
C13—N1—C12—N11	−1.7 (3)	−4.3 (3)
C6—C7—C8—C9	−2.0 (4)	−3.6 (4)
C7—C8—C9—C13	−3.2 (3)	−3.3 (3)

		Distance of atom to plane	
Fragment	Atom	(III)	(IV)
N2—C3—N4—O5	C6	−0.391 (2)	−0.405 (2)
C13—N1—C12—N11	C9	−0.866 (2)	−0.884 (2)
C13—N1—C12—N11	O10	−0.257 (2)	−0.287 (1)
C6—C7—C8—C9—C13	N1	1.111 (2)	1.117 (2)
C6—C7—C8—C9—C13	N2	0.855 (2)	0.885 (2)

Structure solution was completed by Fourier synthesis. H atoms were introduced at idealized positions in the calculations before the last refinement cycle but not refined. Refinement was by full-matrix least-squares methods including anisotropic displacement parameters for all non-H atoms. Despite the large differences in cell parameters [*e.g.* b = 8.748 (3) in (III) and 9.908 (3) Å in (IV)], the two crystals are isostructural and the crystal structure of (IV) was obtained directly from the coordinates of (III) refined with the X-ray intensities measured on the crystal of (IV).

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structures: *MULTAN*11/82 (Main *et al.*, 1982); program(s) used to refine structures: *SDP-Plus* (Frenz, 1985); molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1199). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Baouid, A., Benharref, A., Hasnaoui, A. & Lavergne, J. P. (1994). *Bull. Soc. Chim. Belg.* **103**, 743–751.

El Messaoudi, M., Hasnaoui, A., El Mouhtadi, M. & Lavergne, J. P. (1992). *Bull. Soc. Chim. Belg.* **101**, 977–985.

El Messaoudi, M., Hasnaoui, A., El Mouhtadi, M., Goupil, J. M. & Lavergne, J. P. (1988). *J. Heterocycl. Chem.* **25**, 453–457.

El Messaoudi, M., Hasnaoui, A. & Lavergne, J. P. (1994). *Synth. Commun.* **24**, 513–520.

El Messaoudi, M., Hasnaoui, A., Lavergne, J. P. & Pierrot, M. (1995). *Synth. Commun.* In the press.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Hasnaoui, A., Baouid, A. & Lavergne, J. P. (1991). *J. Heterocycl. Chem.* **28**, 73–76.

Hasnaoui, A., El Messaoudi, M. & Lavergne, J. P. (1985). *Recl Trav. Chim. Pays-Bas*, **104**, 129–131.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England, and Louvain, Belgium.

Acta Cryst. (1996). C**52**, 739–743

cis,trans-4,5-Diphenyl-1,3,2-dioxathiolane 2-Oxide, *cis,cis*-4,5-Diphenyl-1,3,2-dioxathiolane 2-Oxide and 4,4-Diphenyl-1,3,2-dioxathiolane 2-Oxide

DESMOND G. HELLIER* AND MAJID MOTEVALLI

Chemistry Department, Queen Mary and Westfield College, Mile End Road, London E1 4NS, England

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Abstract

All three title compounds, $C_{14}H_{12}O_3S$, adopt half-chair (envelope) conformations with the S=O group and the phenyl groups in pseudoaxial and pseudoequatorial positions, respectively. The steric effects of the phenyl groups are discussed in terms of S—O/C—O bond lengths and ring torsion angles.

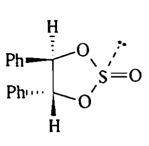
Comment

The conformational analyses of methyl- and phenyl-1,3,2-dioxathiolane 2-oxides (methyl- and phenylethylene sulfites) have been thoroughly investigated by IR and ^{1}H and ^{13}C NMR solution studies (Hellier & Green, 1973*a*,*b*). It was concluded that rapid interconversion between various envelope forms is possible but is restricted to that involving rotation about the C—C bond. Complete pseudorotatory circuits around the ring are prevented by the relatively high potential barrier imposed by the sulfite group.

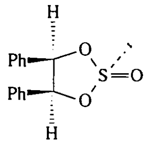
The crystal structure determinations of *trans*-4(*S*)-phenyl-1,3,2-dioxathiolane 2-oxide, (IV), and *trans,trans*-4,5-diphenyl-1,3,2-dioxathiolane 2-oxide, (V), have been reported previously (Lowe, Jones & Salamone, 1984) and fully confirm the half-chair conformation of these compounds.

In view of our interest in cyclic sulfites and the fact that neither the molecular structures of five-membered ring sulfites nor the effect of substituent groups have yet been studied in detail, we decided to investigate the structures of *cis,trans*-4,5-diphenyl-1,3,2-dioxathiolane 2-oxide, (I), *cis,cis*-4,5-diphenyl-1,3,2-dioxathiolane 2-

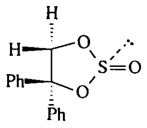
oxide, (II), and 4,4-diphenyl-1,3,2-dioxathiolane 2-oxide, (III). This paper reports the single-crystal X-ray data for these three title compounds.



(I)



(II)



(III)

PLUTON (Spek, 1993) drawings of the molecular structures of compounds (I), (II) and (II) are shown in Figs. 1 to 3, respectively. The summarization of data in Table 2 shows several points of interest. For instance, the S=O bond lengths are shorter (average 1.433 Å) than those found in comparable six-membered ring sulfites, typically 1.445 Å. The S—O bond lengths show only minor variation within the range 1.612–1.620 Å; these values do not appear to be dependent on the orientation of phenyl groups. The C—O bond lengths are considerably longer than the normally accepted values found in ethers and alcohols (1.43–1.44 Å). Similar elongations have been observed in other anomeric (1,3-dioxo-) systems, *e.g* acetals (Lenstra & van de Mieroop, 1978) and phosphates (Geise, Lenstra & van Nuffel, 1982).

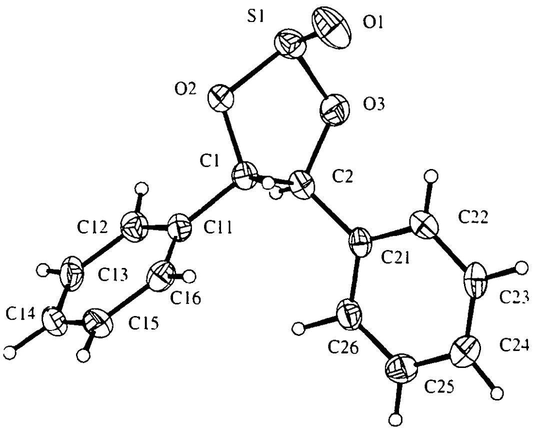


Fig. 1. View of compound (I) showing the atom-numbering scheme and displacement ellipsoids plotted at the 30% probability level.

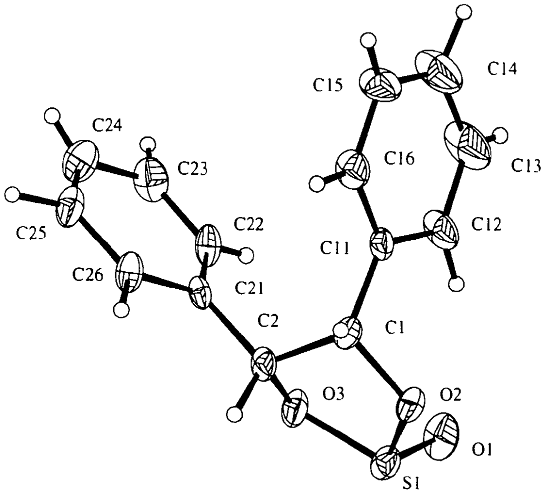


Fig. 2. View of compound (II) showing the atom-numbering scheme and displacement ellipsoids plotted at the 30% probability level.

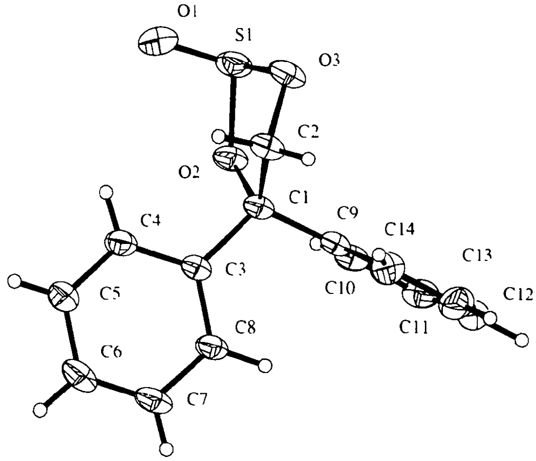


Fig. 3. View of compound (III) showing the atom-numbering scheme and displacement ellipsoids plotted at the 30% probability level.

All three title sulfites give very similar average ring valency angles of *ca* 105°. Additionally, the sum of angles around the S atom for compounds (I) and (III) of *ca* 309° appears to be typical, but the *cis,cis* isomer (II) gives a smaller value of *ca* 308°, presumably due to the particular steric effect of the geminal phenyl groups. As expected from the different substitution patterns, the ring torsion angles around C1—C2 show some, but only slight, variation (31.73–33.97°). These values may be compared with that of 1,3,2-dioxathiolane 2-oxide (ethylene sulfite), reported to have a value of 44° (Hellier & Green, 1975). The latter value reveals evidence of the intramolecular stress which results from accommodating phenyl groups on C1 and C2. Finally, interaction between the phenyl groups is potentially greatest in compound (III), but is minimized by a virtual right angle between the phenyl groups of 85.37°.

Experimental

The title compounds (I), (II) and (III) have been previously prepared and characterized (Hellier & Green, 1975).

Compound (I)

Crystal data

$C_{14}H_{12}O_3S$
$M_r = 260.30$
Orthorhombic
$P2_12_12_1$
$a = 5.8090\,(10)$ Å
$b = 15.514\,(3)$ Å
$c = 13.883\,(2)$ Å
$V = 1251.1\,(4)$ Å^3
$Z = 4$
$D_x = 1.382$ Mg m^{-3}
$D_m = 1.40$ Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12\text{–}15°$
$\mu = 0.255$ mm^{-1}
$T = 293\,(2)$ K
Transparent rhomb
$0.35 \times 0.30 \times 0.25$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.872$, $T_{\max} = 0.973$
1334 measured reflections
1303 independent reflections
827 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0116$
$\theta_{\max} = 24.97°$
$h = 0 \rightarrow 6$
$k = -7 \rightarrow 18$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0286$
$wR(F^2) = 0.0820$
$S = 0.921$
1303 reflections
211 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.161$ e Å^{-3}
$\Delta\rho_{\min} = -0.171$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter $= -0.06\,(15)$

Compound (II)

Crystal data

$C_{14}H_{12}O_3S$
$M_r = 260.30$
Triclinic
$P\bar{1}$
$a = 6.4560\,(10)$ Å
$b = 7.8080\,(10)$ Å
$c = 12.636\,(2)$ Å
$\alpha = 93.860\,(10)°$
$\beta = 98.970\,(10)°$
$\gamma = 98.810\,(10)°$
$V = 619.0\,(2)$ Å^3
$Z = 2$
$D_x = 1.396$ Mg m^{-3}
$D_m = 1.4$ Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10\text{–}14°$
$\mu = 0.258$ mm^{-1}
$T = 293\,(2)$ K
Transparent rhomb
$0.40 \times 0.35 \times 0.25$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.960$, $T_{\max} = 0.988$
2436 measured reflections
2178 independent reflections
867 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0554$
$\theta_{\max} = 25.06°$
$h = -1 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0633$
$wR(F^2) = 0.1767$
$S = 0.862$
2178 reflections
212 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1019P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.370$ e Å^{-3}
$\Delta\rho_{\min} = -0.504$ e Å^{-3}
Extinction correction: $F_c^* = kF_c/[1 + (0.001\chi \times F_c^2\lambda^3/\sin 2\theta)]^{1/4}$
Extinction coefficient: $\chi = 0.084\,(11)$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Compound (III)

Crystal data

$C_{14}H_{12}O_3S$
$M_r = 260.30$
Monoclinic
$P2_1/a$
$a = 8.7480\,(10)$ Å
$b = 17.697\,(2)$ Å
$c = 8.4180\,(10)$ Å
$\beta = 109.01\,(3)°$
$V = 1232.1\,(2)$ Å^3
$Z = 4$
$D_x = 1.403$ Mg m^{-3}
$D_m = 1.45$ Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12\text{–}15°$
$\mu = 0.259$ mm^{-1}
$T = 293\,(2)$ K
Transparent rhombic
$0.3 \times 0.3 \times 0.2$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.956$, $T_{\max} = 0.976$
2356 measured reflections
2159 independent reflections
1592 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0174$
$\theta_{\max} = 24.97°$
$h = -2 \rightarrow 10$
$k = 0 \rightarrow 21$
$l = -9 \rightarrow 9$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0357$
$wR(F^2) = 0.1284$
$S = 1.017$
2159 reflections
211 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.359$
$\Delta\rho_{\max} = 0.178$ e Å^{-3}
$\Delta\rho_{\min} = -0.310$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	*y*	*z*	$U_{\rm eq}$
Compound (I)				
S1	−0.9005 (2)	−0.19149 (6)	−0.92148 (7)	0.0539 (3)
O1	−0.6680 (5)	−0.2081 (2)	−0.8940 (2)	0.0810 (10)
O2	−0.9907 (5)	−0.10732 (14)	−0.8640 (2)	0.0509 (7)
O3	−1.0580 (5)	−0.25733 (15)	−0.8604 (2)	0.0601 (8)
C1	−1.0555 (7)	−0.1303 (2)	−0.7659 (2)	0.0409 (9)
C2	−1.1718 (7)	−0.2182 (2)	−0.7778 (3)	0.0454 (9)
C11	−1.2053 (7)	−0.0607 (2)	−0.7250 (2)	0.0381 (9)
C12	−1.4091 (7)	−0.0387 (2)	−0.7709 (3)	0.0472 (9)
C13	−1.5483 (8)	0.0258 (2)	−0.7344 (3)	0.0546 (11)
C14	−1.4828 (9)	0.0683 (3)	−0.6522 (4)	0.0628 (14)
C15	−1.2833 (10)	0.0475 (3)	−0.6061 (3)	0.0601 (13)
C16	-1.1417 (8)	−0.0171 (2)	−0.6427 (3)	0.0489 (10)
C21	−1.1534 (7)	−0.2754 (2)	−0.6911 (3)	0.0393 (9)
C22	−0.9636 (7)	−0.3272 (2)	−0.6738 (3)	0.0445 (10)
C23	−0.9558 (8)	−0.3778 (2)	−0.5927 (3)	0.0544 (11)
C24	−1.1288 (9)	−0.3772 (3)	−0.5274 (3)	0.0583 (11)
C25	−1.3166 (8)	−0.3244 (3)	−0.5430 (3)	0.0580 (11)
C26	−1.3298 (7)	−0.2744 (2)	−0.6249 (3)	0.0513 (10)
Compound (II)				
S1	0.2328 (2)	0.8414 (2)	0.45926 (12)	0.0496 (5)
O1	0.4100 (6)	0.8323 (6)	0.4039 (4)	0.0669 (12)
O2	0.0621 (5)	0.9353 (4)	0.3874 (3)	0.0479 (10)
O3	0.0899 (5)	0.6495 (5)	0.4317 (3)	0.0556 (12)
C1	−0.1292 (8)	0.8182 (7)	0.3307 (4)	0.0427 (14)
C2	−0.1355 (7)	0.6592 (7)	0.3964 (4)	0.0424 (14)
C11	−0.1217 (8)	0.7846 (7)	0.2142 (4)	0.0425 (13)
C12	0.0621 (10)	0.7942 (9)	0.1719 (5)	0.062 (2)
C13	0.0501 (14)	0.7588 (13)	0.0641 (6)	0.097 (3)
C14	−0.1362 (11)	0.7166 (11)	−0.0066 (6)	0.087 (2)
C15	−0.3164 (12)	0.7096 (10)	0.0368 (6)	0.073 (2)
C16	−0.3131 (9)	0.7428 (8)	0.1443 (5)	0.054 (2)
C21	−0.2400 (8)	0.4886 (7)	0.3389 (4)	0.0421 (14)
C22	−0.1402 (9)	0.3885 (8)	0.2770 (5)	0.054 (2)
C23	−0.2382 (10)	0.2318 (9)	0.2239 (5)	0.061 (2)
C24	−0.4502 (10)	0.1746 (8)	0.2321 (6)	0.064 (2)
C25	−0.5546 (10)	0.2711 (8)	0.2921 (5)	0.060 (2)
C26	−0.4529 (8)	0.4290 (8)	0.3454 (5)	0.0489 (14)
Compound (III)				
S1	0.02629 (7)	0.10994 (4)	0.02237 (7)	0.0568 (2)
O1	0.1664 (2)	0.09828 (12)	0.1668 (2)	0.0771 (6)
O2	0.0720 (2)	0.08025 (8)	−0.1385 (2)	0.0471 (4)
O3	0.0215 (2)	0.19770 (10)	−0.0339 (2)	0.0608 (4)
C1	0.1207 (2)	0.13988 (10)	−0.2339 (2)	0.0394 (4)
C2	0.1389 (3)	0.20862 (14)	−0.1182 (3)	0.0495 (5)
C3	0.2812 (2)	0.11543 (10)	−0.2522 (2)	0.0392 (4)
C4	0.4089 (3)	0.09581 (12)	−0.1097 (3)	0.0489 (5)
C5	0.5543 (3)	0.07283 (14)	−0.1234 (3)	0.0557 (6)
C6	0.5755 (3)	0.06821 (14)	−0.2782 (3)	0.0573 (6)
C7	0.4502 (3)	0.08741 (13)	−0.4187 (3)	0.0542 (6)
C8	0.3033 (3)	0.11068 (11)	−0.4071 (3)	0.0458 (5)
C9	−0.0134 (2)	0.14941 (11)	−0.4022 (2)	0.0407 (5)
C10	−0.1130 (3)	0.08970 (13)	−0.4742 (3)	0.0477 (5)
C11	−0.2310 (3)	0.0991 (2)	−0.6310 (3)	0.0589 (6)
C12	−0.2494 (3)	0.1667 (2)	−0.7135 (3)	0.0630 (7)
C13	−0.1476 (4)	0.2252 (2)	−0.6440 (3)	0.0706 (8)
C14	−0.0288 (3)	0.21650 (14)	−0.4896 (3)	0.0611 (6)

Table 2. *Selected bond lengths (Å), angles (°), average ring valency angles (°), average ring torsion angles (°) and phenyl–phenyl dihedral angles (°) of compounds (I), (II) and (III)*

Compound (I)			
S1—O1	1.427 (3)	O2—C1	1.457 (4)
S1—O3	1.612 (3)	O3—C2	1.457 (4)
S1—O2	1.618 (2)	C1—C2	1.531 (5)
O1—S1—O3	106.4 (2)	C2—O3—S1	114.1 (2)
O1—S1—O2	108.7 (2)	O2—C1—C2	103.4 (3)
O3—S1—O2	93.89 (13)	O3—C2—C1	104.8 (3)
C1—O2—S1	110.3 (2)		
O3—S1—O2—C1	29.2 (3)	S1—O3—C2—C1	−12.3 (3)
O2—S1—O3—C2	−9.0 (3)	O2—C1—C2—O3	30.5 (3)
S1—O2—C1—C2	−39.0 (3)		
Average ring valency angle		105.2	
Average ring tosion angle		24.0	
Phenyl–phenyl dihedral angle		63.05 (11)	
Compound (II)			
S1—O1	1.439 (4)	O2—C1	1.472 (6)
S1—O2	1.613 (4)	O3—C2	1.469 (6)
S1—O3	1.619 (4)	C1—C2	1.538 (7)
O1—S1—O2	108.7 (2)	C1—O2—S1	115.1 (3)
O1—S1—O3	104.0 (2)	C2—O3—S1	111.6 (3)
O2—S1—O3	94.0 (2)	O2—C1—C2	102.7 (4)
O1—S1—O2—C1	104.8 (4)	S1—O3—C2—C1	36.3 (5)
O2—S1—O3—C2	−21.6 (3)	O2—C1—C2—O3	−34.0 (5)
S1—O2—C1—C2	21.8 (5)		
Average ring valency angle		105.4	
Average ring tosion angle		23.0	
Phenyl–phenyl dihedral angle		48.4 (2)	
Compound (III)			
S1—O1	1.432 (2)	O3—C2	1.439 (3)
S1—O3	1.620 (2)	C1—C3	1.524 (3)
S1—O2	1.6191 (15)	C1—C9	1.526 (3)
O2—C1	1.471 (2)	C1—C2	1.534 (3)
O1—S1—O3	108.66 (10)	C2—O3—S1	108.55 (14)
O1—S1—O2	106.70 (10)	O2—C1—C2	102.15 (15)
O3—S1—O2	93.24 (8)	O3—C2—C1	105.3 (2)
C1—O2—S1	114.73 (12)		
O3—S1—O2—C1	12.19 (13)	S1—O3—C2—C1	42.8 (2)
O2—S1—O3—C2	−32.65 (14)	O2—C1—C2—O3	−31.8 (2)
S1—O2—C1—C2	10.3 (2)		
Average ring valency angle		104.8	
Average ring tosion angle		25.9	
Phenyl–phenyl dihedral angle		85.37 (8)	

The H atoms of all three compounds were identified in difference maps and included at geometrically idealized positions. Refinement was on F^2 for all reflections. Weighted *R*, *wR* and all goodness-of-fit values, *S*, were based on F^2, while the conventional *R* factor was based on *F*, with *F* set to zero for negative F^2.

For all compounds, data collection: CAD-4/PC software; cell refinement: CAD-4/PC software; data reduction: CAD-4/PC software; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLUTON* (Spek, 1993); software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: HU1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Geise, H. J., Lenstra, A. T. H. & van Nuffel, P. (1982). *Bull. Soc. Chim. Belg.* **91**, 43–48.

Hellier, D. G. & Green, C. H. (1973*a*). *J. Chem. Soc. Perkin Trans.* 2, pp. 243–252.

Hellier, D. G. & Green, C. H. (1973*b*). *J. Chem. Soc. Perkin Trans.* 2, pp. 1966–1969.
Hellier, D. G. & Green, C. H. (1975). *J. Chem. Soc. Perkin Trans.* 2, pp. 190–193.
Lenstra, A. T. H. & van de Mieroop, W. (1978). *Cryst. Struct. Commun.* **7**, 577–581.
Lowe, G., Jones, R. H. & Salamone, S. J. (1984). *J. Chem. Soc. Chem. Commun.* pp. 262–263.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 478–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1993). *PLUTON. Molecular Graphics Program.* University of Utrecht, The Netherlands.

Acta Cryst. (1996). C**52**, 743–746

$3^1,3^2$-Didehydrorhodochlorin-15-acetic Acid Trimethyl Ester

Aarne Pajunen, Maria E. Stapelbroek-Möllmann and Paavo H. Hynninen

Department of Chemistry, University of Helsinki, Box 55, FIN-00014 University of Helsinki, Finland. E-mail: aarne.pajunen@cc.helsinki.fi

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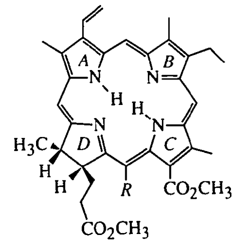
Abstract

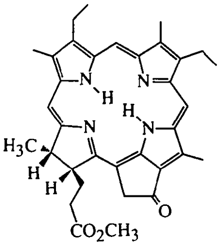
The structure of the title compound, methyl (2*S*,3*S*)-8-ethenyl-13-ethyl-2,3-dihydro-18-methoxycarbonyl-20-methoxycarbonylmethyl-3,7,12,17-tetramethylporphyrin-2-propionate, $C_{37}H_{42}N_4O_6$, containing no solvent molecules of crystallization, has been determined at 193 (2) K. The subrings *A*, *B* and *C* of the chlorin macrocycle are approximately in the least-squares plane defined by the four N atoms. The reduced ring *D* is distorted owing to the steric repulsion between the C17 and C15 substituents. The crystal packing is dominated by π–π interactions between subrings *A* and *C* of adjacent molecules in a slipped parallel orientation.

Comment

Chlorin e$_6$ trimethyl ester, (I), has played an important role in chlorophyll chemistry (Willstätter & Stoll, 1913; Fischer & Stern, 1940; Stoll & Wiedemann, 1952; Seely, 1966; Inhoffen, 1968; Woodward *et al.*, 1990; Smith, 1991; Hynninen, 1991*a*). It was the actual end product in Woodward's total synthesis of chlorophyll a (Woodward *et al.*, 1990). The three final steps (formation of the isocyclic ring, phytylation and Mg insertion) were considered by Woodward to proceed along 'well trodden paths', worked out earlier by Fischer (Fischer & Stern, 1940). The investigations of Inhoffen (1968) and his group concerned the electrochemical reduction of chlorin (I) and subsequent photo-oxygenation. These reactions rendered it possible to functionalize ring *B* and led finally to the invention of partial synthetic routes to bacteriochlorin derivatives and to chlorophyll b. Recently, the tetrasodium salt of mono-L-aspartyl chlorin e$_6$ was proposed as a promising photosensitizer for the photodynamic therapy of cancer (Aizawa *et al.*, 1987).



(I) $R = CH_2CO_2CH_3$
(II) $R = H$



(III)

Considering the important position of compound (I) among chlorophyll derivatives [two additional examples are given by structures (II) and (III)] and the fact that well formed crystals had been reported for free chlorin e$_6$ earlier this century (Willstätter & Stoll, 1913; Stoll & Wiedemann, 1952), it is surprising that no X-ray diffraction data have been available for it thus far. We have now succeeded in obtaining good crystals of (I) by allowing methanol to diffuse into a concentrated solution of (I) in acetone. Here, we describe the results from our X-ray crystallographic analysis of (I).

The subrings *A*, *B* and *C* of the chlorin macrocycle are approximately in the least-squares plane defined by the four N atoms. The reduced ring *D* is distorted as a result of steric repulsion between the C15 and C17 substituents. The C18 atom is situated below the plane composed of the N21, N22, N23 and N24 atoms by 0.19 (1) Å, C17 is raised out of the plane by 0.22 (1) Å, while the methoxycarbonylmethyl group at C15 is simultaneously oriented in the opposite direction to relieve steric strain. The torsion angle between the *trans* C17 and C18 H atoms is 107.7 (1)°. Regarding rotation about the C17^1—C17 bond, the most favoured conformational rotamer is the antiperiplanar form and, regarding rotation about the C17^2—C17^1 bond, the most populated rotamer is the *gauche*$^+$ form (for the Newman projections of the conformers, see Helaja, Hyvärinen, Heikkinen, Kilpeläinen & Hynninen, 1995). The predominant conformation for all three ester groups is *trans* (*Z*) (Eliel, Wilen & Mander, 1994).

The C_β—C_β bond length in ring *B* [1.346 (8) Å] is shorter than those in rings *A* [1.371 (8) Å] and *C* [1.412 (7) Å]. The C_α—C_β bond lengths in ring *B* are 1.476 (7) and 1.477 (7) Å. These values for ring *B* are consistent with the concept that the C7═C8 double