Absorption correction:
ψ scan (TEXSAN;
Molecular Structure
Corporation, 1990)
T_{min} = 0.85, T_{max} = 1.00
3556 measured reflections
3323 independent reflections
2996 observed reflections
[$I > 3\sigma(I)$]

$h = 0 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -10 \rightarrow 10$
3 standard reflections
monitored every 150
reflections
intensity decay: none

Refinement

Refinement on F
R = 0.035
wR = 0.046
S = 4.2
2996 reflections
227 parameters
H atoms refined as riding,
C—H = 0.98 Å
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.02

$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = -0.27 e Å^{-3}
Extinction correction:
Zachariasen (1968) type
2 Gaussian isotropic
Extinction coefficient:
0.14 × 10^{-4}
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)

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

	x	y	z	U_{eq}
Cl1	0.33673 (5)	-0.01704 (5)	0.03519 (6)	0.0505 (3)
O1	0.5148 (1)	0.1164 (1)	0.4323 (2)	0.045 (1)
O2	0.5649 (1)	0.2909 (1)	0.3478 (2)	0.053 (1)
O3	0.3360 (1)	0.2885 (1)	0.7822 (2)	0.050 (1)
O4	0.5145 (1)	0.3905 (1)	0.7187 (2)	0.058 (1)
C1	0.2053 (2)	-0.0100 (1)	0.1359 (2)	0.033 (1)
C2	0.0940 (2)	-0.1216 (1)	0.0806 (2)	0.038 (1)
C3	-0.0132 (2)	-0.1178 (1)	0.1566 (2)	0.040 (1)
C4	-0.0126 (2)	-0.0039 (1)	0.2858 (2)	0.033 (1)
C4a	0.1004 (1)	0.1048 (1)	0.3413 (2)	0.027 (1)
C5	-0.0957 (2)	0.3434 (1)	0.3372 (2)	0.035 (1)
C6	-0.1383 (2)	0.4269 (2)	0.2446 (2)	0.041 (1)
C7	-0.0402 (2)	0.4930 (2)	0.1917 (2)	0.043 (1)
C8	0.1040 (2)	0.4773 (1)	0.2304 (2)	0.038 (1)
C8a	0.1465 (2)	0.3949 (1)	0.3236 (2)	0.031 (1)
C9	0.2940 (2)	0.3708 (1)	0.3912 (2)	0.032 (1)
C9a	0.2111 (1)	0.1029 (1)	0.2679 (2)	0.027 (1)
C10	0.1215 (1)	0.2421 (1)	0.4725 (2)	0.028 (1)
C10a	0.0476 (1)	0.3296 (1)	0.3781 (2)	0.029 (1)
C11	0.3255 (1)	0.2270 (1)	0.3592 (2)	0.029 (1)
C12	0.2842 (1)	0.2995 (1)	0.5147 (2)	0.030 (1)
C13	0.4819 (2)	0.2181 (2)	0.3780 (2)	0.035 (1)
C14	0.6612 (2)	0.0938 (3)	0.4512 (3)	0.068 (1)
C15	0.3923 (2)	0.3334 (1)	0.6814 (2)	0.036 (1)
C16	0.4328 (3)	0.3068 (3)	0.9466 (3)	0.072 (1)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

C—Cl	1.738 (2)
C—C (aromatic)	1.381-1.398 (2)
C—CO$_2$Me	1.506 (2), 1.485 (2)
C=O	1.198, 1.197 (2)
C—OMe	1.332, 1.333 (2)
O—Me	1.444, 1.453 (2)
C—C—C (external)	128.8, 128.4, 130.4, 129.2 (1)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1990). Program(s)

used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Dimethyl 4b,8b,8c,8d-Tetrahydrodibenzo[a,f]cyclopropa[cd]pentalene-8b-carboxylate-8c-thionocarboxylate and the Corresponding 8c-Thiolocarboxylate

Ray Jones, A. Graham M. Rattray, John R. Scheffer and James Trotter

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

Abstract
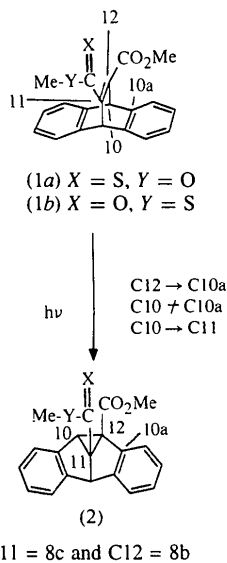
The title compounds, methyl 8c-[methoxy(thiocarbonyl)]-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[cd]pentalene-8b-carboxylate, C$_{20}$H$_{16}$O$_3$S, and methyl 8c-[(methylthio)]carbonyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[cd]pentalene-8b-carboxylate, C$_{20}$H$_{16}$O$_3$S, are the photoproducts in the photolysis of the dibenzobarrelene thiono and thiolo esters. The geometry and dimensions of the molecules are similar

to those of related materials. Only one photoproduct (of two possible) is formed in each case, with initial vinyl–benzo bond formation involving the vinyl C atom carrying the non-thioester group; intermediate biradicals are stabilized by resonance interaction with the thioester groups.

C11 bond. The intermediate biradicals have an unpaired electron at C11 and are thus stabilized by resonance interaction with the COSMe groups. This resonance stabilization is likely to be greater than in the alternate pathway with resonance involving the CO$_2$Me groups, thus accounting for the formation of only one photoproduct.

Comment

As part of a study of the effects of different substituents on the di-π-methane rearrangement of dibenzobarrelenes, two thio esters were prepared, namely, dimethyl 9,10-dihydro-9,10-ethenoanthracene-12-carboxylate-11-thionocarboxylate, (1a), and the corresponding 11-thiolocarboxylate, (1b) [thionocarboxylate = methoxy(thiocarbonyl); thiolocarboxylate = (methylthio)carbonyl] (Rattray, 1992; see deposit material for synthesis and spectral details). Photolysis of each of these compounds in solution results in only one (of two possible) regioisomeric photoproducts (Rattray, Yang, Gudmundsdottir & Scheffer, 1993). The photolyses require rigorous degassing, since the starting materials and photoproducts are susceptible to photooxidation. IR, MS and NMR data were inconclusive, but suggested that the two thio-ester groups in the photoproducts were bonded at position 8b (dibenzosemibullvalene numbering; C12 in the dibenzobarrelene numbering system; Fig. 1) (Rattray, 1992). The X-ray crystal structure analyses have shown the photoproducts to be the 8c-thiono (2a) and 8c-thiolo (2b) esters.

(2a)

(1a) X = S, Y = O
(1b) X = O, Y = S

hν   C12 → C10a
      C10 ≠ C10a
      C10 → C11

(2)

C11 = 8c and C12 = 8b

(2b)

Fig. 1. Views of the title molecules (33% probability displacement ellipsoids; dibenzobarrelene numbering system). (2b) is shown in the same orientation and with the same chirality as in the reaction scheme; (2a) is rotated by 180°.

The proposed mechanism for the di-π-methane reaction to give the observed photoproducts involves initial C12—C10a bond formation, followed by C10—C10a bond breaking and finally formation of a C10—
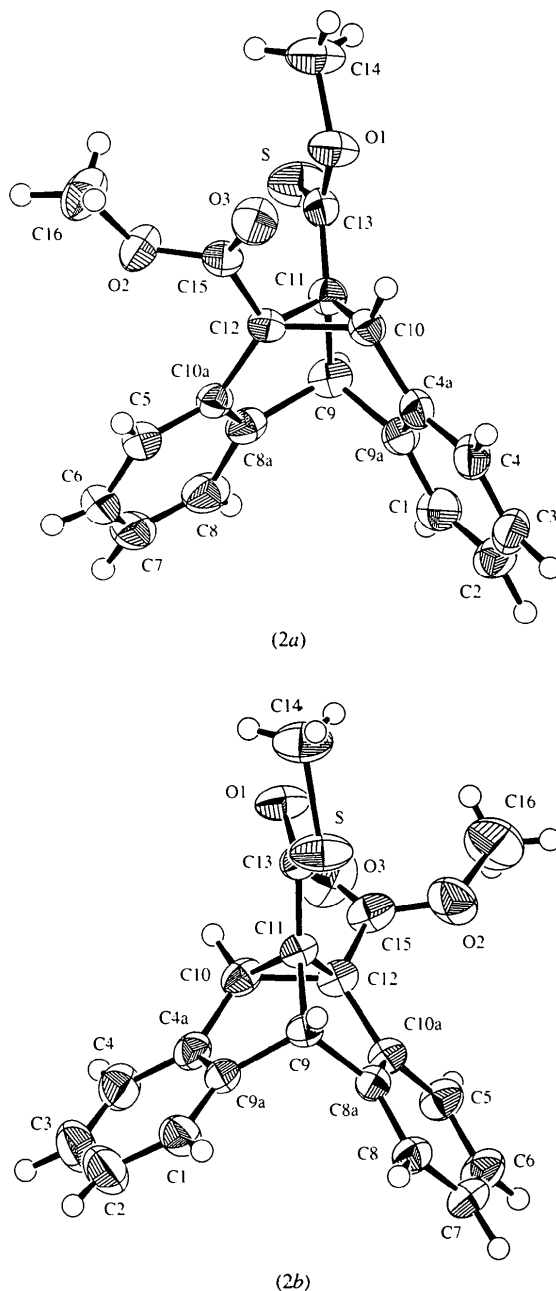
Experimental

Compound (1a) was irradiated on a preparative scale in benzene solution, using benzene which had been distilled under nitrogen. Nitrogen was also bubbled through the substrate solution for an hour before commencing and during irradiation. Concentration of the photolysized material resulted in the recovery of a bright yellow oil. Purification of the photoproduct was accomplished by column chromatography (hexanes/EtOAc 98:2). The photoproduct was recrystallized from chloroform/hexanes (m.p. 415.5–417 K) and was subsequently identified as compound (2a).

Compound (1b) was irradiated in a similar manner to (1a) using acetone solution. After photolysis the solvent was removed *in vacuo* leaving a yellow oil. The photoproduct was purified by column chromatography (hexanes/EtOAc 95:5), recrystallized from ethanol/chloroform (m.p. 400 K) and identified as compound (2b).

Compound (2a)

Crystal data

$C_{20}H_{16}O_3S$	Mo $K\alpha$ radiation
$M_r = 336.40$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 24
$P2_1/c$	reflections
$a = 12.452\,(2)$ Å	$\theta = 17.6–19.6°$
$b = 16.182\,(2)$ Å	$\mu = 0.20$ mm^{-1}
$c = 8.118\,(2)$ Å	$T = 294$ K
$\beta = 90.68\,(2)°$	Prism
$V = 1635.7\,(5)$ Å^3	$0.45 \times 0.35 \times 0.25$ mm
$Z = 4$	Colorless
$D_x = 1.366$ Mg m^{-3}	

Data collection

Rigaku AFC-6S diffractometer	$R_{int} = 0.06$
$\omega–2\theta$ scans	$\theta_{max} = 30°$
Absorption correction:	$h = 0 \rightarrow 17$
ψ scan (North, Phillips & Mathews, 1968)	$k = 0 \rightarrow 22$
	$l = -11 \rightarrow 11$
$T_{min} = 0.95$, $T_{max} = 1.00$	3 standard reflections
6208 measured reflections	monitored every 200
4938 independent reflections	reflections
2642 observed reflections	intensity decay: 0.1%
$[I > 3\sigma(I)]$	

Refinement

Refinement on F	Extinction correction:
$R = 0.048$	Zachariasen (1968) type
$wR = 0.055$	2 Gaussian isotropic
$S = 3.0$	Extinction coefficient:
2642 reflections	0.96×10^{-6}
282 parameters	Atomic scattering factors
H atoms refined isotropically	from *International Tables*
$w = 1/\sigma^2(F)$	*for X-ray Crystallography*
$(\Delta/\sigma)_{max} = 0.0002$	(1974, Vol. IV)
$\Delta\rho_{max} = 0.23$ e Å^{-3}	
$\Delta\rho_{min} = -0.25$ e Å^{-3}	

Compound (2b)

Crystal data

$C_{20}H_{16}O_3S$	Cu $K\alpha$ radiation
$M_r = 336.40$	$\lambda = 1.54178$ Å
Monoclinic	Cell parameters from 20
$P2_1/n$	reflections
$a = 7.911\,(1)$ Å	$\theta = 54.0–57.3°$
$b = 14.457\,(1)$ Å	$\mu = 1.8$ mm^{-1}
$c = 14.813\,(1)$ Å	$T = 294$ K
$\beta = 90.90\,(1)°$	Plate
$V = 1693.9\,(3)$ Å^3	$0.50 \times 0.30 \times 0.15$ mm
$Z = 4$	Colorless
$D_x = 1.319$ Mg m^{-3}	

Data collection

Rigaku AFC-6S diffractometer	$R_{int} = 0.018$
$\omega–2\theta$ scans	$\theta_{max} = 77.4°$
Absorption correction:	$h = 0 \rightarrow 10$
ψ scan (North, Phillips & Mathews, 1968)	$k = 0 \rightarrow 18$
	$l = -16 \rightarrow 16$
$T_{min} = 0.92$, $T_{max} = 1.00$	3 standard reflections
3837 measured reflections	monitored every 200
3592 independent reflections	reflections
2880 observed reflections	intensity decay: 0.05%
$[I > 3\sigma(I)]$	

Refinement

Refinement on F	Extinction correction:
$R = 0.042$	Zachariasen (1968) type
$wR = 0.064$	2 Gaussian isotropic
$S = 2.8$	Extinction coefficient:
2880 reflections	0.53×10^{-5}
282 parameters	Atomic scattering factors
H atoms refined isotropically	from *International Tables*
$w = 1/\sigma^2(F)$	*for X-ray Crystallography*
$(\Delta/\sigma)_{max} = 0.12$	(1974, Vol. IV)
$\Delta\rho_{max} = 0.25$ e Å^{-3}	
$\Delta\rho_{min} = -0.39$ e Å^{-3}	

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

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

	x	y	z	U_{eq}
S	0.82702 (8)	0.11226 (5)	-0.0276 (1)	0.0627 (5)
O1	0.7317 (2)	0.1641 (1)	0.2398 (2)	0.049 (1)
O2	0.5148 (1)	0.0241 (1)	0.1942 (2)	0.048 (1)
O3	0.5544 (2)	0.0866 (1)	0.4331 (2)	0.053 (1)
C1	0.9825 (2)	-0.1353 (2)	0.3894 (4)	0.047 (1)
C2	1.0094 (2)	-0.1595 (2)	0.5478 (4)	0.051 (1)
C3	0.9557 (2)	-0.1259 (2)	0.6790 (4)	0.053 (2)
C4	0.8743 (2)	-0.0678 (2)	0.6567 (4)	0.046 (1)
C4a	0.8497 (2)	-0.0440 (2)	0.4959 (3)	0.038 (1)
C5	0.5874 (2)	-0.1503 (2)	0.2353 (3)	0.043 (1)
C6	0.6000 (3)	-0.2231 (2)	0.1483 (4)	0.054 (2)
C7	0.6963 (3)	-0.2417 (2)	0.0736 (4)	0.057 (2)
C8	0.7814 (3)	-0.1884 (2)	0.0820 (4)	0.051 (1)
C8a	0.7693 (2)	-0.1141 (2)	0.1639 (3)	0.037 (1)
C9	0.8520 (2)	-0.0483 (2)	0.2022 (3)	0.039 (1)
C9a	0.9040 (2)	-0.0774 (2)	0.3627 (3)	0.037 (1)
C10	0.7670 (2)	0.0163 (2)	0.4377 (3)	0.035 (1)
C10a	0.6729 (2)	-0.0956 (1)	0.2416 (3)	0.033 (1)
C11	0.7848 (2)	0.0278 (2)	0.2540 (3)	0.034 (1)
C12	0.6773 (2)	-0.0114 (1)	0.3175 (3)	0.032 (1)

	x	y	z	U_{eq}
C13	0.7807 (2)	0.1041 (2)	0.1586 (3)	0.037 (1)
C14	0.7044 (4)	0.2402 (2)	0.1552 (5)	0.065 (2)
C15	0.5774 (2)	0.0398 (2)	0.3245 (3)	0.035 (1)
C16	0.4086 (3)	0.0602 (3)	0.1919 (5)	0.062 (1)

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

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

	x	y	z	U_{eq}
S	0.64182 (8)	0.18083 (4)	0.85445 (4)	0.0600 (4)
O1	0.8484 (2)	0.0486 (1)	0.8058 (1)	0.052 (1)
O2	0.7124 (2)	0.0166 (1)	0.5708 (1)	0.064 (1)
O3	0.9789 (3)	−0.0161 (1)	0.6103 (1)	0.079 (1)
C1	1.0246 (3)	0.4209 (2)	0.7136 (1)	0.051 (1)
C2	1.1946 (4)	0.4453 (2)	0.7099 (2)	0.067 (1)
C3	1.3158 (3)	0.3814 (2)	0.6896 (2)	0.068 (1)
C4	1.2735 (3)	0.2903 (2)	0.6717 (2)	0.057 (1)
C4a	1.1054 (2)	0.2638 (1)	0.6773 (1)	0.041 (1)
C5	0.7783 (3)	0.1991 (1)	0.4601 (1)	0.046 (1)
C6	0.6985 (3)	0.2710 (2)	0.4139 (1)	0.052 (1)
C7	0.6490 (3)	0.3505 (2)	0.4587 (1)	0.049 (1)
C8	0.6775 (2)	0.3599 (1)	0.5505 (1)	0.040 (1)
C8a	0.7522 (2)	0.2876 (1)	0.5974 (1)	0.033 (1)
C9	0.8090 (2)	0.2841 (1)	0.6956 (1)	0.032 (1)
C9a	0.9821 (2)	0.3294 (1)	0.6978 (1)	0.037 (1)
C10	1.0311 (2)	0.1695 (1)	0.6771 (1)	0.039 (1)
C10a	0.8030 (2)	0.2077 (1)	0.5521 (1)	0.036 (1)
C11	0.8521 (2)	0.1804 (1)	0.7113 (1)	0.033 (1)
C12	0.8817 (2)	0.1407 (1)	0.6166 (1)	0.036 (1)
C13	0.7932 (2)	0.1248 (1)	0.7888 (1)	0.036 (1)
C14	0.6206 (5)	0.1016 (2)	0.9464 (2)	0.063 (1)
C15	0.8659 (3)	0.0381 (1)	0.5998 (1)	0.046 (1)
C16	0.6836 (6)	−0.0797 (2)	0.5466 (3)	0.087 (2)

Table 3. *Selected bond lengths (Å) and angles (°)*

	(2a)	(2b)
C=S	1.630 (3)	
C—SMe		1.753 (2)
S—Me		1.790 (3)
C—C(aromatic)	1.367 (5)–1.395 (4)	1.368 (4)–1.398 (3)
C—COSMe	1.458 (4)	1.483 (3)
C—CO$_2$Me	1.496 (4)	1.509 (3)
C=O	1.199 (3)	1.210 (2), 1.197 (3)
C—OMe	1.326 (3), 1.331 (3)	1.319 (3)
O—Me	1.448 (4), 1.446 (4)	1.455 (4)
C—S—C		101.5 (1)
C—O—C	119.6 (2), 117.4 (2)	116.5 (2)
C—C—C (external)	128.4 (2)–130.0 (3)	128.7 (2)–129.3 (2)

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1990). Program(s) used to solve structures: *TEXSAN*. Program(s) used to refine structures: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with synthesis and spectral details for compounds (1a), (1b), (2a) and (2b), have been deposited with the IUCr (Reference: FG1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Styrylboronic Acid

Graeme J. Gainsford, Richard H. Meinhold and Anthony D. Woolhouse

The New Zealand Institute for Industrial Research and Development, PO Box 31-310, Lower Hutt, New Zealand

Abstract

Styrylboronic acid, $C_8H_9BO_2$, was one of several organoboron compounds investigated for their wood-preservation properties following *in situ* polymerization. The structure consists of independent monomeric molecules bound together by strong hydrogen bonds (B—O—H···O). The planes of the styryl and boronic acid moieties are twisted by 26(1)° with respect to each other, apparently as a result of the hydrogen-bonding requirements.

Comment

The title compound, (I), was synthesized by reaction of the Grignard reagent prepared from 4-bromostyrene with tri-*n*-butyl borate, followed by hydrolysis (full details in supplementary material). Extremely thin (< 0.03 mm) large plates and intergrown needles were isolated by re-crystallization from water. Recrystallization from other solvents gave unsatisfactory crystals.

(I)