Crystal structure of dimethyl (1α,2β,3α,4β,7β,8α,9β,10α)-13-di(methylthio)methylidene-pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene-2,9-dicarboxylate, $C_{21}H_{24}O_4S_2$

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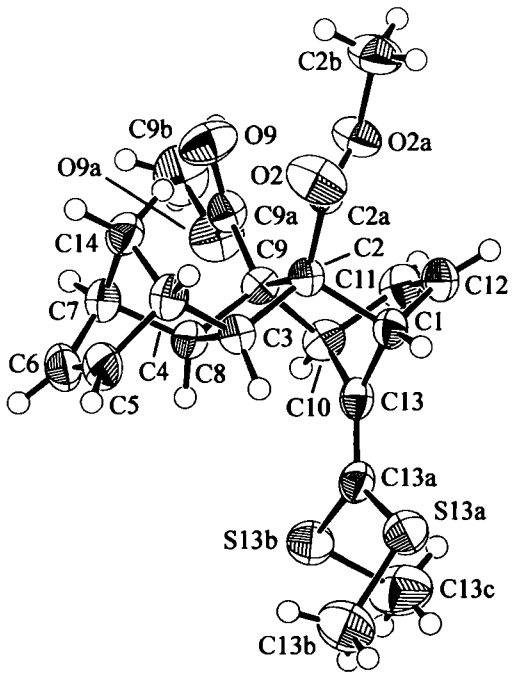
Received January 21, 2002, accepted and available on-line March 22, 2002; CCDC-No. 1267/789



Abstract

$C_{21}H_{24}O_4S_2$, monoclinic, $P12_1/c1$ (No. 14), a = 10.962(3) Å, b = 12.797(2) Å, c = 15.189(4) Å, β = 110.14(2)°, V = 2000.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.046, $wR_{ref}(F^2)$ = 0.119, T = 293 K.

Source of material

This compound was prepared by the cycloaddition of equimolar quantities of dimethyl-(1α,2β,5β,6α)-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene-3,4-dicarboxylate and 6,6-di(methylthio)fulvene in the presence of a small amount of 2,5-di(*t*-butyl) phenol. The reaction was conducted in refluxing chloroform for 7 days and the product isolated by chromatography on silica gel using 10% ethyl acetate in petroleum spirit as an eluent. The product was recrystallised as yellow plates from a petroleum spirit solution of the compound; mp 383 K – 384 K.

Experimental details

The C-bound H atoms were placed in their geometrically calculated positions and included in the final refinement in the riding model approximation.

Discussion

The molecule adopts a staircase motif with successive risers being defined by C11–C12, C1–C13–C10, C2–C9, C3–C8, C4–C14–C7 and C5–C6 connectivities. The ester groups lie to the opposite side of the molecule to the C=C(SMe)$_2$ group.

Table 1. Data collection and handling.

Crystal:	pale-yellow plate, size 0.08 × 0.32 × 0.36 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	2.90 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC6R, $\omega/2\theta$
$2\theta_{max}$:	50.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3919, 3540
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1944
$N(param)_{refined}$:	245
Programs:	SHELXS-86 [1], SHELXL-97 [2], teXsan [3], DIBABS [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.5608	0.1040	0.7944	0.079(3)
H(2a)	4e	0.9623	0.0512	0.6825	0.094(3)
H(2b)	4e	0.9490	0.0018	0.7732	0.094
H(2c)	4e	1.0322	0.1032	0.7804	0.094
H(3)	4e	0.6237	0.2828	0.8910	0.079
H(4)	4e	0.8681	0.2773	0.9936	0.079
H(10)	4e	0.7653	0.4277	1.0501	0.063(2)
H(6)	4e	0.7334	0.5721	0.9423	0.063
H(7)	4e	0.8053	0.5192	0.8084	0.079
H(8)	4e	0.5849	0.4273	0.7905	0.079
H(9a)	4e	0.6890	0.5000	0.4849	0.094
H(9b)	4e	0.7891	0.4076	0.5095	0.094
H(9c)	4e	0.8157	0.5073	0.5733	0.094
H(10)	4e	0.4780	0.3515	0.6137	0.079
H(11)	4e	0.5312	0.1946	0.5336	0.063
H(12)	4e	0.5783	0.0477	0.6403	0.063
H(13a)	4e	0.2237	0.2413	0.9230	0.094
H(13b)	4e	0.1775	0.3103	0.8322	0.094
H(13c)	4e	0.3133	0.3308	0.9094	0.094
H(13d)	4e	0.0674	0.3695	0.5804	0.094
H(13e)	4e	0.0904	0.2752	0.6501	0.094
H(13f)	4e	0.1482	0.2726	0.5690	0.094
H(14a)	4e	0.9750	0.4217	0.9363	0.079
H(14b)	4e	0.9166	0.3426	0.8513	0.079

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(13a)	4*e*	0.32447(9)	0.18842(8)	0.82136(7)	0.0661(6)	0.0549(6)	0.0707(7)	–0.0081(5)	0.0394(5)	–0.0042(6)
S(13b)	4*e*	0.27387(9)	0.37717(8)	0.68887(8)	0.0447(5)	0.0533(6)	0.0736(7)	0.0083(5)	0.0129(5)	0.0001(5)
O(2)	4*e*	0.8869(2)	0.1269(2)	0.8847(2)	0.070(2)	0.074(2)	0.040(2)	0.033(2)	0.010(1)	0.016(1)
O(2a)	4*e*	0.8423(2)	0.1295(2)	0.7307(2)	0.049(1)	0.059(2)	0.041(1)	0.016(1)	0.013(1)	–0.002(1)
O(9)	4*e*	0.8676(2)	0.3431(2)	0.6836(2)	0.051(2)	0.081(2)	0.070(2)	0.002(1)	0.030(1)	0.024(2)
O(9a)	4*e*	0.6823(2)	0.4136(2)	0.5915(2)	0.069(2)	0.065(2)	0.041(1)	0.004(1)	0.022(1)	0.025(1)
C(1)	4*e*	0.5739(3)	0.1558(2)	0.7510(2)	0.041(2)	0.031(2)	0.042(2)	–0.003(1)	0.014(2)	0.001(2)
C(2a)	4*e*	0.8206(3)	0.1564(2)	0.8083(2)	0.040(2)	0.035(2)	0.037(2)	–0.001(2)	0.011(2)	0.003(2)
C(2b)	4*e*	0.9560(3)	0.0661(3)	0.7427(3)	0.051(2)	0.074(3)	0.072(3)	0.021(2)	0.021(2)	–0.004(2)
C(2)	4*e*	0.7013(3)	0.2246(2)	0.7887(2)	0.038(2)	0.031(2)	0.031(2)	0.000(1)	0.010(1)	0.003(1)
C(3)	4*e*	0.6963(3)	0.2984(2)	0.8694(2)	0.040(2)	0.034(2)	0.030(2)	0.001(2)	0.010(1)	0.004(2)
C(4)	4*e*	0.8215(3)	0.3322(3)	0.9500(2)	0.045(2)	0.047(2)	0.028(2)	–0.005(2)	0.002(2)	0.000(2)
C(5)	4*e*	0.7773(3)	0.4261(3)	0.9924(2)	0.059(2)	0.060(3)	0.038(2)	–0.013(2)	0.015(2)	–0.020(2)
C(6)	4*e*	0.7589(3)	0.5048(3)	0.9333(3)	0.056(2)	0.041(2)	0.056(2)	–0.005(2)	0.014(2)	–0.012(2)
C(7)	4*e*	0.7866(3)	0.4658(3)	0.8482(2)	0.047(2)	0.035(2)	0.047(2)	–0.006(2)	0.015(2)	–0.001(2)
C(8)	4*e*	0.6690(3)	0.3937(2)	0.8004(2)	0.037(2)	0.034(2)	0.034(2)	–0.001(1)	0.011(1)	0.002(2)
C(9)	4*e*	0.6684(3)	0.3197(2)	0.7185(2)	0.033(2)	0.035(2)	0.030(2)	0.000(1)	0.009(1)	0.004(2)
C(9a)	4*e*	0.7537(3)	0.3562(2)	0.6641(2)	0.048(2)	0.036(2)	0.036(2)	0.000(2)	0.015(2)	0.004(2)
C(9b)	4*e*	0.7497(4)	0.4611(3)	0.5350(3)	0.111(3)	0.071(3)	0.049(3)	–0.006(3)	0.040(2)	0.019(2)
C(10)	4*e*	0.5280(3)	0.2933(3)	0.6509(2)	0.037(2)	0.049(2)	0.032(2)	0.002(2)	0.005(1)	0.006(2)
C(11)	4*e*	0.5403(3)	0.1970(3)	0.5967(2)	0.043(2)	0.064(3)	0.031(2)	–0.006(2)	0.005(2)	–0.010(2)
C(12)	4*e*	0.5665(3)	0.1165(3)	0.6554(2)	0.046(2)	0.047(2)	0.043(2)	–0.006(2)	0.011(2)	–0.013(2)
C(13)	4*e*	0.4728(3)	0.2431(3)	0.7192(2)	0.039(2)	0.036(2)	0.034(2)	–0.005(2)	0.006(2)	–0.004(2)
C(13a)	4*e*	0.3696(3)	0.2675(3)	0.7417(2)	0.037(2)	0.040(2)	0.043(2)	–0.006(2)	0.009(2)	–0.003(2)
C(13b)	4*e*	0.2513(4)	0.2780(4)	0.8780(3)	0.096(3)	0.095(4)	0.076(3)	0.000(3)	0.049(3)	–0.016(3)
C(13c)	4*e*	0.1280(3)	0.3166(4)	0.6133(3)	0.050(2)	0.119(4)	0.067(3)	0.012(3)	0.004(2)	–0.002(3)
C(14)	4*e*	0.8967(3)	0.3879(3)	0.8957(2)	0.040(2)	0.046(2)	0.046(2)	–0.007(2)	0.010(2)	–0.004(2)

Acknowledgment. The Australian Research Council is thanked for support.

References

1. Sheldrick, G. M.: SHELXS-86. Program for the solution of crystal structure. University of Göttingen, Germany 1986.
2. Sheldrick, G. M.: SHELXL-97. Program for crystal structure refinement.University of Göttingen, Germany 1997.
3. teXsan: Single Crystal Structure Analysis Software. Version 1.04. Molecular Structure Corporation. The Woodlands, TX, USA 1997.
4. Walker, N.; Stuart, D.: An empirical method for correcting diffractometer data for absorption effects. Acta Crystallogr. A**39** (1983) 159-166.