the National Institute of Diabetes and Digestive and Kidney Diseases, Grant No. DK26546-22.

References

DUAX, W. L., GRIFFIN, J. F., STRONG, P. D. & WOOD, K. J. (1989). *Acta Cryst.* C**45**, 930–932.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

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

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

SEGALOFF, A., GABBARD, R. B., FLORES, A., BORNE, R. F., BAKER, J. K., DUAX, W. L., STRONG, P. D. & ROHRER, D. C. (1980). *Steroids*, **35**, 335–349.

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Two Chlorinated Thiophene Derivatives, $C_{13}H_{11}Cl_4NO_6S$ and $C_9H_6Cl_4O_4S$

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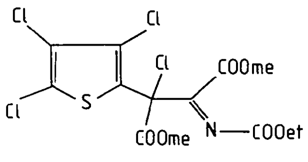
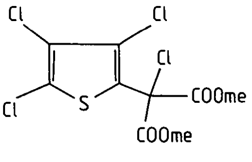
Abstract. Dimethyl 2-chloro-3-ethoxycarbonylimino-2-(3,4,5-trichlorothien-2-yl)succinate, $C_{13}H_{11}Cl_4NO_6S$ (1), $M_r = 451{\cdot}1$, monoclinic, $P2_1/c$, $a = 12{\cdot}208\,(2)$, $b = 10{\cdot}413\,(1)$, $c = 14{\cdot}849\,(1)$ Å, $\beta = 104{\cdot}97\,(1)°$, $V = 1823{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}64$ g cm^{-3}, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71073$ Å), $F(000) = 912$, $\mu = 7{\cdot}2$ cm^{-1}, $T = 298$ K, $R = 0{\cdot}068$ for 4375 reflections. Dimethyl 2-chloro-2-(3,4,5-trichlorothien-2-yl)malonate, $C_9H_6Cl_4O_4S$ (2), $M_r = 352{\cdot}0$, monoclinic, $P2_1$, $a = 6{\cdot}742\,(3)$, $b = 8{\cdot}068\,(1)$, $c = 12{\cdot}555\,(1)$ Å, $\beta = 97{\cdot}84\,(2)°$, $V = 676{\cdot}5$ Å^3, $Z = 2$, $D_x = 1{\cdot}73$ g cm^{-3}, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71073$ Å), $F(000) = 352$, $\mu = 10{\cdot}3$ cm^{-1}, $T = 298$ K, $R = 0{\cdot}031$ for 1561 reflections. The S—C bond of the chlorinated thiophene ring is significantly shorter than the corresponding bond in related (S,N)-ylides.

Experimental. Both compounds were synthesized as described by Dillen, Meth-Cohn & van Vuuren (1987).



(1)



(2)

Compound (1), crystal *ca* 0·12 × 0·31 × 0·31 mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; ω scan; variable scan speed with a maximum of 5·49° min^{-1}, and a minimum corresponding to 50 s measuring time per reflection; the ω-scan angle changed as (0·53 +

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent thermal factors* (Å$^2 \times 10^3$)

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

	x	y	z	U_{eq}
(*a*) Molecule (1)				
S(1)	379 (1)	1792 (1)	8828 (1)	49 (1)
C(2)	60 (2)	3338 (2)	8465 (2)	49 (1)
C(3)	674 (2)	4216 (2)	9045 (2)	48 (1)
C(4)	1428 (2)	3620 (2)	9823 (2)	44 (1)
C(5)	1381 (2)	2325 (2)	9810 (1)	39 (1)
C(6)	2074 (2)	1414 (2)	10519 (1)	38 (1)
C(7)	3344 (2)	1744 (2)	10744 (1)	37 (1)
N(8)	3851 (2)	2179 (2)	11528 (1)	44 (1)
C(9)	5007 (2)	2553 (3)	11767 (2)	50 (1)
O(10)	5089 (1)	3731 (2)	11473 (1)	63 (1)
C(11)	6235 (3)	4294 (3)	11742 (2)	88 (1)
C(12)	6186 (3)	5492 (4)	11225 (3)	102 (1)
O(13)	5735 (1)	1923 (2)	12266 (1)	68 (1)
C(14)	3938 (2)	1518 (2)	9975 (2)	45 (1)
O(15)	3211 (1)	1146 (2)	9200 (1)	50 (1)
C(16)	3651 (3)	883 (3)	8396 (2)	70 (1)
O(17)	4931 (2)	1639 (2)	10099 (1)	74 (1)
C(18)	1911 (2)	−11 (2)	10233 (2)	41 (1)
O(19)	2768 (1)	−691 (1)	10744 (1)	50 (1)
C(20)	2708 (3)	−2083 (3)	10578 (2)	63 (1)
O(21)	1125 (1)	−425 (1)	9663 (1)	57 (1)
Cl(22)	1589 (1)	1501 (1)	11569 (1)	52 (1)
Cl(23)	−956 (1)	3632 (1)	7459 (1)	73 (1)
Cl(24)	576 (1)	5838 (1)	8864 (1)	72 (1)
Cl(25)	2259 (1)	4544 (1)	10697 (1)	64 (1)
(*b*) Molecule (2)				
S(1)	876 (1)	3669	6361 (1)	49 (1)
C(2)	1271 (6)	3059 (5)	5098 (3)	49 (1)
C(3)	2959 (6)	2197 (5)	5091 (3)	45 (1)
C(4)	4002 (5)	2005 (5)	6146 (3)	43 (1)
C(5)	3052 (5)	2711 (5)	6921 (3)	37 (1)
C(6)	3743 (5)	2678 (4)	8114 (3)	36 (1)
C(7)	4513 (5)	944 (5)	8503 (3)	39 (1)
O(8)	3206 (4)	−187 (3)	8110 (2)	44 (1)
C(9)	3769 (8)	−1897 (5)	8382 (4)	53 (1)
O(10)	6030 (4)	700 (3)	9098 (2)	53 (1)
C(11)	2094 (5)	3248 (5)	8761 (3)	42 (1)
O(12)	2104 (4)	2345 (3)	9639 (2)	47 (1)
C(13)	603 (8)	2778 (6)	10319 (4)	59 (1)
O(14)	998 (4)	4375 (4)	8499 (2)	62 (1)
Cl(15)	5760 (1)	4135 (2)	8441 (1)	51 (1)
Cl(16)	−426 (2)	3599 (2)	4017 (1)	74 (1)
Cl(17)	3759 (2)	1359 (2)	3977 (1)	70 (1)
Cl(18)	6258 (1)	1007 (2)	6385 (1)	62 (1)

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Table 2. *Bond lengths* (Å) *and valence angles* (°)

(*a*) Molecule (1)			
S(1)—C(2)	1·710 (2)	S(1)—C(5)	1·735 (2)
C(2)—C(3)	1·344 (3)	C(2)—Cl(23)	1·705 (2)
C(3)—C(4)	1·420 (3)	C(3)—Cl(24)	1·710 (2)
C(4)—C(5)	1·349 (3)	C(4)—Cl(25)	1·720 (2)
C(5)—C(6)	1·505 (3)	C(6)—C(7)	1·539 (3)
C(6)—C(18)	1·542 (3)	C(6)—Cl(22)	1·808 (2)
C(7)—N(8)	1·253 (2)	C(7)—C(14)	1·519 (3)
N(8)—C(9)	1·417 (3)	C(9)—O (10)	1·315 (3)
C(9)—O(13)	1·195 (3)	O(10)—C(11)	1·474 (3)
C(11)—C(12)	1·458 (5)	C(14)—O(15)	1·317 (2)
C(14)—O(17)	1·186 (2)	O(15)—C(16)	1·456 (3)
C(18)—O(19)	1·327 (2)	C(18)—O(21)	1·185 (2)
O(19)—C(20)	1·469 (3)		
C(2)—S(1)—C(5)	91·0 (1)	S(1)—C(2)—C(3)	113·3 (2)
S(1)—C(2)—Cl(23)	120·0 (1)	C(3)—C(2)—Cl(23)	126·8 (2)
C(2)—C(3)—C(4)	111·2 (2)	C(2)—C(3)—Cl(24)	124·5 (2)
C(4)—C(3)—Cl(24)	124·3 (2)	C(3)—C(4)—C(5)	114·1 (2)
C(3)—C(4)—Cl(25)	120·1 (2)	C(5)—C(4)—Cl(25)	125·8 (2)
S(1)—C(5)—C(4)	110·5 (2)	S(1)—C(5)—C(6)	122·2 (2)
C(4)—C(5)—C(6)	127·3 (2)	C(5)—C(6)—C(7)	111·3 (2)
C(5)—C(6)—C(18)	113·9 (2)	C(7)—C(6)—C(18)	109·0 (2)
C(5)—C(6)—Cl(22)	108·8 (1)	C(7)—C(6)—Cl(22)	109·8 (1)
C(18)—C(6)—Cl(22)	103·8 (1)	C(6)—C(7)—N(8)	120·7 (2)
C(6)—C(7)—C(14)	116·9 (2)	N(8)—C(7)—C(14)	122·5 (2)
C(7)—N(8)—C(9)	123·6 (2)	N(8)—C(9)—O(10)	109·2 (2)
N(8)—C(9)—O(13)	122·5 (2)	O(10)—C(9)—O(13)	127·6 (2)
C(9)—O(10)—C(11)	115·4 (2)	O(10)—C(11)—C(12)	106·9 (3)
C(7)—C(14)—O(15)	111·0 (2)	C(7)—C(14)—O(17)	122·3 (2)
O(15)—C(14)—O(17)	126·7 (2)	C(14)—O(15)—C(16)	117·6 (2)
C(6)—C(18)—O(19)	109·2 (2)	C(6)—C(18)—O(21)	124·7 (2)
O(19)—C(18)—O(21)	126·0 (2)	C(18)—O(19)—C(20)	115·7 (2)
(*b*) Molecule (2)			
S(1)—C(2)	1·716 (4)	S(1)—C(5)	1·722 (3)
C(2)—C(3)	1·335 (5)	C(2)—Cl(16)	1·708 (4)
C(3)—C(4)	1·421 (5)	C(3)—Cl(17)	1·706 (4)
C(4)—C(5)	1·361 (4)	C(4)—Cl(18)	1·711 (4)
C(5)—C(6)	1·507 (5)	C(6)—C(7)	1·548 (5)
C(6)—C(11)	1·534 (5)	C(6)—Cl(15)	1·803 (3)
C(7)—O(8)	1·316 (4)	C(7)—O(10)	1·198 (4)
O(8)—C(9)	1·459 (5)	C(11)—O(12)	1·320 (4)
C(11)—O(14)	1·189 (4)	O(12)—C(13)	1·454 (5)
C(2)—S(1)—C(5)	91·0 (2)	S(1)—C(2)—C(3)	113·3 (3)
S(1)—C(2)—Cl(16)	119·3 (2)	C(3)—C(2)—Cl(16)	127·4 (3)
C(2)—C(3)—C(4)	111·4 (3)	C(2)—C(3)—Cl(17)	125·2 (3)
C(4)—C(3)—Cl(17)	123·4 (3)	C(3)—C(4)—C(5)	113·6 (3)
C(3)—C(4)—Cl(18)	122·0 (3)	C(5)—C(4)—Cl(18)	124·4 (3)
S(1)—C(5)—C(4)	110·7 (2)	S(1)—C(5)—C(6)	123·0 (2)
C(4)—C(5)—C(6)	126·3 (3)	C(5)—C(6)—C(7)	112·0 (3)
C(5)—C(6)—C(11)	111·9 (3)	C(7)—C(6)—C(11)	109·9 (3)
C(5)—C(6)—Cl(15)	109·6 (2)	C(7)—C(6)—Cl(15)	107·9 (2)
C(11)—C(6)—Cl(15)	105·2 (2)	C(6)—C(7)—O(8)	109·2 (3)
C(6)—C(7)—O(10)	124·5 (3)	O(8)—C(7)—O(10)	126·2 (3)
C(7)—O(8)—C(9)	115·3 (3)	C(6)—C(11)—O(12)	110·7 (3)
C(6)—C(11)—O(14)	123·4 (3)	O(12)—C(11)—O(14)	125·8 (3)
C(11)—O(12)—C(13)	115·7 (3)		

$0{\cdot}35\tan\theta)^\circ$; horizontal aperture fixed to 1·3 mm, vertical slit to 4 mm. Cell dimensions determined by fitting the setting angles of 25 reflections with $6 \leq \theta \leq 20^\circ$. Monoclinic data set collected up to $\theta = 30^\circ$ ($\sin\theta/\lambda = 0{\cdot}7035$ Å^{-1}, $h = 0{:}17$, $k = 0{:}14$, $l = -20{:}20$); 5577 reflections measured of which 2170 were unobserved [$I < \sigma(I)$], $R_{\rm int} = 0{\cdot}0024$. Intensity control every hour (no significant loss), orientation control every 200 reflections (allowed deviation 0·1°). Data corrected for Lorentz and polarization effects. Empirical absorption correction using ψ scans (correction factors min. 0·96, max. 1·00).

Compound (2), crystals *ca* $0{\cdot}37 \times 0{\cdot}44 \times 0{\cdot}85$ mm; diffractometer, radiation and scan mode as for (1); ω-scan angle changed as $(0{\cdot}61 + 0{\cdot}35\tan\theta)^\circ$; horizontal aperture 1·3 mm, vertical slit 4 mm. Cell dimensions determined by fitting the setting angles of 25 reflections with $6 \leq \theta \leq 19^\circ$. Monoclinic data set collected up to $\theta = 27^\circ$ ($\sin\theta/\lambda = 0{\cdot}6388$ Å^{-1}, $h = 0{:}8$, $k = 0{:}10$, $l = -16{:}16$); 1582 reflections measured of which 49 were unobserved [$I < \sigma(I)$], $R_{\rm int} = 0{\cdot}0406$. Intensity and orientation control as for (1). Data corrected for Lorentz and polarization effects, and for absorption (correction factor min. 0·87, max. 1·00).

The crystal structures for both compounds were solved by direct methods with *MULTAN*80 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All H atoms were located from subsequent Fourier analysis. Non-H atoms were refined anisotropically, H atoms with a common temperature factor; *SHELX*76 (Sheldrick, 1976); full-matrix method with $\sigma^{-2}(F)$ weights, refinement on F values. For compound (2), the y coordinate of the S atom was fixed to define the origin. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Data for (1): 4375 reflections used for 260 variables, $R = 0{\cdot}068$, $wR = 0{\cdot}026$, $U_{\rm iso} = 0{\cdot}147\ (4)$ Å^2

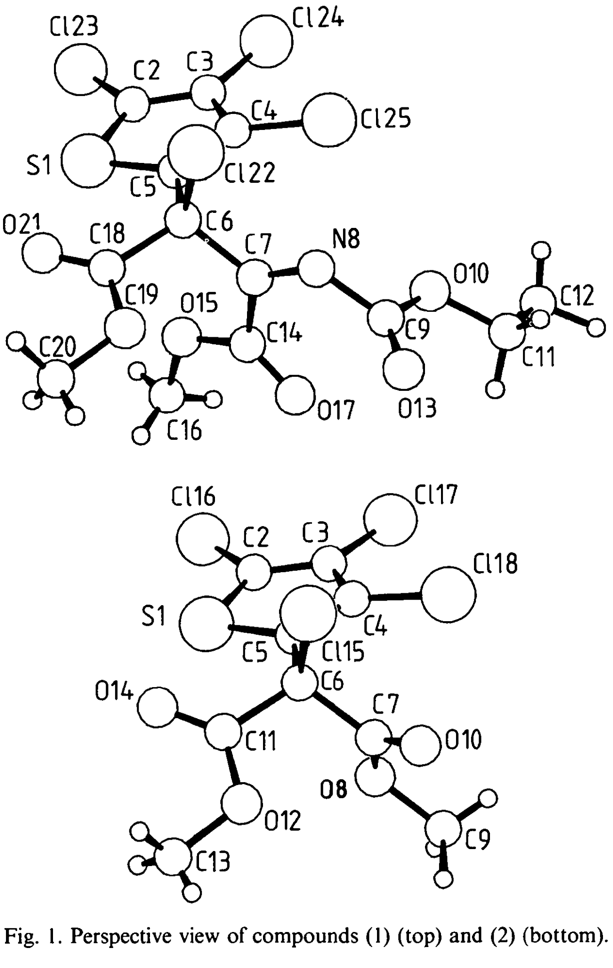

Fig. 1. Perspective view of compounds (1) (top) and (2) (bottom).

for H atoms, $(\Delta/\sigma)_{\max} = 0{\cdot}4$, $(\Delta\rho)_{\max} = 0{\cdot}47$, $(\Delta\rho)_{\min} = -0{\cdot}49$ e Å^{-3}. For (2): 1561 reflections for 181 variables; $R = 0{\cdot}031$, $wR = 0{\cdot}026$, $U_{\rm iso} = 0{\cdot}086\,(6)$ Å^2 for H atoms, $(\Delta/\sigma)_{\max} = 0{\cdot}1$, $(\Delta\rho)_{\max} = 0{\cdot}20$, $(\Delta\rho)_{\min} = -0{\cdot}38$ e Å^{-3}.

Fractional coordinates for the non-H atoms of both compounds are given in Table 1, bond lengths and angles in Table 2.* The structures are shown in Fig. 1.

Related literature. The crystal structures of three related ylides are described by Dillen, Meth-Cohn & van Rooyen (1987), and reactions of possible interest in Dillen, Meth-Cohn, Moore & van Rooyen (1988).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52619 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Dillen, J. L. M., Meth-Cohn, O., Moore, C. & van Rooyen, P. H. (1988). *Tetrahedron*, **44**, 3127–3138.

Dillen, J. L. M., Meth-Cohn, O. & van Rooyen, P. H. (1987). *S. Afr. J. Chem.* **40**, 51–56.

Dillen, J. L. M., Meth-Cohn, O. & van Vuuren, G. (1987). *J. Chem. Soc. Perkin Trans.* 1, pp. 2659–2661.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Sheldrick, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

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A Bichromophoric Difulvene from 3,7-Bicyclo[3.3.0]octadione

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Abstract. 3,7-Bis(2,4-cyclopentadien-1-ylidene)bicyclo[3.3.0]octane, $C_{18}H_{18}$, $M_r = 234{\cdot}3$, monoclinic, $I2/a$, $a = 15{\cdot}2830\,(11)$, $b = 5{\cdot}1918\,(3)$, $c = 16{\cdot}8990\,(13)$ Å, $\beta = 96{\cdot}397\,(6)^\circ$, $V = 1332{\cdot}6\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}168$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 4{\cdot}58$ cm^{-1}, $F(000) = 504$, $T = 295$ K, $R = 0{\cdot}036$ for 1042 observations with $I > 3\sigma(I)$ (of 1377 unique data). The bicyclo[3.3.0]octane ring system adopts a flattened half-chair conformation with a crystallographic twofold axis bisecting the ring fusion bond. The bond angle of the C=C exocyclic to the cyclopentadienylidene ring is 108·72 (8)°. The intramolecular distance between the electrophilic fulvene carbons is 3·822 (2) Å. The cyclopentadienylidene rings are planar, with maximum deviation of 0·001 (1) Å.

Experimental. The title compound was prepared by condensing 3,7-bicyclo[3.3.0]octadione and 1,3-cyclopentadiene with pyrrolidine as a catalyst in methanol (Stone & Little, 1984). Suitable crystals (m.p. 395–397 K) were grown by slow cooling of refluxing hexane; a yellow crystal with dimensions 0·06 × 0·35 × 0·43 mm was mounted in a capillary on an Enraf–Nonius CAD-4 diffractometer with Cu $K\alpha$ radiation and a graphite monochromator. Cell dimensions were determined from setting angles of 25 reflections having $30 > \theta > 20^\circ$. The ω–2θ scans were designed for $I = 50\sigma(I)$, subject to maximum scan time = 90 s, scan rates varied 0·61–3·30° min^{-1}. Two quadrants of data having $2 \le \theta \le 75^\circ$, $-26 \le h \le 26$, $0 \le k \le 6$, $-19 \le l \le 19$, were measured and corrected for background, Lorentz, polarization and absorption. Absorption corrections were based on ψ scans, with minimum relative transmission coefficient 0·884. Three standard reflections (200, 020, 002) showed only a random fluctuation in intensity so no correction for decay was applied. Data from two equivalent quadrants were averaged, $R_{\rm int} = 0{\cdot}018$. Systematic absences hkl with $h + k + l$ odd and $h0l$ with h odd indicated space groups $I2/a$ or Ia. The former was confirmed by successful refinement of a centrosymmetric model. The structure was solved by direct methods, refined by full-matrix least squares based upon F, using data for which $I > 3\sigma(I)$, weights $w = 4F_o^2[\sigma^2(I) + (0{\cdot}02F_o^2)^2]^{-1}$ using the *Enraf–Nonius Structure Determination Package* (Frenz & Okaya, 1980), scattering factors of Cromer

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