

0.3 and  $-0.2 \text{ e } \text{\AA}^{-3}$ . Atomic scattering factors calculated by  $\sum [a_i \exp(-b_i \lambda^{-2} \sin^2 \theta)] + c$  ( $i = 1, \dots, 4$ ) (*International Tables for X-ray Crystallography*, 1974, Vol. IV). Calculations performed on VAX station 3100 computer. The final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.\* C30 – O32 are the atoms in the solvent molecules. Bond lengths and angles are listed in Table 2. A perspective view of the molecule with the atom labeling is presented in Fig. 1.

\* Lists of H-atom coordinates, anisotropic temperature factors of the non-H atoms and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53988 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Related literature.** The structure of the title compound reported here has been referred to in the chemical synthesis of 6-hydroxy corticosteroids (Terasawa & Okada, 1991).

The author thanks Drs Terasawa and Okada for supplying the crystals.

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## 1/1 Charge-Transfer Complex of 5-Chloro-2-isopropyl-2H-1-benzothieno-[2,3-c]pyrrole with 1,3,5-Trinitrobenzene

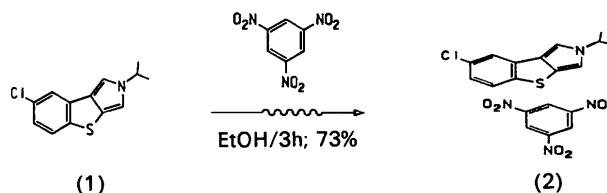
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**Abstract.** 5-Chloro-2-isopropyl-2H-1-benzothieno-[2,3-c]pyrrole–trinitrobenzene (1/1),  $\text{C}_{13}\text{H}_{12}\text{ClNS} \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_6$ ,  $M_r = 462.86$ , triclinic,  $P\bar{1}$ ,  $a = 6.891$  (3),  $b = 11.498$  (4),  $c = 14.223$  (3) Å,  $\alpha = 71.53$  (2),  $\beta = 76.77$  (3),  $\gamma = 82.23$  (3)°,  $V = 1038.1$  (6) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.481 \text{ Mg m}^{-3}$ ,  $F(000) = 476$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu = 0.32 \text{ mm}^{-1}$ ,  $T = 291$  (1) K, final  $R = 0.076$  for 1566 unique observed [ $F \geq 4.0\sigma(F)$ ] diffractometer data.  $\text{C}_6\text{H}_3\text{N}_3\text{O}_6$  (I) and  $\text{C}_{13}\text{H}_{12}\text{ClNS}$  (II) are nearly planar with maximum deviations from planarity of 0.221 (9) Å in (I) and 0.075 (11) Å in (II) [C(methyl) atoms not considered] and the molecules are stacked  $\dots(\text{I})\dots(\text{II})\dots(\text{I})\dots(\text{II})\dots$  along the  $x$  axis with distances of 3.36 and 3.29 Å between the planes. The plane-parallel pairing of the molecular components clearly demonstrates the expected  $\pi-\pi^*$  interaction between the  $14\pi$ -donor and the  $6\pi$ -acceptor system; the plane-to-plane distances are characteristic for a weak molecular charge-transfer complex without additional hydrogen bonding. Molecular orientation leads to the conclusion that the electron-rich S atom in the five-membered ring and the unsubstituted C atoms of the trinitrobenzene (TNB) play a dominant role in the complex geometry.

**Experimental.** Electron donor–acceptor complexes with polynitroarenes as  $\pi$  acceptors are useful in stabilizing and characterizing unstable quinoid and benzenoid hetarenes and give reliable information about donor properties. To prove the donor activity of 5-chloro-2-isopropyl-2H-1-benzothieno[2,3-c]pyrrole (1), an example of the hitherto unknown  $14\pi$ -hetarene, complexation was carried out with 1,3,5-trinitrobenzene (TNB) in ethanol (3 h; reflux).



In order to determine the orientation and distance of the acceptor molecule in relation to the tricyclic  $14\pi$ -hetarene, an X-ray analysis of the crystalline 1/1 complex (2) (m.p. 435 K from ethanol) was performed; red crystals were obtained from methanol solution by slow evaporation (3 d) from methanol at 298 K. A well developed crystal platelet of size  $\sim 0.29 \times 0.10 \times 0.03 \text{ mm}$  was used. Its quality was

Table 1. Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^4$ )

	$x$	$y$	$z$	$U_{eq}/U$
S(1)	0.3115 (3)	0.9026 (2)	0.6118 (2)	374
Cl(1)	0.2759 (5)	0.8654 (3)	1.0614 (2)	946
C(1)	0.261 (1)	0.5695 (7)	0.7800 (6)	422
C(1')	0.193 (1)	1.0806 (7)	0.3027 (6)	355
C(2)	0.204 (1)	1.1507 (9)	0.2030 (6)	484
C(3)	0.279 (1)	0.6510 (7)	0.6145 (6)	393
C(3')	0.217 (1)	1.276 (1)	0.1832 (7)	564
C(3a)	0.290 (1)	0.7449 (7)	0.6523 (6)	317
C(4')	0.223 (1)	1.3296 (9)	0.2549 (8)	554
C(4a)	0.302 (1)	0.9037 (7)	0.7367 (6)	346
C(5)	0.311 (1)	1.0044 (7)	0.7656 (7)	445
C(5')	0.211 (1)	1.2542 (8)	0.3542 (7)	464
C(6)	0.302 (1)	0.9935 (9)	0.8629 (8)	573
C(6')	0.199 (1)	1.1307 (8)	0.3796 (6)	449
C(7)	0.287 (1)	0.880 (1)	0.9350 (7)	579
C(8)	0.276 (1)	0.7752 (8)	0.9081 (6)	470
C(8a)	0.284 (1)	0.7856 (7)	0.8073 (6)	350
C(8b)	0.278 (1)	0.6922 (7)	0.7603 (6)	344
C(9)	0.265 (1)	0.4235 (7)	0.6796 (8)	562
C(10)	0.463 (2)	0.353 (1)	0.690 (1)	1146
C(11)	0.096 (2)	0.3509 (9)	0.753 (1)	804
N(1)	0.262 (1)	0.5456 (6)	0.6936 (5)	424
N(2)	0.184 (1)	0.9487 (7)	0.3278 (6)	511
N(3)	0.227 (1)	1.355 (1)	0.0777 (8)	907
N(4)	0.211 (1)	1.3078 (9)	0.4359 (8)	609
O(1)	0.203 (1)	0.8850 (6)	0.4129 (5)	772
O(2)	0.161 (1)	0.9049 (7)	0.2644 (6)	779
O(3)	0.219 (1)	1.303 (1)	0.0143 (7)	1219
O(4)	0.252 (2)	1.461 (1)	0.0596 (7)	1394
O(5)	0.204 (1)	1.4189 (7)	0.4139 (7)	949
O(6)	0.227 (1)	1.2367 (8)	0.5180 (6)	821

checked by optical polarizing microscopy. Intensity data were collected with  $\omega/2\theta$  scans, variable scan speed  $0.5\text{--}8.1^\circ\text{min}^{-1}$  in  $\theta$ , scan width  $1.2^\circ +$  dispersion. A Nicolet R3m/V diffractometer with graphite-monochromated Mo  $K\alpha$  radiation was used. The lattice parameters were determined from a symmetry-constrained least-squares fit of 50 reflections with  $2\theta_{\text{max}} = 26.18^\circ$ .  $\omega$  scans of low-order reflections along the three crystal axes showed acceptable mosaicity. Six standard reflections (200,  $\bar{1}20$ , 003,  $\bar{2}00$ ,  $1\bar{2}0$ , 00 $\bar{3}$ ) were recorded every 300 reflections, only random deviations were detected during 235.5 h of X-ray exposure; 3895 reflections with  $2.0 \leq 2\theta \leq 44.0^\circ$  (4692 accessible),  $-8 \leq h \leq 2$ ,  $-13 \leq k \leq 13$ ,  $-15 \leq l \leq 15$  were measured. The data were corrected for Lorentz-polarization but not for absorption effects because of the small absorption coefficient and averaged ( $R_{\text{int}} = 0.116$ ) to 2273 unique reflections, 1566 of which had  $F \geq 4.0\sigma(F)$ . The structure was solved *via* direct methods and  $\Delta\rho$  maps. It was refined (on  $F$ ) using full-matrix least squares with anisotropic displacement parameters for all non-H atoms and for each molecular unit a common isotropic one for the H atoms, which were placed in geometrically calculated positions (C—H  $0.96 \text{ \AA}$ ). 283 parameters were refined. Weights  $w = 1.0/[\sigma^2(F) + (0.007F^2)]$  led to a featureless analysis of variance in terms of  $\sin\theta$  and  $F_o$ . The refinement converged to  $S = 1.03$ ,  $R = 0.076$ ,  $wR = 0.082$ ,  $(\Delta/\sigma)_{\text{max}} = 0.005$  (no extinction correction). The relatively high values of the  $R$  factors can be attributed

Table 2. Bond distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ), torsion angles ( $^\circ$ ), least-squares planes and dihedral angles, possible hydrogen bonds and short intermolecular contacts ( $\text{\AA}$ )

S(1)—C(3a)	1.736 (8)	C(5)—C(6)	1.34 (2)
S(1)—C(4a)	1.767 (9)	C(5')—C(6')	1.36 (1)
Cl(1)—C(7)	1.74 (1)	C(5')—N(4)	1.48 (2)
C(1)—C(8b)	1.36 (1)	C(6)—C(7)	1.38 (1)
C(1)—N(1)	1.34 (1)	C(7)—C(8)	1.39 (2)
C(1')—C(2')	1.38 (1)	C(8)—C(8a)	1.39 (1)
C(1')—C(6')	1.40 (1)	C(8a)—C(8b)	1.44 (1)
C(1')—N(2)	1.45 (1)	C(9)—C(10)	1.50 (2)
C(2')—C(3')	1.39 (2)	C(9)—C(11)	1.52 (1)
C(3)—C(3a)	1.37 (1)	C(9)—N(1)	1.48 (1)
C(3)—N(1)	1.365 (9)	N(2)—O(1)	1.23 (1)
C(3')—C(4')	1.36 (2)	N(2)—O(2)	1.21 (1)
C(3')—N(3)	1.48 (1)	N(3)—O(3)	1.24 (2)
C(3a)—C(8b)	1.45 (1)	N(3)—O(4)	1.20 (2)
C(4')—C(5')	1.39 (1)	N(4)—O(5)	1.21 (1)
C(4a)—C(5)	1.36 (1)	N(4)—O(6)	1.21 (1)
C(4a)—C(8a)	1.41 (1)		
C(3a)—S(1)—C(4a)	91.2 (4)	C(6)—C(7)—C(8)	120.5 (9)
C(8b)—C(1)—N(1)	109.3 (8)	Cl(1)—C(7)—C(8)	118.7 (7)
C(6')—C(1')—N(2)	118.6 (7)	C(7)—C(8)—C(8a)	119.3 (9)
C(2')—C(1')—N(2)	118.5 (8)	C(4a)—C(8a)—C(8)	117.7 (8)
C(2')—C(1')—C(6')	122.8 (8)	C(8)—C(8a)—C(8b)	130.0 (8)
C(1')—C(2')—C(3')	115.9 (8)	C(4a)—C(8a)—C(8b)	112.3 (7)
C(1')—C(2')—H(2')	122 (1)	C(3a)—C(8b)—C(8a)	111.1 (7)
C(3a)—C(3)—N(1)	107.4 (7)	C(1)—C(8b)—C(8a)	143.2 (8)
C(2')—C(3')—N(3)	118 (1)	C(1)—C(8b)—C(3a)	105.7 (7)
C(2')—C(3')—C(4')	124 (1)	C(11)—C(9)—N(1)	110.9 (8)
C(4')—C(3')—N(3)	118 (1)	C(10)—C(9)—N(1)	111.1 (9)
S(1)—C(3a)—C(3)	140.1 (7)	C(10)—C(9)—C(11)	110.6 (9)
C(3)—C(3a)—C(8b)	107.2 (7)	C(3)—N(1)—C(9)	122.4 (7)
S(1)—C(3a)—C(8b)	112.7 (6)	C(1)—N(1)—C(9)	126.9 (7)
C(3')—C(4')—C(5')	118 (1)	C(1)—N(1)—C(3)	110.4 (7)
S(1)—C(4a)—C(8a)	112.7 (6)	C(1')—N(2)—O(2)	119.5 (8)
S(1)—C(4a)—C(5)	125.8 (7)	C(1')—N(2)—O(1)	118.2 (8)
C(5)—C(4a)—C(8a)	121.6 (8)	O(1)—N(2)—O(2)	122.3 (9)
C(4a)—C(5)—C(6)	120.2 (9)	C(3')—N(3)—O(4)	118 (1)
C(4')—C(5')—N(4)	120.1 (9)	C(3')—N(3)—O(3)	117 (1)
C(4')—C(5')—C(6')	122.1 (9)	O(3)—N(3)—O(4)	125 (1)
C(6')—C(5')—N(4)	117.8 (9)	C(5')—N(4)—O(6)	117 (1)
C(5)—C(6)—C(7)	121 (1)	C(5')—N(4)—O(5)	117 (1)
C(1')—C(6')—C(5')	117.7 (8)	O(5)—N(4)—O(6)	126 (1)
Cl(1)—C(7)—C(6)	120.8 (8)		
C(6')—C(1')—N(2)—O(1)	-7 (1)	C(11)—C(9)—N(1)—C(1)	54 (1)
C(2')—C(3')—N(3)—O(3)	1 (2)	C(10)—C(9)—N(1)—C(1)	-69 (1)
C(4')—C(5')—N(4)—O(5)	7 (1)		

No.	Plane through atoms	Equation of the plane	$\chi^2$
1	N(1), C(1), C(3), C(3a), C(8b)	$0.966x - 0.209y - 0.151z = 1.47 \text{ \AA}$	0.3
2	S(1), C(3a), C(4a), C(8a), C(8b)	$0.970x - 0.197y - 0.141z = 1.72 \text{ \AA}$	0.6
3	C(4a), C(5), C(6), C(7), C(8), C(8a)	$0.9700x - 0.196y - 0.144z = 1.69 \text{ \AA}$	2.2
4	C(1'), C(2'), C(3'), C(4'), C(5'), C(6')	$0.966x - 0.197y - 0.168z = 0.52 \text{ \AA}$	2.8

Dihedral angles: 1,2  $0.9(2)^\circ$ , 1,3  $0.9(3)^\circ$ , 1,4  $1.2(3)^\circ$ , 2,3  $0.2(2)^\circ$ , 2,4  $1.6(2)^\circ$ , 3,4  $1.4(2)^\circ$ .

## Possible hydrogen bonds

$D \cdots A$ ( $\text{\AA}$ )	$H \cdots A$ ( $\text{\AA}$ )	$D-H \cdots A$ ( $^\circ$ )
C(3) $\cdots$ O(1) <sup>i</sup>	H(3) $\cdots$ O(1) <sup>i</sup>	C(3)—H(3) $\cdots$ O(1) <sup>i</sup>
3.34 (1)	2.760 (9)	119.5 (8)
C(10) $\cdots$ O(5) <sup>ii</sup>	H(10c) $\cdots$ O(5) <sup>ii</sup>	C(10)—H(10c) $\cdots$ O(5) <sup>ii</sup>
3.46 (1)	2.62 (1)	146 (1)

## Short intermolecular contacts

Cl(1) $\cdots$ O(2)	( $x, y, 1+z$ )	2.977 (9)	S(1) $\cdots$ O(1)	3.159 (9)
S(1) $\cdots$ H(6')		2.761 (8)		

Symmetry codes: (i)  $x, y, z$ ; (ii)  $-x+1, -y+2, -z+1$ .

to the fact that the crystal diffracted very weakly and had a great number of non-significant measurements. The correctness of the space-group choice was checked by using *MISSYM* (Le Page, 1987). The largest peaks in final  $\Delta\rho$  map were  $\pm 0.4(2) \text{ e \AA}^{-3}$ . Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography* (1974,

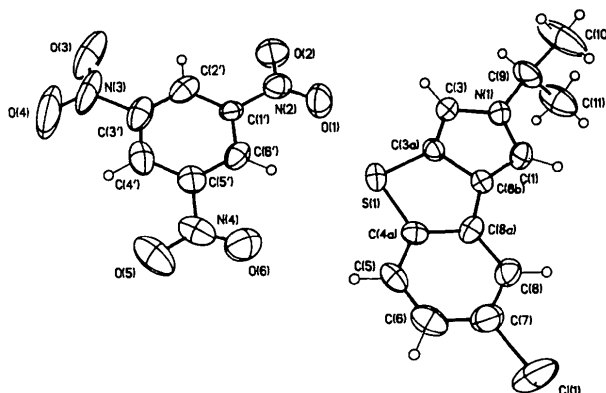


Fig. 1. General view (*SHELXTL-Plus* graphic) of the molecule, showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries.

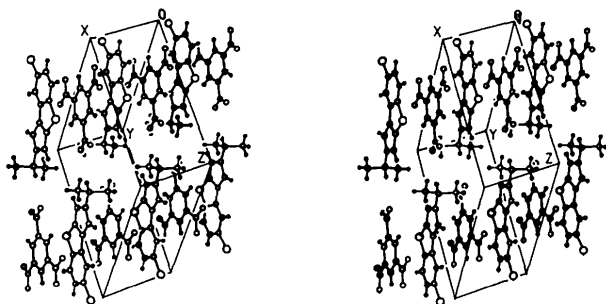


Fig. 2. Stereoscopic view (*SHELXTL-Plus* graphic) of the unit cell. Dashed lines correspond to short intermolecular contacts.

Vol. IV). The programs used were *PARST* (Nardelli, 1983), *SHELX76* (Sheldrick, 1976), *SHELXTL-Plus* (Sheldrick, 1987), *PCK83* (Williams, 1984), *PLATON* (Spek, 1982), and *MISSYM* (Le Page, 1987). The molecule and the numbering scheme are shown in Fig. 1 and a stereoscopic view of the unit-cell contents is in Fig. 2. Positional parameters and the equivalent values of the anisotropic dis-

placement parameters for the non-H atoms are given in Table 1.\* Bond lengths, bond angles, torsion angles, least-squares planes, dihedral angles, possible hydrogen bonds and short intermolecular contacts are given in Table 2.

**Related literature.** For charge-transfer complexes see Parini (1962), Thesing, Melchior & Schäfer (1964), Foster (1976), Bleidelis, Shvets & Freimanis (1976) and Jelitto (1989). For preparation and spectroscopic data of tricyclic  $14\pi$ -hetarenes see Dyker (1988) and Götte (1990).

\* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54023 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## The Diels–Alder Diadduct of Hexachlorocyclopentadiene with Cyclooctatetraene

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**Abstract.** *endo,endo*-1,5,6,7,8,14,15,16,17,17,18,18-Dodecachlorohexacyclo[12.2.1.1<sup>5,8</sup>.0<sup>2,13</sup>.0<sup>3,12</sup>.0<sup>4,9</sup>]octa-

deca-6,10,15-triene,  $C_{18}H_8Cl_{12}$ ,  $M_r = 649.7$ , orthorhombic,  $P2_12_12_1$ ,  $a = 13.028$  (2),  $b = 13.0214$  (12),  $c = 14.252$  (2) Å,  $V = 2417.7$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.785$  g cm<sup>-3</sup>;  $\lambda(\text{Cu } K\alpha) = 1.54184$  Å,  $\mu =$

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