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

C(1)—C(2)	1·333 (7)	C(13)—C(14)	1·543 (7)
C(1)—C(10)	1·500 (7)	C(13)—C(17)	1·564 (7)
C(2)—C(3)	1·460 (7)	C(13)—C(19)	1·528 (7)
C(3)—C(4)	1·444 (7)	C(14)—C(15)	1·509 (7)
C(3)—O(25)	1·236 (7)	C(15)—C(16)	1·552 (7)
C(4)—C(5)	1·336 (7)	C(16)—C(17)	1·566 (7)
C(5)—C(6)	1·513 (7)	C(16)—C(22)	1·509 (9)
C(5)—C(10)	1·511 (7)	C(17)—C(20)	1·543 (7)
C(6)—C(7)	1·511 (7)	C(17)—O(29)	1·458 (6)
C(6)—O(26)	1·401 (6)	C(20)—C(21)	1·504 (8)
C(7)—C(8)	1·527 (7)	C(20)—O(28)	1·192 (7)
C(8)—C(9)	1·538 (7)	C(21)—Cl(24)	1·771 (8)
C(8)—C(14)	1·518 (7)	O(29)—C(30)	1·325 (6)
C(9)—C(10)	1·577 (7)	C(30)—O(31)	1·219 (7)
C(9)—C(11)	1·553 (6)	C(30)—C(32)	1·449 (7)
C(9)—Cl(23)	1·841 (5)	C(32)—C(33)	1·333 (11)
C(10)—C(18)	1·555 (7)	C(32)—O(36)	1·355 (6)
C(11)—C(12)	1·530 (6)	C(33)—C(34)	1·389 (13)
C(11)—O(27)	1·413 (5)	C(34)—C(35)	1·331 (11)
C(12)—C(13)	1·533 (7)	C(35)—O(36)	1·356 (7)

C(2)—C(1)—C(10)	124·7 (4)	C(12)—C(13)—C(17)	117·3 (4)
C(1)—C(2)—C(3)	120·7 (5)	C(12)—C(13)—C(19)	111·1 (4)
C(2)—C(3)—C(4)	117·1 (5)	C(14)—C(13)—C(17)	98·9 (4)
C(2)—C(3)—O(25)	122·1 (5)	C(14)—C(13)—C(19)	112·8 (4)
C(4)—C(3)—O(25)	120·9 (5)	C(17)—C(13)—C(19)	108·4 (4)
C(3)—C(4)—C(5)	123·0 (5)	C(8)—C(14)—C(13)	113·9 (4)
C(4)—C(5)—C(6)	121·8 (4)	C(8)—C(14)—C(15)	118·2 (4)
C(4)—C(5)—C(10)	122·4 (4)	C(13)—C(14)—C(15)	104·4 (4)
C(6)—C(5)—C(10)	115·7 (4)	C(14)—C(15)—C(16)	103·9 (4)
C(5)—C(6)—C(7)	112·5 (4)	C(15)—C(16)—C(17)	106·0 (4)
C(5)—C(6)—O(26)	111·9 (4)	C(15)—C(16)—C(22)	112·4 (5)
C(7)—C(6)—O(26)	112·2 (4)	C(17)—C(16)—C(22)	117·0 (5)
C(6)—C(7)—C(8)	115·2 (4)	C(13)—C(17)—C(16)	103·5 (4)
C(7)—C(8)—C(9)	111·7 (4)	C(13)—C(17)—C(20)	113·2 (4)
C(7)—C(8)—C(14)	110·6 (4)	C(13)—C(17)—O(29)	104·8 (4)
C(9)—C(8)—C(14)	111·1 (4)	C(16)—C(17)—C(20)	113·0 (4)
C(8)—C(9)—C(10)	110·4 (4)	C(16)—C(17)—O(29)	111·8 (4)
C(8)—C(9)—C(11)	113·0 (4)	C(20)—C(17)—O(29)	110·3 (4)
C(8)—C(9)—Cl(23)	108·1 (3)	C(17)—C(20)—C(21)	116·0 (4)
C(10)—C(9)—C(11)	115·9 (4)	C(17)—C(20)—O(28)	122·2 (5)
C(10)—C(9)—Cl(23)	105·9 (3)	C(21)—C(20)—O(28)	121·5 (5)
C(11)—C(9)—Cl(23)	102·7 (3)	C(20)—C(21)—Cl(24)	114·2 (5)
C(1)—C(10)—C(5)	112·0 (4)	C(17)—O(29)—C(30)	120·8 (4)
C(1)—C(10)—C(9)	110·9 (4)	O(29)—C(30)—O(31)	124·8 (5)
C(1)—C(10)—C(18)	106·2 (4)	O(29)—C(30)—C(32)	110·9 (4)
C(5)—C(10)—C(9)	107·3 (4)	O(31)—C(30)—C(32)	124·3 (5)
C(5)—C(10)—C(18)	106·9 (4)	C(30)—C(32)—C(33)	134·4 (6)
C(9)—C(10)—C(18)	113·6 (4)	C(30)—C(32)—O(36)	116·0 (4)
C(9)—C(11)—C(12)	113·3 (3)	C(33)—C(32)—O(36)	109·5 (5)
C(9)—C(11)—O(27)	108·9 (3)	C(32)—C(33)—C(34)	107·3 (8)
C(12)—C(11)—O(27)	111·2 (3)	C(33)—C(34)—C(35)	106·9 (8)
C(11)—C(12)—C(13)	113·5 (4)	C(34)—C(35)—O(36)	109·7 (6)
C(12)—C(13)—C(14)	107·8 (4)	C(32)—O(36)—C(35)	106·5 (4)

angles are listed in Table 2. A perspective view of the molecule with atom labeling is presented in Fig. 1.

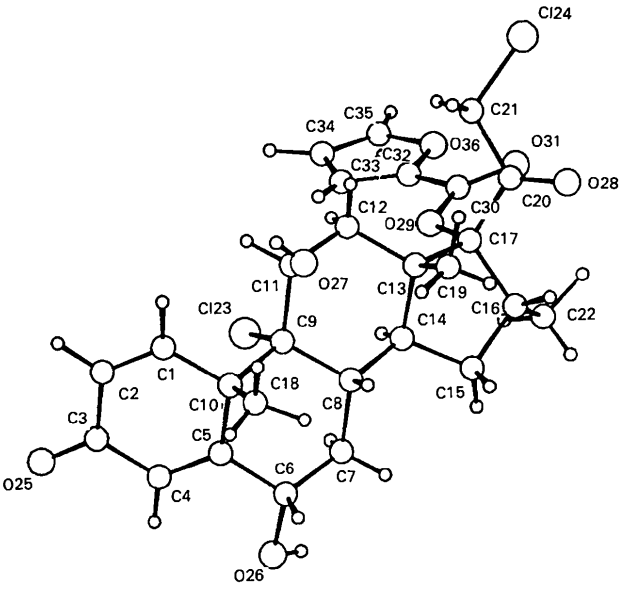

Fig. 1. Perspective view drawn by *PLUTO* (Motherwell & Clegg, 1978).

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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Acta Cryst. (1991). C**47**, 1767–1769

Structure of a 1,4-Dien-3-one-6β-hydroxy Steroid Methanol Solvate

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(*Received* 10 *January* 1991; *accepted* 6 *February* 1991)

Abstract. 9α,21-Dichloro-6β,11β,17α-trihydroxy-16α-methylpregna-1,4-diene-3,20-dione methanol solvate, $C_{22}H_{28}Cl_2O_5.\frac{1}{2}CH_3OH$, $M_r = 459{\cdot}385$, monoclinic, $C2$, $a = 25{\cdot}506\ (5)$, $b = 8{\cdot}371\ (1)$, $c = 15{\cdot}035\ (3)$ Å, $\beta = 136{\cdot}99\ (1)°$, $V = 2189{\cdot}8\ (8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}393$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ =

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Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2), *and occupancies for solvents*

$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}	S.o.f.
C(1)	0·6048 (1)	0·7076 (3)	−0·0781 (2)	3·2 (1)	
C(2)	0·5964 (1)	0·7757 (3)	−0·1686 (2)	3·5 (1)	
C(3)	0·5897 (1)	0·6777 (3)	−0·2569 (2)	3·2 (1)	
C(4)	0·5947 (1)	0·5055 (3)	−0·2399 (2)	3·3 (1)	
C(5)	0·6015 (1)	0·4353 (3)	−0·1517 (2)	2·9 (1)	
C(6)	0·6062 (1)	0·2550 (3)	−0·1404 (2)	3·4 (1)	
C(7)	0·6687 (1)	0·1990 (3)	0·0016 (2)	3·6 (1)	
C(8)	0·6744 (1)	0·2943 (2)	0·0950 (2)	2·5 (1)	
C(9)	0·6770 (1)	0·4764 (2)	0·0808 (2)	2·4 (1)	
C(10)	0·6033 (1)	0·5311 (3)	−0·0637 (2)	2·7 (1)	
C(11)	0·6976 (1)	0·5776 (3)	0·1895 (2)	2·9 (1)	
C(12)	0·7651 (1)	0·5086 (3)	0·3279 (2)	2·9 (1)	
C(13)	0·7568 (1)	0·3300 (2)	0·3381 (2)	2·4 (1)	
C(14)	0·7448 (1)	0·2418 (2)	0·2345 (2)	2·5 (1)	
C(15)	0·7536 (1)	0·0645 (3)	0·2692 (2)	3·3 (1)	
C(16)	0·8117 (1)	0·0625 (3)	0·4199 (2)	3·4 (1)	
C(17)	0·8315 (1)	0·2412 (3)	0·4620 (2)	2·8 (1)	
C(18)	0·5270 (1)	0·4985 (4)	−0·1068 (2)	3·6 (1)	
C(19)	0·6913 (1)	0·3011 (3)	0·3238 (2)	3·3 (1)	
C(20)	0·8512 (1)	0·2735 (3)	0·5849 (2)	3·0 (1)	
C(21)	0·9050 (2)	0·4103 (4)	0·6691 (2)	3·9 (1)	
C(22)	0·8817 (2)	−0·0441 (4)	0·4908 (3)	5·2 (2)	
Cl(23)	0·75825 (3)	0·51935	0·10646 (5)	3·25 (3)	
Cl(24)	0·93102 (4)	0·43048 (10)	0·81452 (6)	4·22 (3)	
O(25)	0·5817 (1)	0·7410 (3)	−0·3407 (2)	4·3 (1)	
O(26)	0·5344 (1)	0·1878 (3)	−0·2053 (2)	5·3 (1)	
O(27)	0·6295 (1)	0·5925 (3)	0·1562 (1)	4·0 (1)	
O(28)	0·8244 (1)	0·1947 (3)	0·6104 (2)	5·0 (1)	
O(29)	0·8981 (1)	0·2946 (2)	0·4979 (1)	3·3 (1)	
C(30)	1·0000	0·6149 (8)	0·5000	8·3 (6)	0·5
O(31)	0·9773 (5)	0·5881 (9)	0·5587 (7)	5·7 (5)	0·3
O(32)	0·9725 (9)	0·5731 (16)	0·4044 (11)	6·7 (9)	0·2

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

C(1)—C(2)	1·340 (4)	C(10)—C(18)	1·561 (5)
C(1)—C(10)	1·498 (4)	C(11)—C(12)	1·545 (4)
C(2)—C(3)	1·460 (4)	C(11)—O(27)	1·418 (4)
C(3)—C(4)	1·453 (4)	C(12)—C(13)	1·533 (4)
C(3)—O(25)	1·238 (4)	C(13)—C(14)	1·539 (4)
C(4)—C(5)	1·341 (4)	C(13)—C(17)	1·569 (4)
C(5)—C(6)	1·514 (4)	C(13)—C(19)	1·540 (4)
C(5)—C(10)	1·519 (4)	C(14)—C(15)	1·534 (4)
C(6)—C(7)	1·530 (4)	C(15)—C(16)	1·556 (4)
C(6)—O(26)	1·417 (4)	C(16)—C(17)	1·558 (4)
C(7)—C(8)	1·527 (4)	C(16)—C(22)	1·529 (6)
C(8)—C(9)	1·547 (4)	C(17)—C(20)	1·543 (4)
C(8)—C(14)	1·519 (4)	C(17)—O(29)	1·427 (4)
C(9)—C(10)	1·578 (4)	C(20)—C(21)	1·502 (6)
C(9)—C(11)	1·552 (4)	C(20)—O(28)	1·197 (4)
C(9)—Cl(23)	1·845 (3)	C(21)—Cl(24)	1·768 (5)

C(2)—C(1)—C(10)	124·4 (3)	C(9)—C(11)—C(12)	113·6 (2)
C(1)—C(2)—C(3)	120·6 (3)	C(9)—C(11)—O(27)	107·0 (2)
C(2)—C(3)—C(4)	117·4 (3)	C(12)—C(11)—O(27)	112·3 (2)
C(2)—C(3)—O(25)	120·5 (3)	C(11)—C(12)—C(13)	113·6 (2)
C(4)—C(3)—O(25)	122·1 (3)	C(12)—C(13)—C(14)	107·8 (2)
C(3)—C(4)—C(5)	122·7 (3)	C(12)—C(13)—C(17)	116·4 (2)
C(4)—C(5)—C(6)	119·4 (3)	C(12)—C(13)—C(19)	110·8 (2)
C(4)—C(5)—C(10)	122·0 (3)	C(14)—C(13)—C(17)	98·3 (2)
C(6)—C(5)—C(10)	118·6 (3)	C(14)—C(13)—C(19)	113·0 (2)
C(5)—C(6)—C(7)	112·2 (2)	C(17)—C(13)—C(19)	110·1 (2)
C(5)—C(6)—O(26)	111·2 (3)	C(8)—C(14)—C(13)	114·7 (2)
C(7)—C(6)—O(26)	110·0 (3)	C(8)—C(14)—C(15)	118·7 (3)
C(6)—C(7)—C(8)	115·1 (2)	C(13)—C(14)—C(15)	104·4 (2)
C(7)—C(8)—C(9)	111·9 (2)	C(14)—C(15)—C(16)	104·6 (2)
C(7)—C(8)—C(14)	109·9 (2)	C(15)—C(16)—C(17)	105·2 (2)
C(9)—C(8)—C(14)	110·4 (2)	C(15)—C(16)—C(22)	113·9 (3)
C(8)—C(9)—C(10)	110·3 (2)	C(17)—C(16)—C(22)	114·3 (3)
C(8)—C(9)—C(11)	114·1 (2)	C(13)—C(17)—C(16)	102·8 (2)
C(8)—C(9)—Cl(23)	108·5 (2)	C(13)—C(17)—C(20)	112·8 (2)
C(10)—C(9)—C(11)	115·9 (2)	C(13)—C(17)—O(29)	112·1 (2)
C(10)—C(9)—Cl(23)	104·9 (2)	C(16)—C(17)—C(20)	112·3 (2)
C(11)—C(9)—Cl(23)	102·1 (2)	C(16)—C(17)—O(29)	113·4 (2)
C(1)—C(10)—C(5)	112·5 (2)	C(20)—C(17)—O(29)	103·7 (2)
C(1)—C(10)—C(9)	110·8 (2)	C(17)—C(20)—C(21)	116·1 (3)
C(1)—C(10)—C(18)	105·6 (2)	C(17)—C(20)—O(28)	121·6 (3)
C(5)—C(10)—C(9)	107·0 (2)	C(21)—C(20)—O(28)	122·3 (3)
C(5)—C(10)—C(18)	108·2 (2)	C(20)—C(21)—Cl(24)	113·6 (3)
C(9)—C(10)—C(18)	112·9 (2)		

2·96 mm^{-1}, $F(000) = 972$, $T = 295$ K, $R = 0{\cdot}032$ for 2125 observed reflections [$F_o > 3\sigma(F_o)$]. The molecules are linked by intermolecular hydrogen bonds O(28)—HO(27)($\frac{3}{2}-x, y-\frac{1}{2}, 1-z$) = 2·897 (4) [2·11 (5) for O···H] and O(25)—HO(29)($\frac{3}{2}-x, \frac{1}{2}+y, -z$) = 2·799 (4) Å [2·05 (5) Å]. Disordered solvent molecules are contained in the crystal structure.

Experimental. Colorless plate crystals obtained from methanol. Crystal of dimensions 0·3 × 0·3 × 0·2 mm. Rigaku AFC-5R diffractometer, graphite-monochromatized Cu $K\alpha$. Cell dimensions determined from 2θ angles for 25 reflections in the range $27 < 2\theta < 44°$. Intensities measured up to $\theta = 70°$ in h 0/30, k 0/10 and l −18/12, ω–2θ scans, ω-scan width $(1 + 0{\cdot}2\tan\theta)°$, three standard reflections monitored every 100 measurements showed no significant change. 2180 unique reflections measured, 2125 intensities observed [$F_o \leq 3\sigma(F_o)$ and 11 very strong reflections rejected], no absorption corrections. Structures solved by *MULTAN*84 (Main, Germain & Woolfson, 1984). H atoms and three peaks located on a difference density map. One of these three peaks was on a twofold axis and two were near the axis. These peaks explained four disordered methanol molecules. Occupancies of the methanol molecules from thermal parameters in least-squares refinements. Positional parameters of all atoms and anisotropic thermal parameters of non-H atoms refined by block-diagonal least squares. Temperature factors of each H atom equal to B_{eq} of the bonded atom. $\sum(w|\Delta F|^2)$ minimized, $w = 1/[\sigma^2(F_o) + 0{\cdot}00111|F_o|^2]$, $w = 0$ for 55 reflections with $w^{1/2}|\Delta F| \geq 3$. The final $R = 0{\cdot}032$, $wR = 0{\cdot}039$, $S = 1{\cdot}0691$. Max. Δ/σ in the final cycle 0·03. Max. and min. peaks in the final difference map

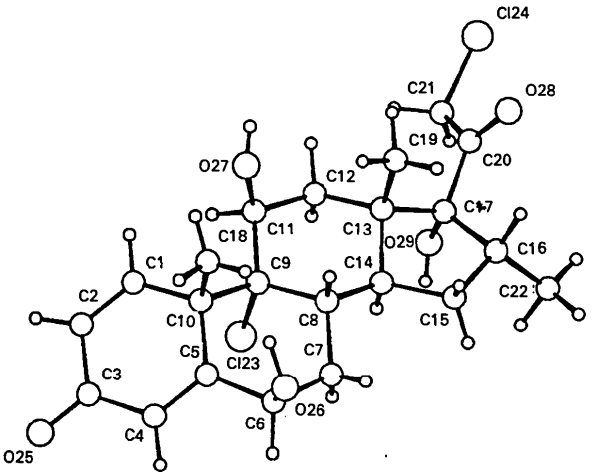

Fig. 1. Perspective view drawn by *PLUTO* (Motherwell & Clegg, 1978).

0·3 and −0·2 e Å^{-3}. Atomic scattering factors calculated by $\sum[a_i\exp(-b_i\lambda^{-2}\sin^2\theta)] + c$ ($i = 1,...,4$) (*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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Acta Cryst. (1991). C**47**, 1769–1771

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

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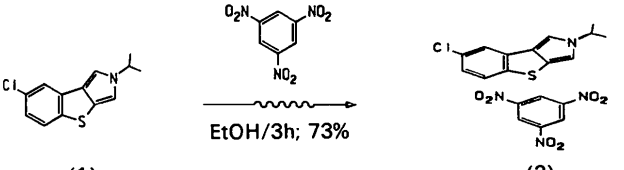
(*Received* 14 *January* 1991; *accepted* 20 *February* 1991)

Abstract. 5-Chloro-2-isopropyl-2*H*-1-benzothieno-[2,3-*c*]pyrrole–trinitrobenzene (1/1), $C_{13}H_{12}ClNS.C_6H_3N_3O_6$, $M_r = 462{\cdot}86$, triclinic, $P\bar{1}$, $a = 6{\cdot}891$ (3), $b = 11{\cdot}498$ (4), $c = 14{\cdot}223$ (3) Å, $\alpha = 71{\cdot}53$ (2), $\beta = 76{\cdot}77$ (3), $\gamma = 82{\cdot}23$ (3)°, $V = 1038{\cdot}1$ (6) Å^3, $Z = 2$, $D_x = 1{\cdot}481$ Mg m^{-3}, $F(000) = 476$, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}32$ mm^{-1}, $T = 291$ (1) K, final $R = 0{\cdot}076$ for 1566 unique observed [$F \geq 4{\cdot}0\sigma(F)$] diffractometer data. $C_6H_3N_3O_6$ (I) and $C_{13}H_{12}ClNS$ (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 ···(I)···(II)···(I)···(II)··· 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 π–π^* interaction between the 14π-donor and the 6π-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 π 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-2*H*-1-benzothieno[2,3-*c*]pyrrole (1), an example of the hitherto unknown 14π-hetarene, complexation was carried out with 1,3,5-trinitrobenzene (TNB) in ethanol (3 h; reflux).



(1) (2)

In order to determine the orientation and distance of the acceptor molecule in relation to the tricyclic 14π-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 ~0·29 × 0·10 × 0·03 mm was used. Its quality was

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