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The Structure of the Charge-Transfer Complex Skatole–Tetracyanoethylene

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Abstract. $C_9H_9N.C_6N_4$, monoclinic, $C2/c$, $Z = 8$, $a = 10{\cdot}07\,(1)$, $b = 9{\cdot}97\,(1)$, $c = 26{\cdot}45\,(2)$ Å, $\beta = 88{\cdot}91\,(5)^\circ$, $D_x = 1{\cdot}297\,(3)$, $D_m = 1{\cdot}30\,(1)$ Mg m^{-3}. Refinement in two blocks gave $R = 0{\cdot}111$ for 1852 counter reflections with $F/\sigma(F) > 2{\cdot}5$. The structure consists of two symmetry-related donor–acceptor stacks of skatole and TCNE molecules.

Introduction. Solution studies of the skatole–TCNE complex showed a well defined charge-transfer band at 550 nm (18 000 cm^{-1}). The rate of complex formation appears to be very fast, because of the immediate development of a deep-blue color.

Blue prismatic crystals were obtained from the solution by slow evaporation of the 1,2-dichloroethane solvent. When left in air at room temperature for several days, the crystals turned light brown.

Weissenberg photographs showed the systematic extinctions hkl for $h + k \neq 2n$ and $h0l$ for $l \neq 2n$. A statistical analysis of $|E_2 - 1|$ for visually estimated data indicated the space group $C2/c$. The R factor between symmetry-related structure factors ($R_{\rm sym}$) was 0·24 for the visually estimated data, indicating poor crystal quality.

The intensities were collected with a Nonius CAD-4 four-circle diffractometer using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å) and the $\omega/2\theta$ variable-scan method. $R_{\rm sym}$ was 0·14 for the best crystal available, also indicating poor crystal quality. The 1951 unique reflections measured were corrected for Lorentz and polarization effects but not for absorption or extinction ($\mu = 0{\cdot}587$ mm^{-1}). $R_{\rm sym}$ could not be improved by varying data-collection parameters.

The structure was solved by direct methods using *SHELX* (Sheldrick, 1975). The initial solutions showed hexagonal lattices of electron density typical of incorrect solutions of planar structures containing hexagonal rings.

E values were therefore renormalized using the equation:

$$\mathrm{new}(E^2) = \mathrm{old}(E^2)[\underset{A}{0{\cdot}99} - \underset{B}{0{\cdot}03}\cos(\underset{x}{0{\cdot}32}\,h + \underset{y}{0{\cdot}12}\,k + \underset{z}{0{\cdot}017}\,l)]$$

where A and B are refined by least squares, h,k,l are the Miller indices of the reflection and x,y,z are the components in fractional coordinates of a vector normal to the molecular plane (as observed in the incorrect solution) with length equal to the observed interplanar distance.

This new normalization led to a solution which showed two skatole molecules, one with much higher peaks than the other, with positions related by a non-crystallographic center of symmetry. These molecules were translated until the non-crystallographic inversion coincided with a crystallographic one. A Fourier map phased with these atomic positions showed the TCNE molecule

For refinement by least squares, the complex was divided in two blocks, one for the skatole molecule and the other for the TCNE molecule. H atoms were located using stereochemical considerations. After anisotropic refinement using weights $w = 1/[\sigma^2(F) + 0{\cdot}0001F^2]$, the final R was 0·111 for the 1852 reflections with $F > 2{\cdot}5\sigma(F)$ and 0·118 for all 1951

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Table 1. *Final atomic positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *with standard deviations in parentheses*

The stereochemistry of the methyl group was held rigid and therefore no standard deviations are quoted.

	x	y	z
C(1)	2593 (4)	676 (4)	4108 (2)
C(2)	3060 (5)	1808 (6)	4366 (2)
C(3)	3425 (5)	2882 (5)	4070 (3)
C(4)	3347 (5)	2861 (5)	3549 (3)
C(5)	2907 (4)	1753 (5)	3298 (2)
C(6)	2519 (4)	637 (4)	3579 (2)
C(7)	2016 (4)	−675 (4)	3443 (2)
C(8)	1815 (4)	−1327 (5)	3883 (2)
C(9)	1746 (5)	−1133 (5)	2912 (2)
N(1)	2174 (4)	−567 (4)	4289 (1)
C(10)	90 (5)	3424 (5)	4114 (2)
C(11)	3 (4)	3338 (5)	3629 (2)
C(12)	−370 (5)	2320 (5)	4431 (2)
C(13)	666 (4)	4592 (5)	4346 (2)
C(14)	490 (5)	4419 (5)	3301 (2)
C(15)	−514 (5)	2140 (5)	3377 (2)
N(2)	−712 (4)	1521 (5)	4700 (2)
N(3)	1123 (4)	5462 (4)	4550 (2)
N(4)	843 (5)	5235 (5)	3036 (2)
N(5)	−876 (5)	1255 (5)	3154 (2)
H(1)	208 (5)	−73 (5)	461 (2)
H(2)	298 (5)	173 (5)	475 (2)
H(3)	379 (5)	371 (5)	423 (2)
H(4)	367 (5)	372 (5)	332 (2)
H(5)	286 (5)	167 (5)	290 (2)
H(6)	195	−18	273
H(7)	73	−142	285
H(8)	137 (5)	−221 (5)	393 (2)
H(9)	240	−189	275

measured unique reflections. Several weighting schemes were tried but R could not be lowered further; its high value is probably due to the poor quality of the crystal, as shown previously by the high value of R_{sym}. The r.m.s. value of the shift/e.s.d. for all parameters was 0·02. The scattering factors were taken from Cromer & Mann (1968).

The final fractional coordinates with e.s.d.'s are listed in Table 1.* Fig. 1 shows the bond distances and angles for both molecules, which are similar to those previously reported (Ikemoto & Kuroda, 1967; Hanson, 1964).

Discussion. The two molecules of the complex are planar within experimental error. The r.m.s. distances to the mean molecular plane are 0·03 Å for the TCNE and 0·01 Å for the skatole non-hydrogen atoms. The angle between the mean planes of the skatole and TCNE molecules is 4·0°, and both planes are close to the [310] direction.

Fig. 2 shows the superposition of the skatole molecule with the two neighboring TCNE molecules. One TCNE molecule is stacked on top of the six-membered ring of the skatole, at a distance of 3·32 Å, and the other is stacked on top of the five-membered ring, at a distance of 3·49 Å. The TCNE molecule located on top of the phenyl-type ring of the skatole is oriented with the central double bond of the TCNE parallel to the short axis of the skatole molecule, and shifted with respect to the center. A similar feature has been observed in the perylene–TCNE (Ikemoto & Kuroda, 1967) and naphthalene–TCNE complexes

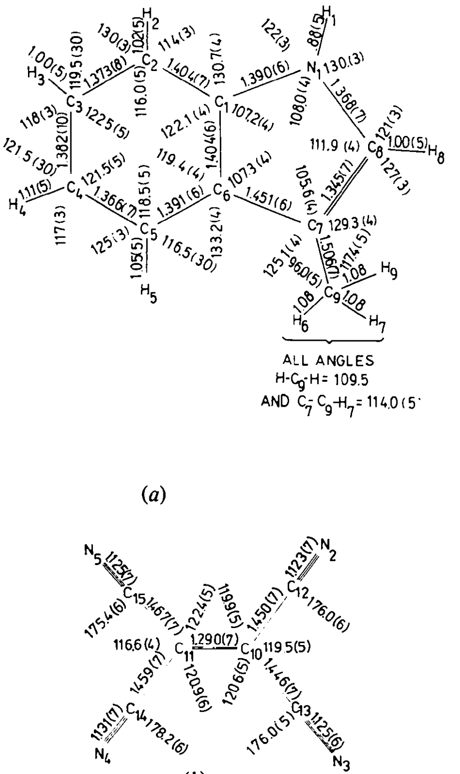

Fig. 1. Bond distances (Å) and angles (°) for (*a*) the skatole molecule and (*b*) the TCNE molecule.

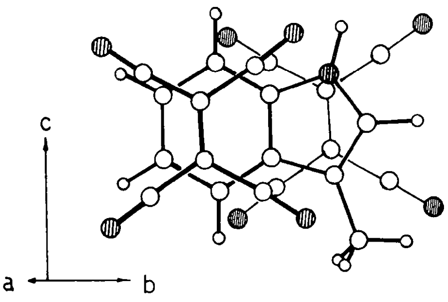

Fig. 2. Projection on the molecular plane of the skatole molecule of the two neighboring TCNE molecules.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34912 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Williams & Wallwork, 1967); in the latter it was interpreted as a specific interaction between the C=C group of TCNE and the 1,4 position in naphthalene.

The distance of 3·32 Å between the molecular planes is similar to that reported for the pyrene–TCNE complex (Ikemoto & Kuroda, 1968). The 18 000 $\mathrm{cm^{-1}}$ band observed for skatole–TCNE is close to the 20 000 $\mathrm{cm^{-1}}$ band observed for pyrene–TCNE corresponding to the electron transfer from the second highest orbital of pyrene to the lowest vacant orbital of TCNE.

A decomposition mechanism (Foster & Hanson, 1965) was suggested for the indole–TCNE complex *via* a complex to 3-tricyanovinylindole. We conclude that the C atom at the 3-substituted position in the skatole molecule plays a decisive role in stabilizing the charge-transfer crystal. This is consistent with the observation (Bruzzone & Roselli, 1980) that indole–TCNE and 2-methylindole–TCNE do not form crystals.

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The Structure of Methyl 6-(Diphenylphosphinyl)-3,4-dimethyl-3-cyclohexene-1-carboxylate

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Abstract. $C_{22}H_{25}O_3P$, M_r = 368·42, monoclinic, $P2_1/c$, Z = 4, a = 14·235 (3), b = 12·768 (2), c = 11·062 (2) Å, β = 90·48 (2)°, V = 2010·5 Å^3, D_o = 1·222 (by flotation), D_c = 1·217 Mg m^{-3}, $F(000)$ = 782. The structure was solved with *MULTAN* and refined by full-matrix least squares to a final R of 0·048 (R_w = 0·063) for 2027 intensities collected on a four-circle diffractometer with Cu radiation. The cyclohexene ring is in a slightly distorted half-chair conformation with asymmetry parameters ΔC_2 = 4·2 (5), ΔC_s = 17·8 (5), $\bar{\varphi}$ = 30·0 (5)°. The carboxyl group is *trans* to the diphenylphosphinyl group with a P–C–C–$COOCH_3$ torsional angle of 59·8 (6)°.

Introduction. The title compound is a model for studying the mechanism of the stereospecific synthesis of the optically active 17-phosphasteroid system used by Dr Bodalski and his group at the Institute of Organic Chemistry, Technical University of Łódź. Also, the present study forms part of our X-ray investigation of the structures and conformations of phosphine oxides (Gałdecki & Główka, 1977*a*,*b*, 1978; Główka, 1978; Gałdecki, Główka, Bodalski & Pietrusiewicz, 1979).

Colourless crystals of the compound were kindly supplied by Dr J. Koszuk. Intensities from a spherical crystal (about 0·3 mm in diameter) were recorded on a Syntex diffractometer with graphite-monochromated Cu $K\alpha$ radiation. From 2027 collected reflections, 1896 had $|F| \geq 3\sigma(F)$. The intensities were not corrected for absorption (μr = 2·0).

The calculations were performed using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) on a RIAD 32 computer, and *MULTAN* (Germain, Main & Woolfson, 1971) on an ODRA 1305 machine. The weighting scheme applied in the refinement of the structure was $w^{-1} = [\sigma(F_o)]^2$. Neutral-atom scattering factors given by Doyle & Turner (1968) for P, O and C

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