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The Structure of the 1/1 Molecular Complex of Acridine with 1,2,4,5-Benzenetetracarbonitrile

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Abstract. $C_{10}H_2N_4.C_{13}H_{19}N$, $M_r = 367.4$, triclinic, $P1$, $a = 7.447$ (4), $b = 7.885$ (5), $c = 8.072$ (9) Å, $\alpha = 73.93$ (9), $\beta = 84.59$ (9), $\gamma = 85.85$ (6)°, $V = 452$ (1) Å^3, $Z = 1$, $D_x = 1.35$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.078$ mm^{-1}, $F(000) = 194$, $T = 293$ K, $wR = 0.042$ for 1241 observations. The donor molecule does not lie symmetrically above the acceptor. Some of the bond lengths in the acridine molecule do not agree with expected values. This is due to disorder in the acridine–TCNB complex. The mean interplanar spacing between acridine and TCNB is 3.48 (9) Å, which is in agreement with that in similar compounds.

Introduction. Molecular charge-transfer (CT) complexes have recently received a great deal of attention. The crystal structures of most of them exhibit quasi-one-dimensional stacking. In many structural studies evidence of large anisotropic thermal motions and/or disorder has been found and considerable effort has gone into establishing the important parameters regarding the motion and disorder (Luty & Kuchta, 1986; Boeyens & Levendis, 1984, 1986; Tsuchiya, Marumo & Saito, 1972). Molecular and crystal disorder is important because it influences most of the solid state properties, including energy and charge transport.

This acridine–TCNB complex should in principle be similar (in structural aspect) to the complex of anthracene–TCNB, because acridine is a nitrogen analog of anthracene. Much data has been collected on the anthracene–TCNB complex. Its structure has been studied by X-ray diffraction (Tsuchiya, Marumo & Saito, 1972; Stezowski, 1980), electron para-

magnetic resonance (Erdle & Moehwald, 1978; Park & Reddoch, 1981), Raman spectroscopy (Bernstein, Dalal, Murphy, Reddoch, Sunder & Williams, 1987; Moehwald, Erdle & Thaer, 1978), differential scanning calorimetry (Dalal, Ripmeester, Reddoch & Williams, 1978), nuclear magnetic resonance (Auch, Steudle, Von Schuetz & Wolf, 1978) and infrared spectroscopy (Umemura, Haley, Cameron, Murphy, Ingold & Williams, 1981).

To our knowledge no similar studies have been devoted to the acridine–TCNB complex apart from fluorescence measurements (Miniewicz & Williams, unpublished results). This paper presents the room-temperature crystallographic structure of the title compound.

Experimental. 1,2,4,5-Benzenetetracarbonitrile (TCNB) was prepared by the method described by Lawton & McRitchie (1959); commercialy available acridine was purified by multiple vacuum sublimation and zone melting. Small (1 × 2 × 3 mm) crystals of the acridine–TCNB complex were obtained by slow evaporation of equimolar acetone solutions of donor and acceptor.

The sample (prism shaped $0 \cdot 15 \times 0 \cdot 20 \times 0 \cdot 22$ mm) was studied with an automatic Enraf–Nonius CAD-4 diffractometer. The cell parameters are obtained by fitting of a set of 24 reflections ($8 < \theta < 10°$). The data collection ($2\theta_{max} = 50°$, scan $\omega/2\theta = 1$, $t_{max} = 60$ s, range hkl: h −8,8; k −9,9; l 0,10, intensity controls $21\bar{1}$, $\bar{2}21$, 130 without appreciable decay) gives 1723 reflections [1241 independent ($R_{int} = 0 \cdot 007$) with $I > (I)$]. After Lorentz and polarization corrections (no absorption correction) the structure was solved with direct methods (MULTAN82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) which reveal all the non-H atoms. After isotropic then anisotropic refinements, the H atoms are located between 0·39 and 0·16 e Å⁻³ with a difference Fourier synthesis then their coordinates refined. The best full-matrix least-squares refinement (use of F magnitudes) of the structure (x, y, z, β_{ij} for C and N atoms, x, y, z for H atoms) gives {251 variables 1241 observations, $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0 \cdot 04 F_o^2)^2]^{-1/2}$} $R = 0 \cdot 047$, $wR = 0 \cdot 042$ and $wS = 2 \cdot 13$ (residual $\Delta\rho \leq 0 \cdot 18$ e Å⁻³. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a Digital PDP 11/60 computer with the *SDP* package (Frenz, 1985). Final positional parameters are given in Table 1.*

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes, H-atom coordinates and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51832 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and their e.s.d.'s*

	x	y	z	$B_{eq}*(Å^2)$
N1	0·577	−0·218	1·048	5·89 (8)
N2	0·9405 (4)	0·0893 (4)	0·6460 (4)	5·47 (7)
N3	1·2203 (5)	−0·5990 (4)	1·3071 (4)	6·26 (8)
N4	1·2369 (4)	−0·2782 (4)	1·6058 (4)	5·85 (8)
N5	0·9459 (4)	0·4215 (4)	0·9402 (4)	5·37 (7)
C1	0·5298 (4)	−0·0503 (5)	0·0653 (5)	5·05 (9)
C2	0·4675 (5)	−0·0020 (7)	0·7939 (5)	7·2 (1)
C3	0·4177 (6)	0·1809 (8)	0·7212 (6)	12·5 (2)
C4	0·4329 (7)	0·3004 (8)	0·8045 (8)	13·2 (2)
C5	0·4882 (6)	0·2634 (6)	0·9568 (8)	9·2 (2)
C6	0·5355 (5)	0·0817 (5)	1·0479 (5)	4·62 (8)
C7	0·5986 (5)	0·0492 (4)	1·2091 (5)	4·47 (8)
C8	0·6442 (4)	−0·1228 (5)	1·2922 (4)	4·44 (8)
C9	0·7060 (5)	−0·1645 (7)	1·4582 (5)	8·2 (1)
C10	0·7473 (6)	−0·3192 (8)	1·5431 (6)	8·4 (1)
C11	0·7409 (6)	−0·4701 (6)	1·4716 (6)	9·2 (1)
C12	0·6843 (6)	−0·4351 (6)	1·3020 (6)	6·5 (1)
C13	0·6292 (4)	−0·2647 (5)	1·2118 (5)	4·99 (9)
C14	1·0768 (4)	−0·2047 (4)	1·0262 (3)	3·08 (6)
C15	1·1322 (4)	−0·2712 (3)	1·1941 (4)	3·40 (6)
C16	1·1398 (4)	−0·1502 (4)	1·2928 (3)	3·14 (6)
C17	1·0918 (5)	0·0254 (4)	1·2341 (4)	4·41 (7)
C18	1·0390 (4)	0·0884 (4)	1·0665 (4)	3·40 (6)
C19	1·0324 (4)	−0·0240 (4)	0·9581 (4)	3·76 (7)
C20	1·1847 (4)	−0·4498 (4)	1·2573 (4)	3·71 (7)
C21	1·1943 (5)	−0·2258 (4)	1·4723 (4)	4·07 (7)
C22	0·9925 (5)	0·2801 (4)	0·9946 (4)	4·57 (8)
C23	0·9791 (4)	0·0375 (4)	0·7897 (4)	4·05 (7)

* Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
$(4/3)[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)]$.

Discussion. Bond lengths and bond angles are given in Table 2 and atom numbering is displayed in Fig. 1(a) (Johnson, 1965). As is seen from Fig. 2, the crystal of acridine–TCNB is built up of stacks along the *a* axis of alternating donor and acceptor molecules. Such an arrangement is characteristic of π–π^* electron donor-acceptor complexes.

In the acridine molecule, some bond lengths are not in good agreement with expected values (C15—C20, C16—C21, C21—N4, C3—C4, C10—C11). A static disorder between C7 and N1 was then considered but the corresponding calculations in space group $P\bar{1}$ did not give satisfactory results (R values and e.s.d.'s). It is well known that average structures obtained by non-critical refinement of apparent atomic arrangements invariably produce unacceptable bond parameters. It is also commonly found that the donor does not lie symmetrically above the acceptor, the consequence of which is unsymmetrical interactions between nitrile groups and the acridine molecule (Fig. 1b). These features actually constitute a reliable diagnostic for disorder in crystals, thus one may assume that the bond lengths mentioned above are artifacts of the disorder in the acridine–TCNB complex.

The TCNB molecule is planar. The angle between the best planes through acridine and TCNB is 2·5 (4)°. The mean interplanar spacing between acridine and

Table 2. *Bond distances* (Å) *and bond angles* (°)

Numbers in parentheses are e.s.d.'s in the least significant digits.

N1	C1	1·345 (7)	C8	C13	1·456 (8)
N1	C13	1·359 (7)	C9	C10	1·255 (11)
N2	C23	1·174 (6)	C10	C11	1·465 (14)
N3	C20	1·153 (6)	C11	C12	1·418 (8)
N4	C21	1·109 (6)	C12	C13	1·392 (8)
N5	C22	1·122 (6)	C14	C15	1·401 (6)
C1	C2	1·441 (9)	C14	C19	1·405 (6)
C1	C6	1·388 (8)	C15	C16	1·409 (6)
C2	C3	1·435 (13)	C15	C20	1·398 (6)
C3	C4	1·32 (2)	C16	C17	1·366 (6)
C4	C5	1·283 (15)	C16	C21	1·489 (7)
C5	C6	1·453 (8)	C17	C18	1·390 (7)
C6	C7	1·376 (8)	C18	C19	1·412 (7)
C7	C8	1·370 (7)	C18	C22	1·490 (7)
C8	C9	1·402 (8)	C19	C23	1·397 (7)

|							
C1	N1	C13	122·1 (5)	C8	C13	C12	117·8 (5)
N1	C1	C2	122·2 (6)	N1	C13	C8	117·2 (5)
N1	C1	C6	119·7 (5)	C15	C14	C19	121·3 (4)
C2	C1	C6	118·1 (6)	C14	C15	C20	120·8 (4)
C1	C2	C3	116·9 (8)	C14	C15	C16	117·4 (4)
C2	C3	C4	121·7 (9)	C16	C15	C20	121·8 (4)
C3	C4	C5	123·1 (1)	C15	C16	C17	123·2 (4)
C4	C5	C6	120·1 (1)	C15	C16	C21	116·1 (4)
C1	C6	C5	119·5 (6)	C17	C16	C21	120·6 (3)
C1	C6	C7	122·2 (5)	C16	C17	C18	118·2 (4)
C5	C6	C7	118·1 (7)	C17	C18	C19	121·9 (4)
C6	C7	C8	117·2 (4)	C17	C18	C22	120·0 (4)
C7	C8	C9	119·8 (6)	C19	C18	C22	118·1 (4)
C7	C8	C13	121·3 (5)	C14	C19	C18	117·9 (4)
C9	C8	C13	118·9 (6)	C14	C19	C23	119·6 (4)
C8	C9	C10	123·3 (8)	C18	C19	C23	122·5 (4)
C9	C10	C11	121·8 (6)	N3	C20	C15	176·7 (5)
C10	C11	C12	117·3 (6)	N4	C21	C16	178·2 (5)
C11	C12	C13	120·7 (7)	N5	C22	C18	175·3 (6)
N1	C13	C12	124·7 (7)	N2	C23	C19	177·7 (5)
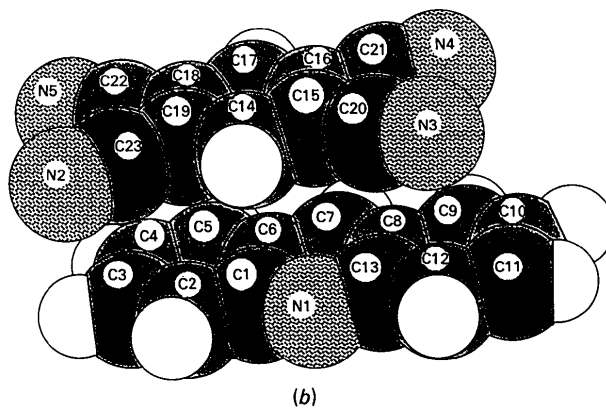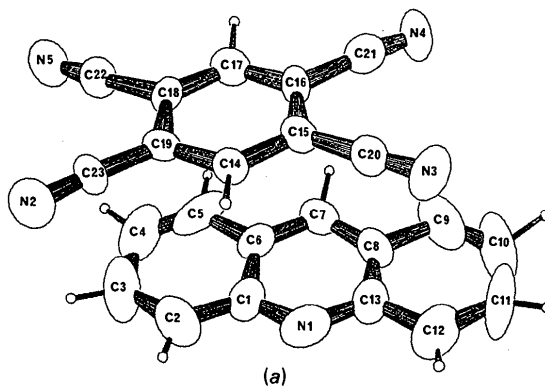
Fig. 1. (*a*) Atom-numbering scheme and thermal ellipsoids for acridine and TCNB molecules. (*b*) Perspective view of the complex with 80% van der Waals radii.

TCNB [3·48 (9) Å] is close to that in anthracene [3·42 Å (Muehle, Krzystek, Von Schuetz, Wolf, Stigler & Stezowski, 1986)], naphthalene [3·43 Å (Kumakura, Iwasaki & Saito, 1967)] and phenanthrene [3·45 Å (Wright, Kyuya & Kuroda, 1978)] complexes with benzenetetracarbonitrile, and is typical for weak CT interaction (*i.e.* expected for an aromatic plane-to-plane van der Waals contact). The relative orientation of the molecules in the acridine–TCNB crystal suggests that the overlap integral and hence charge-transfer energy is almost minimized. There is near center-on-center arrangement of donor and acceptor (abour 95% of CT stabilization). It seems that lattice packing and charge-transfer interactions determine the observed structure.

Examination of the thermal ellipsoid plot for acridine (*cf.* Fig. 1 and Table 2) evidenced a kind of disorder. Larger anisotropic thermal parameters, especially for acridine, might represent either an arrangement of disordered acridine molecules or an acridine molecule executing large thermal oscillations. The 'static' disorder corresponds to a *W*-shaped potential well with a barrier large compared with kT at room temperature and the oscillation ('dynamic disorder') to a flat-bottomed potential well. The third possibility, a *W*-shaped well with a barrier lower than kT at room
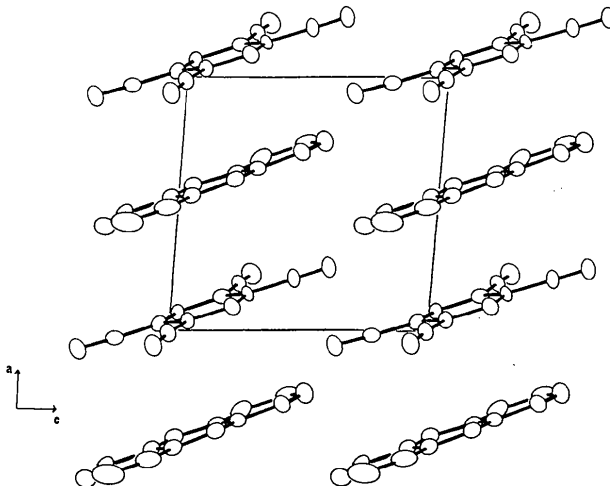
Fig. 2. Projection of the acridine–TCNB structure along **b**.

temperature, would lead to a dynamic situation at high temperature which could be frozen in at low temperature [as was observed and predicted in the anthracene–TCNB complex (Luty & Kuchta, 1986)]. On lowering the temperature the first case would lead to approximately the same apparent oscillation as at room temperature, but the second case would show a considerable reduction in the molecular oscillation. The third case might or might not lead to a significant reduction of thermal motion. Low-temperature structure determination is planned in order to establish which kind of disorder occurs in the acridine–TCNB complex.

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Conformation of Multiflorine*

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Abstract. $C_{15}H_{22}N_2O$, $M_r = 246\cdot3$, monoclinic, $P2_1$, $a = 12\cdot008$ (2), $b = 7\cdot568$ (2), $c = 8\cdot297$ (2) Å, $\beta = 114\cdot70$ (1)°, $V = 685\cdot0$ (3) Å^3, $Z = 2$, $D_x = 1\cdot19$ (4) g cm^{-3}, λ(Cu $K\alpha$) = $1\cdot54178$ Å, $\mu = 5\cdot55$ cm^{-1}, $F(000) = 268$, room temperature, $R = 0\cdot039$ for 892 unique observed reflections. The configuration of both A/B and C/D ring junctions is *trans*. The γ-keto-α,β-enamine ring A adopts a slightly distorted half-chair conformation, ring B a distorted chair conformation, ring C is a boat and ring D is in almost ideal chair conformation. Protonation of the free base changes the C/D-junction configuration into *cis* and the C-ring conformation into chair.