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Structure of a Benzanthracene–1,2,4,5-Tetracyanobenzene Complex, $C_{18}H_{12}.C_{10}H_2N_4$

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Abstract. Benz[*a*]anthracene–1,2,4,5-benzenetetracarbonitrile, $M_r = 406.45$, monoclinic, $P2_1/n$, $a = 8.216 (4)$, $b = 7.965 (3)$, $c = 30.709 (6)$ Å, $\beta = 91.56 (2)°$, $V = 2009 (2)$ Å^3, $Z = 4$, $D_x = 1.34$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, μ(Mo $K\alpha$) = 0.8 cm^{-1}, $F(000) = 840$, $T = 123$ K; refinement with 1444 observed diffractometer data converged to $R = 0.057$. The molecules lie in ribbons in the (20$\overline{6}$) plane and the benzanthracene component is disordered over two sites. The stacking of molecules in the crystal is similar to that found in a benzanthracene–pyromellitic dianhydride complex, there being two different environments for each donor and acceptor atom.

Introduction. Benz[*a*]anthracene is the parent compound of a large series of carcinogenic compounds but is not regarded as being an active compound itself. No accurate structure determination of benz[*a*]anthracene has been reported to date although the unit cell and space group were first published in 1938 (Iball, 1938) and a two-dimensional structure in 1956 (Friedlander & Sayre, 1956). In an effort to obtain good molecular data for the benz[*a*]anthracene (BA)

nucleus and to study complexes of BA (an electron donor) with various electron acceptors, 1:1 complexes of BA with pyromellitic dianhydride (PMDA) (Foster, Iball, Scrimgeour & Williams, 1976) and with 1,2,4,5-tetracyanobenzene (TCNB) were prepared. We now report the structure of the BA–TCNB complex.
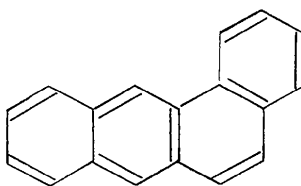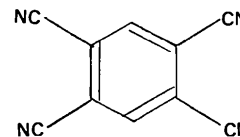
BA   TCNB

Experimental. The crystals were obtained as bright orange rectangular plates by mixing saturated solutions of both components in ethyl acetate in a 1:1 molar ratio. The crystals were recrystallized twice from ethyl acetate. All measurements were made with a crystal $0.10 \times 0.50 \times 0.50$ mm cooled to 123 K. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $11 < \theta < 19°$. Intensities of reflections with *h* 0 to 9, *k* 0 to 8 and *l* -33 to 33

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were measured, ω–2θ scans, ω scan width $(0.70 + 0.35\tan\theta)°$, graphite-monochromated Mo $K\alpha$ radiation, $2\theta_{max} = 54°$. Intensities of three reflections measured every 2 h showed no evidence of crystal decay. 2730 reflections were measured, 2215 were unique, 1444 with $I > 3\sigma(I)$ were labelled observed and used in the structure solution and refinement. Data were corrected for Lorentz and polarization factors. Space group $P2_1/n$ was determined uniquely by the systematic absences $(0k0, k = 2n + 1; h0l, h + l = 2n + 1)$. The structure was solved with some difficulty by direct methods with the aid of *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and *SDP-Plus* (Frenz, 1983). The first E maps had the expected 'chicken-wire' appearance often found in E maps of planar aromatic hydrocarbons; after a number of false starts a correct position was determined for the TCNB molecule. It soon became apparent that one of the reasons why the E maps were difficult to interpret was that the BA molecule was disordered over two sites which were subsequently shown (by refinement) to have 0.61/0.39 occupancies. Because of the BA disorder/ overlap it was not possible to refine the atom sites free of constraints. After sites had been carefully selected from difference maps the structure was refined in two blocks (the disordered BA, and the TCNB) with the *SHELX*76 program (Sheldrick, 1976), with bond-length constraints [using the *DFIX* option in *SHELX*76 and ring C—C 1.395 (10), exocyclic C—C 1.443 (8), C—N 1.138 (7) Å]. Hydrogen atoms were included in the structure-factor calculations (as riding atoms, C—H 0.95 Å, U_{iso} 0.04 Å^2) but were not refined. Isotropic followed by anisotropic refinement converged with $R = 0.057$, $wR = 0.055$, $w = 1/[\sigma^2 F_o + 0.05(F_o)^2]$. Max. shift/e.s.d. = 0.13, density in final difference map from $+0.21$ to -0.22 e Å^{-3}, no chemically significant features. Scattering-factor data were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates are given in Table 1.* Figs. 1, 2, 3 and 4 were prepared with the aid of *ORTEP*II (Johnson, 1976) and are views of the complex.

Discussion. Our analysis establishes the overall structure and the general features of the crystal packing of the 1:1 BA–TCNB complex; because of the disorder of the BA molecule which necessitated the use of bond-length constraints in the refinement process, no meaningful discussion of the bond lengths and angles is possible.

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* Tables of molecular dimensions, calculated hydrogen coordinates and thermal parameters, and lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53146 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	x	y	z	$U(Å^2)$†
C1	0.1351 (7)	0.3023 (6)	0.2833 (2)	0.046 (1)
C2	0.0379 (8)	0.2183 (6)	0.2520 (2)	0.039 (1)
C3	0.0182 (7)	0.0420 (6)	0.2540 (2)	0.036 (1)
C4	0.0928 (9)	−0.0469 (6)	0.2874 (2)	0.032 (1)
C5	0.1941 (7)	0.0371 (6)	0.3181 (2)	0.037 (1)
C6	0.2689 (7)	−0.0559 (6)	0.3509 (2)	0.034 (1)
C7	0.3659 (8)	0.0279 (6)	0.3827 (2)	0.030 (1)
C8	0.4388 (7)	−0.0692 (6)	0.4157 (2)	0.037 (1)
C9	0.5380 (7)	0.0075 (7)	0.4472 (2)	0.036 (1)
C10	0.5663 (7)	0.1809 (6)	0.4471 (2)	0.023 (1)
C11	0.6663 (7)	0.2517 (6)	0.4801 (2)	0.030 (1)
C12	0.6975 (7)	0.4229 (6)	0.4789 (2)	0.024 (1)
C13	0.6287 (7)	0.5240 (6)	0.4460 (2)	0.028 (1)
C14	0.5285 (7)	0.4497 (6)	0.4137 (2)	0.033 (1)
C15	0.4956 (8)	0.2766 (6)	0.4137 (2)	0.031 (1)
C16	0.3904 (7)	0.2015 (6)	0.3809 (2)	0.023 (1)
C17	0.3132 (7)	0.2921 (6)	0.3474 (2)	0.036 (1)
C18	0.2143 (7)	0.2106 (6)	0.3160 (2)	0.032 (1)
N1	−0.0988 (4)	0.6145 (5)	0.2283 (1)	0.054 (1)
N2	−0.2209 (4)	0.1994 (4)	0.1613 (1)	0.047 (1)
N3	−0.6418 (4)	0.6730 (4)	0.0110 (1)	0.045 (1)
N4	−0.5559 (4)	1.0874 (4)	0.0838 (1)	0.050 (1)
C21	−0.2803 (4)	0.6334 (4)	0.1585 (1)	0.030 (1)
C22	−0.3187 (4)	0.4897 (4)	0.1346 (1)	0.030 (1)
C23	−0.4155 (4)	0.5006 (4)	0.0969 (1)	0.031 (1)
C24	−0.4733 (4)	0.6556 (4)	0.0829 (1)	0.030 (1)
C25	−0.4377 (4)	0.7998 (4)	0.1073 (1)	0.032 (1)
C26	−0.3394 (4)	0.7885 (4)	0.1448 (1)	0.034 (1)
C27	−0.1792 (4)	0.6232 (5)	0.1974 (1)	0.038 (1)
C28	−0.2625 (4)	0.3281 (5)	0.1494 (1)	0.034 (1)
C29	−0.5684 (4)	0.6658 (5)	0.0432 (1)	0.033 (1)
C30	−0.5026 (4)	0.9612 (5)	0.0941 (1)	0.037 (1)
C1*	0.5669 (11)	0.4843 (7)	0.4252 (3)	0.055 (1)
C2*	0.6665 (10)	0.4995 (7)	0.4626 (3)	0.054 (1)
C3*	0.7037 (10)	0.3571 (7)	0.4877 (3)	0.053 (1)
C4*	0.6498 (11)	0.1994 (7)	0.4740 (3)	0.073 (1)
C5*	0.5457 (11)	0.1868 (7)	0.4372 (3)	0.046 (1)
C6*	0.4831 (10)	0.0300 (7)	0.4253 (3)	0.049 (1)
C7*	0.3813 (11)	0.0147 (7)	0.3882 (3)	0.045 (1)
C8*	0.3124 (10)	−0.1422 (8)	0.3782 (3)	0.064 (1)
C9*	0.2141 (9)	−0.1598 (7)	0.3410 (3)	0.057 (1)
C10*	0.1784 (10)	−0.0221 (8)	0.3147 (3)	0.061 (1)
C11*	0.0780 (10)	−0.0481 (7)	0.2782 (3)	0.039 (1)
C12*	0.0344 (11)	0.0906 (8)	0.2531 (3)	0.085 (1)
C13*	0.0858 (11)	0.2537 (8)	0.2645 (3)	0.092 (1)
C14*	0.1917 (10)	0.2731 (7)	0.3006 (3)	0.058 (1)
C15*	0.2362 (10)	0.1361 (8)	0.3267 (3)	0.047 (1)
C16*	0.3411 (9)	0.1561 (7)	0.3633 (3)	0.028 (1)
C17*	0.4024 (9)	0.3128 (7)	0.3754 (3)	0.045 (1)
C18*	0.5023 (10)	0.3287 (7)	0.4131 (3)	0.042 (1)

† Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $U_{eq} = 0.33(U_{11} + U_{22} + U_{33})$.

The BA molecule is disordered over two sites in the same volume element in the crystal lattice as shown in Fig. 1. The BA and TCNB components are essentially parallel [interplanar angle 1.0 (6)°]. In the crystal structure the $(20\bar{6})$ plane $(F_o = 512)$ gives by far the strongest reflection [cf. $F(000) = 840$]; the constituent molecules lie very close to this plane (Figs. 2 and 3). In the $(20\bar{6})$ plane there are ribbons of BA molecules and parallel ribbons of TCNB molecules. The stacking of the molecules in the crystal is similar to that found in BA–PMDA, there being two different environments for each donor and each acceptor molecule. Usually in such 1:1 $D–A$ complexes the two molecules alternate $A–D–A–D$ so that the overlap between A (electron acceptor) and D (electron donor) is the same as between D and A. In BA–TCNB the overlap (for the principal component
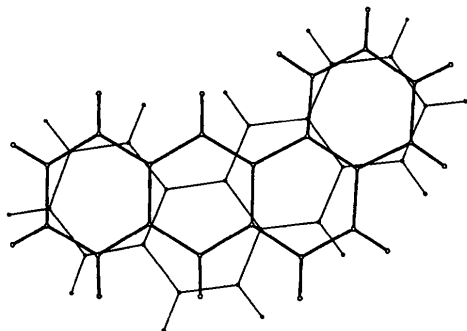
Fig. 1. A view of the two orientations of the disordered BA molecule. The darker bonds belong to the molecule with 0·61 occupancy. Atoms are shown as spheres of arbitrary size.
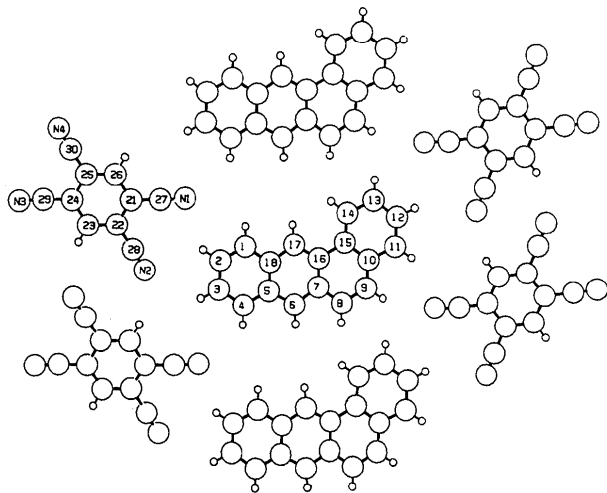

Fig. 2. A view of the BA–TCNB structure projected onto the (20$\bar{6}$) plane; for clarity only the major component of the disordered BA molecule is shown. Atoms are shown as spheres of arbitrary size. The atomic numbering scheme is also shown.
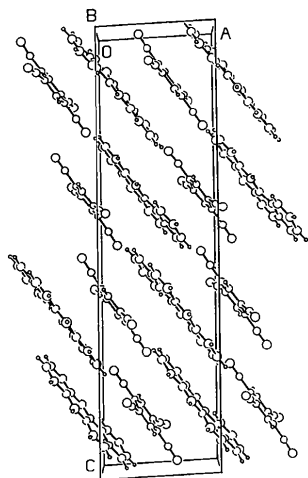

Fig. 3. The unit-cell contents of the BA–TCNB structure viewed along **b**. For clarity, only the major component of the disordered BA molecule is shown.
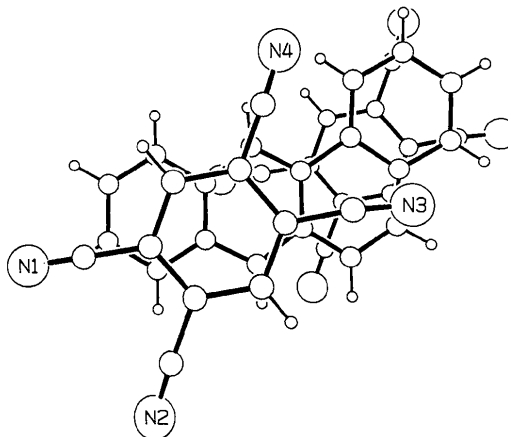

Fig. 4. A view showing the overlap of two TCNB molecules (related by a translation along **a**) with the major BA component.

BA molecule with TCNB) is shown in Fig. 4. One TCNB molecule overlaps the anthracene residue of BA (overlap I) while the TCNB related by a translation in the **a** direction overlaps the phenanthrene residue of BA (overlap II). The angle between the donor and acceptor molecules is the same [2·8 (5)°] in both overlaps and the shortest intermolecular contact in the region of overlap is 3·26 (1) Å (C3···C27); the corresponding value in overlap II is 3·31(1)Å (C11···C24). For the minor BA component, the overlap is entirely similar to the major component, with a 2·4 (6)° angle between planes and shortest intermolecular contacts of C4*···C24 3·24 (1) and C12*···C27 3·34 (1) Å. The shortest intermolecular distance between non-hydrogen atoms in the molecules in the (20$\bar{6}$) plane is between a TCNB nitrogen atom (N1) and adjacent BA carbon C2 [3·42 (1) Å].

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