

## Structure of 1,2-Di(4-pyridyl)ethylene–7,7,8,8-Tetracyano-*p*-quinodimethane (1:1), C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>·C<sub>12</sub>H<sub>4</sub>N<sub>4</sub>

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**Abstract.** DPE–TCNQ,  $M_r = 386.3$ , monoclinic,  $P2_1/c$ ,  $a = 7.262$  (4),  $b = 9.400$  (5),  $c = 14.496$  (4) Å,  $\beta = 91.75$  (5)°,  $V = 989.2$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.28$ ,  $D_x = 1.30$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.046$  mm<sup>-1</sup>,  $F(000) = 400$ ,  $R = 0.076$  for 828 observed reflections. The structure consists of mixed stacks of neutral DPE and TCNQ molecules which alternate on centres of symmetry, the mean interplanar spacing being 3.45 (2) Å.

**Introduction.** 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) forms charge-transfer complexes with a variety of electron donors, the properties of which range from metallic to insulating. For high conductivity it is necessary for the molecules to stack, in segregated columns, with a short uniform spacing between each. The TCNQ complexes of 2,2'-bi(1,3-dithiole) (Kistenmacher, Phillips & Cowan, 1974), 2,2'-bi(1,3-diselenole) (Etemad, Penney, Engler, Scott & Seiden, 1975) and their substituted congeners (Kistenmacher, 1978) satisfy these criteria and exhibit metallic behaviour. In these complexes, charge transfer between donor and acceptor is incomplete and has been estimated as 0.4 to 0.8e, from the dimensions of the TCNQ moiety (Chasseau, 1979) and by X-ray diffuse scattering techniques (Megtert, Pouget & Comes, 1978). In contrast, the insulating mixed-stack complexes are characterized by either weak charge transfer as, for example, in phenazine–TCNQ (Goldberg & Shmueli, 1973) or complete charge transfer as in *N,N,N',N'*-tetramethyl-*p*-phenylenediamine–TCNQ (Hanson, 1965). In this work we report the crystal structure of the mixed-stack complex 1,2-di(4-pyridyl)ethylene–TCNQ, DPE–TCNQ. Our interest in this material stems from the fact that it occurs in two forms, a black conducting form as well as a red mixed-stack insulating form.

**Experimental.** Red insulating needles and black conducting microcrystals were obtained when a hot acetonitrile solution of DPE and TCNQ was allowed to cool slowly to room temperature; the red form:  $0.23 \times 0.15 \times 0.09$  mm, unit-cell parameters from oscillation and Weissenberg photographs;  $1 < \theta < 27.5^\circ$ , crystal mounted with *a* axis coincident with  $\omega$

axis of a Stoe STADI-2 two-circle diffractometer, Mo  $K\alpha$ , background– $\omega$ -scan–background technique; 1936 unique reflexions were measured, 828 with  $I > 3\sigma(I)$  were corrected for Lorentz–polarization effects (not for absorption) and used in refinement; multiresolution direct methods (SHELX: Sheldrick, 1976) gave all non-hydrogen atoms; H atoms located but not refined; common isotropic temperature factor for H atoms refined to  $U = 0.062$  (5) Å<sup>2</sup>; scattering factors from *International Tables for X-ray Crystallography* (1974),  $w = [\sigma^2(F_o) + 0.0101(F_o)^2]^{-1}$ , full-matrix least squares, anisotropic for non-H atoms, gave  $R = 0.076$ ,  $R_w = 0.087$ ; final difference map showed no peaks greater than  $0.54$  e Å<sup>-3</sup>.\*

**Discussion.** The atomic coordinates are listed in Table 1. The crystal structure viewed along **a** and **b** is shown in Figs. 1 and 2. DPE and TCNQ are centrosymmetric and are situated with their centres of symmetry at  $(\frac{1}{2}, \frac{1}{2}, 0)$  and  $(1, \frac{1}{2}, 0)$ , respectively. The molecules stack alternately, in infinite columns, parallel to **a**, the spacing and dihedral angle between the mean planes being 3.45 (2) Å and 1.0 (6)° respectively. All intermolecular contacts between donor and acceptor are greater than the sum of the van der Waals radii, indicating a neutral ground state. This is supported by the dimensions of the TCNQ moiety (Fig. 3) which show bond alternation consistent with the quinonoid structure of the neutral molecule. It is of interest to note that this alternation is even more pronounced in DPE–TCNQ than in homomolecular TCNQ (Long, Sparks & Trueblood, 1965), supporting the view that the geometry is influenced not only by the charge density but also by the molecular environment. The TCNQ molecule is not quite planar, the C–(CN)<sub>2</sub> groups being twisted slightly out of the plane of the ring, the maximum deviations from the mean plane being 0.176 (8) Å for N(1) and –0.062 (7) Å for N(2).

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares planes calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38269 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional positional parameters ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in parentheses

The  $U_{eq}$  values were calculated by reference to Willis & Pryor (1975).

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
C(1)	10620 (7)	3892 (5)	605 (3)	39 (3)
C(2)	10136 (8)	3617 (5)	-357 (3)	45 (3)
C(3)	9566 (8)	4651 (5)	-920 (3)	44 (3)
C(4)	11230 (7)	2832 (5)	1175 (3)	41 (3)
C(5)	11647 (9)	3037 (6)	2149 (4)	51 (4)
C(6)	11508 (10)	1395 (6)	868 (4)	58 (4)
C(7)	6717 (10)	1431 (6)	1383 (5)	61 (4)
C(8)	6084 (10)	2443 (7)	743 (5)	63 (4)
C(9)	5870 (8)	3856 (6)	1036 (4)	58 (4)
C(10)	6318 (9)	4152 (7)	1941 (5)	61 (4)
C(11)	6911 (10)	3084 (7)	2512 (4)	63 (4)
C(12)	5231 (10)	5050 (7)	433 (5)	66 (4)
N(1)	11777 (11)	257 (6)	658 (5)	81 (4)
N(2)	12029 (10)	3141 (6)	2911 (3)	70 (4)
N(3)	7124 (8)	1736 (5)	2256 (3)	61 (4)

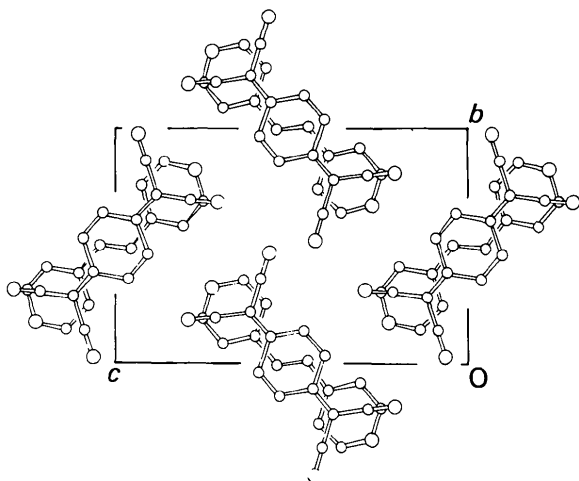


Fig. 1. Projection of the structure along *a*.

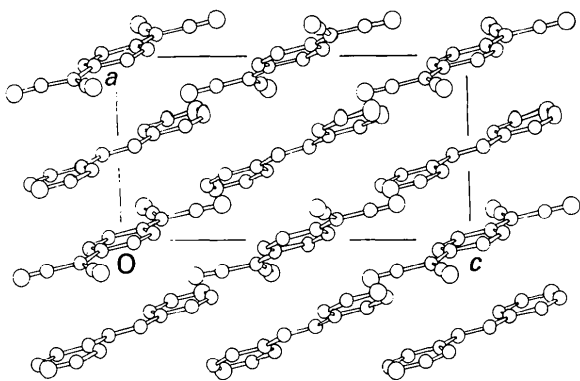


Fig. 2. Projection of the structure along *b*.

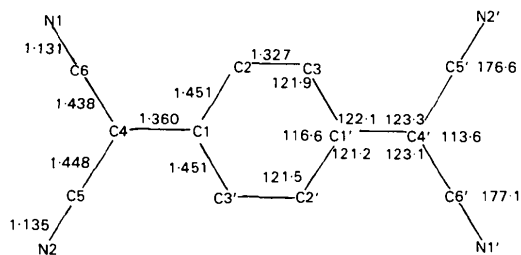


Fig. 3. Dimensions of the TCNQ molecule. The e.s.d.'s of the C-C and C-N bond lengths and the C-C-C and C-C-N angles are 0.007 Å, 0.008 Å, 0.4° and 0.7°, respectively.

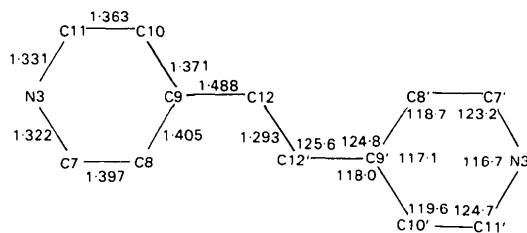


Fig. 4. Dimensions of the DPE molecule. The e.s.d.'s of the bond lengths and angles are 0.009 Å and 0.6°, respectively.

The dimensions of the DPE moiety (Fig. 4) are in close agreement with values reported previously for [4,4'-vinylenbis(1-ethylpyridinium)](TCNQ)<sub>4</sub> (Ashwell, Eley, Fleming, Wallwork & Willis, 1976) and [4,4'-vinylenbis(1-benzylpyridinium)](TCNQ)<sub>5</sub> (Ashwell, Eley Harper, Torrance, Wallwork & Willis, 1977). The donor is planar, the maximum deviation from the least-squares plane being 0.007 (6) Å.

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#### References

- ASHWELL, G. J., ELEY, D. D., FLEMING, R. J., WALLWORK, S. C. & WILLIS, M. R. (1976). *Acta Cryst.* **B32**, 2948-2952.
- ASHWELL, G. J., ELEY, D. D., HARPER, A., TORRANCE, A. C., WALLWORK, S. C. & WILLIS, M. R. (1977). *Acta Cryst.* **B33**, 2258-2263.
- CHASSEAU, D. (1979). Thesis, Docteur d'Etat ès Sciences, Univ. of Bordeaux.
- ETEMAD, S., PENNEY, T., ENGLER, E. M., SCOTT, B. A. & SEIDEN, P. E. (1975). *Phys. Rev. Lett.* **34**, 714-774.
- GOLDBERG, I. & SHMUELI, U. (1973). *Acta Cryst.* **B29**, 440-448.
- HANSON, A. W. (1965). *Acta Cryst.* **19**, 610-613.
- International Tables for X-ray Crystallography* (1974). Vol IV, Table 2.2B. Birmingham: Kynoch Press.
- KISTENMACHER, T. J. (1978). *Ann. NY Acad. Sci.* **313**, 333-342.
- KISTENMACHER, T. J., PHILLIPS, T. E. & COWAN, D. O. (1974). *Acta Cryst.* **B30**, 763-768.
- LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932-939.
- MEGTERT, S., POUGET, J. P. & COMES, R. (1978). *Ann. NY Acad. Sci.* **313**, 234-243.
- SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determinations. Cambridge Univ., England.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). In *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.