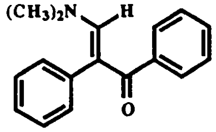
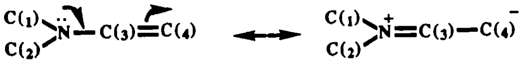
Overill, 1987). The X-ray crystallographic study of (1) represents another example of this type of investigation.



(1)

As may be seen from Table 2, the shortening and lengthening of the N—C(3) [1.390 (3) Å] and C(3)—C(4) [1.380 (3) Å] bond lengths respectively, together with the observed enlargement of the C(4)—C(3)—N angle [130.1 (2)°], is likely to be related to the resonance between the double bond C(3)═C(4) and the electron pair at the N atom (Iida, Yuasa, Kibayashi & Iitaka, 1981). The enaminone system (N—C═C—C═O) is virtually planar. The largest deviations from the mean plane are C(5) 0.053 (2) and C(3) −0.068 (2) Å. Both benzene rings are planar within experimental error with a dihedral angle of 80.00 (7)° between the two benzene planes. Similar behaviour has been observed for other enaminones reported in the literature (Basato, Corain, Veronese, D'Angeli, Valle & Zanotti, 1984).



The conformation of this enaminone is described by the torsion angles given in Table 2.

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References

Bailey, M. D. & Powles, G. R. (1990). US Patent No. 4,916,150, 10 April 1990.

Basato, M., Corain, B., Veronese, A. C., D'Angeli, F., Valle, G. & Zanotti, G. (1984). *J. Org. Chem.* **49**, 4696–4700.

Coppola, G. M., Hardtmann, E. & Huegui, B. S. (1974). *J. Heterocycl. Chem.* **11**, 51–56.

Emsley, J., Freeman, N. J., Parker, R. J., Kuroda, R. & Overill, R. E. (1987). *J. Mol. Struct.* **159**, 173–182.

Greenhill, J. V. (1977). *Chem. Soc. Rev.* pp. 277–294.

Igartua, A. (1991). Doctoral Thesis, Univ. del País Vasco, Bilbao, Spain.

Iida, H., Yuasa, Y., Kibayashi, C. & Iitaka, Y. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2212–2216.

Keller, E. (1988). *SCHAKAL*88. A Fortran program for the graphic representation of molecular models. Univ. of Freiburg, Germany.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1984). *MULTAN*11/84. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Roberts, P. & Sheldrick, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Singer, B. & Mass, G. (1987). *Chem. Ber.* **120**, 1683–1690.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. W. & Hall, S. R. (1972). The *XRAY*72 system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Tilak, B. D., Berde, H., Gogte, V. N. & Ravindranathan, T. (1970). *Indian J. Chem.* **8**, 1–4.

Acta Cryst. (1992). C**48**, 530–533

Structure of a Charge-Transfer Complex of 3,8-Diethyl-5,10-dimethyl-1,6-dioxapyrene (DEDMDOP) with 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ)*

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Abstract. $C_{20}H_{20}O_2.C_{12}H_4N_4$, $M_r = 496.57$, orthorhombic, *Pmnn*, $a = 6.749$ (1), $b = 9.699$ (2), $c = 19.204$ (1) Å, $V = 1257.1$ (3) Å^3, $Z = 2$, $D_x = 1.312$, $D_m = 1.291$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.781$ cm^{-1}, $F(000) = 520$, $T = 294$ K, $R = 0.062$ for 765 observed reflections. The structure is composed of stacks along the *a* axis of alternating DEDMDOP

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* The IUPAC name for TCNQ is 2,2′-(2,5-cyclohexadiene-1,4-diylidene)bispropanedinitrile.

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and TCNQ molecules positioned in mirror planes and regularly spaced by $\frac{1}{2}a = 3.37$ Å. This mixed-stacking arrangement is consistent with the observed low electrical conductivity ($\sigma = 3 \times 10^{-6}$ S m^{-1}).

Introduction. In the search for new organic π-electron donors we have considered chalcogen-substituted polycyclic arenes such as dioxapyrene and dithiapyrene. Previously, we reported the structure of a 1,6-dithiapyrene (DTP) complex with TCNQ (Thorup, Rindorf, Jacobsen, Bechgaard, Johannsen & Mortensen, 1985) which consists of segregated regular stacks of donor and acceptor molecules. The observed metallic conductivity was in good agreement with the crystal packing and an estimated charge transfer of 0.64 e. Nakasuji and coworkers have studied a number of substituted 1,6-dithiapyrene compounds including two 1:1 complexes of 2,7-bis(methylthio)-1,6-dithiapyrene with TCNQ (Nakasuji, Sasaki, Kotani, Murata, Enoki, Imaeda, Inokuchi, Kawamoto, & Tanaka, 1987), one of which is a semiconducting mixed-stack compound and the other is a metallic segregated-stack compound. The title complex is based on the more novel donor 1,6-dioxapyrene (DOP) and the structure presented is the first one containing the DOP skeleton. DOP and its derivatives can also form cation-radical salts which are currently under further study. The dioxapyrenes seem to be slightly better donors than their dithiapyrene counterparts.

Experimental. DEDMDOP was prepared according to Christensen, Johannsen & Bechgaard (1991). Crystals of DEDMDOP-TCNQ were grown by mixing hot saturated solutions of TCNQ in acetonitrile with DEDMDOP in benzonitrile followed by slow cooling. The density of the crystals was measured by flotation in an aqueous solution of $ZnCl_2$. The crystals were generally rather large but of inferior quality as revealed by X-ray photographs. Eventually, a wedge-like single crystal with dimensions 0.13 × 0.15 × 0.25 mm was selected for study on an Enraf–Nonius CAD-4 diffractometer with graphite monochromator. The unit cell was derived from 25 reflections (four settings of each) having $8 < \theta < 13°$. X-ray intensity data were collected in the ω-scan mode with $\Delta\omega = (1.00 + 0.35\tan\theta)°$ within the range $0 < \theta < 35°$, $0 \leq h \leq 10$, $0 \leq k \leq 15$, $-31 \leq l \leq 31$. No decay was found for the intensity control reflections. The intensities were corrected for Lorentz, polarization and absorption effects (transmission in the range 0.98–0.99). After removal of systematic absences the 5821 measured reflections were merged to 2947 unique reflections, $R_{\rm int}(F) = 0.029$, and 765 of these having $F_o > 6\sigma(F_o)$ were later used in the structure refinement. Systematic absences were consistent with the space groups *Pmnn* (non-standard setting of *Pnnm*, No. 58) and *P*2*nn* (non-standard setting of *Pnn*2, No. 34). The structure was solved in the centrosymmetric space group *Pmnn* by direct methods using *SHELXS*86 (Sheldrick, 1990). The equivalent positions for this setting are x, y, z; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$; $x, -y, -z$; $-x, -y, -z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; $-x, y, z$. All non-H atoms appeared in the mirror plane perpendicular to **a**. Refinement and subsequent difference density calculations revealed all H atoms, most of which were also in the mirror plane. In the subsequent refinements C—H distances were restrained to 1.08 Å. The final refinement with anisotropic temperature factors for non-H and isotropic temperature factors for H atoms (145 parameters in total) gave $R(F) = 0.062$, $wR(F) = 0.072$ and $S = 2.38$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $1/w = \sigma_c^2(F_o) + 0.0004|F_o|^2$. The program system *SHELX*76 (Sheldrick, 1976) was used, and complex atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Maximum and minimum residual electron density was 0.31 and -0.28 e Å^{-3} and maximum (Δ/σ) in the final cycle was 0.017. The resultant positional and thermal parameters are given in Table 1.* For molecular geometry calculations *PLATON* (Spek, 1990) was used, and *ORTEP*II (Johnson, 1976) was used to produce crystal structure illustrations.

Table 1. *Fractional coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^4) *for the non*-H *atoms with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
O	0	2101 (3)	4428 (2)	477 (15)
C(1)	0	2470 (6)	3746 (3)	430 (21)
C(2)	0	3782 (5)	3508 (3)	373 (19)
C(3)	0	4906 (5)	4013 (2)	308 (17)
C(4)	0	4495 (5)	4735 (3)	340 (18)
C(5)	0	3113 (5)	4937 (3)	316 (17)
C(6)	0	2685 (5)	5615 (3)	384 (19)
C(7)	0	6275 (5)	3864 (3)	367 (19)
C(8)	0	4120 (6)	2746 (3)	486 (24)
C(9)	0	2905 (9)	2253 (3)	616 (30)
C(10)	0	1190 (6)	5816 (4)	571 (27)
C(11)	0	466 (7)	695 (3)	501 (23)
C(12)	0	−1397 (6)	−181 (3)	481 (22)
C(13)	0	−986 (6)	527 (3)	469 (22)
C(14)	0	−1932 (7)	1055 (3)	574 (20)
C(15)	0	−3408 (11)	926 (4)	787 (34)
C(16)	0	−1549 (10)	1771 (5)	878 (36)
N(1)	0	−4594 (8)	868 (4)	1150 (37)
N(2)	0	−1186 (11)	2324 (4)	1290 (43)

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* Lists of H-atom parameters, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54574 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0239]

Refinement in the noncentrosymmetric space group *P2nn*, where the mirror plane has been removed, was also attempted. The deviations of the resultant x coordinates from zero were on the edge of being significant, and the associated e.s.d.'s became quite large. The space group *Pmnn* was therefore maintained and this choice was justified by the successful refinement. The somewhat high residuals may be caused by small deviations from the planar model, as suggested by some atoms having U values around 0.1 Å^2.

Discussion. The atomic numbering is shown in Fig. 1, which also depicts the molecular overlap. DEDMDOP and TCNQ are both centrosymmetric with their molecular centres at $(0,\frac{1}{2},\frac{1}{2})$ and (0,0,0), respectively. The molecules are strictly planar as they are fixed on a mirror plane, even including as many H atoms as possible. It is a rare observation in crystal structures to find a heterocyclic flat molecule which is positioned orderly on a mirror plane. One such case is 4-methyl-9-oxothioxanthene 10,10-dioxide (Longo & Richardson, 1982) crystallizing in space group *Pnma*.

Bond lengths and angles are listed in Table 2. It is well known that the bond lengths in TCNQ vary with the formal charge of TCNQ. As first suggested by Flandrois & Chasseau (1977) the formal charge can actually be estimated from the observed bond lengths. Application of their method to the present case leads to an estimated charge close to zero; *i.e.* TCNQ and DEDMDOP are neutral or only slightly ionized in their present ground states.

The donor and acceptor molecules are alternately stacked along the a axis. This mixed-stacked arrangement (*DADA*···) is commonly found for charge-transfer complexes of flat molecules and normally associated with very low conductivity. By symmetry the stacking is as regular as possible with an interplanar distance of exactly $\frac{1}{2}a = 3.37$ Å. For comparison, in DTP-TCNQ (which has segregated stacks) the interplanar spacings are 3.39 and 3.27 Å for DTP and TCNQ, respectively (Thorup *et al.*, 1985).

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

O—C(1)	1.358 (7)	O—C(5)	1.385 (6)
C(1)—C(2)	1.352 (8)	C(2)—C(3)	1.459 (7)
C(2)—C(8)	1.500 (8)	C(3)—C(4)	1.445 (7)
C(3)—C(7)	1.358 (7)	C(4)—C(5)	1.395 (7)
C(4)—C(4^{i})	1.410 (8)	C(5)—C(6)	1.367 (8)
C(6)—C(10)	1.500 (8)	C(6)—C(7^{i})	1.421 (8)
C(8)—C(9)	1.512 (10)	N(1)—C(15)	1.156 (13)
N(2)—C(16)	1.119 (13)	C(11)—C(12^{ii})	1.338 (9)
C(11)—C(13)	1.445 (9)	C(12)—C(13)	1.417 (8)
C(13)—C(14)	1.367 (9)	C(14)—C(15)	1.453 (13)
C(14)—C(16)	1.424 (11)		
C(1)—O—C(5)	119.6 (4)	O—C(1)—C(2)	125.0 (5)
C(1)—C(2)—C(3)	118.6 (5)	C(1)—C(2)—C(8)	122.4 (5)
C(3)—C(2)—C(8)	119.0 (5)	C(2)—C(3)—C(4)	115.6 (4)
C(2)—C(3)—C(7)	126.2 (4)	C(4)—C(3)—C(7)	118.2 (4)
C(3)—C(4)—C(5)	122.1 (5)	C(3)—C(4)—C(4^{i})	120.0 (4)
C(5)—C(4)—C(4^{i})	117.9 (5)	O—C(5)—C(4)	119.1 (5)
O—C(5)—C(6)	117.2 (4)	C(4)—C(5)—C(6)	123.7 (5)
C(5)—C(6)—C(10)	122.6 (5)	C(5)—C(6)—C(7^{i})	117.1 (5)
C(10)—C(6)—C(7^{i})	120.3 (5)	C(3)—C(7)—C(6^{i})	123.1 (5)
C(2)—C(8)—C(9)	116.2 (5)	C(13)—C(11)—C(12^{ii})	119.5 (5)
C(13)—C(12)—C(11^{ii})	121.2 (6)	C(11)—C(13)—C(12)	119.2 (5)
C(11)—C(13)—C(14)	119.2 (5)	C(12)—C(13)—C(14)	121.5 (5)
C(13)—C(14)—C(15)	122.3 (6)	C(13)—C(14)—C(16)	122.7 (7)
C(15)—C(14)—C(16)	114.9 (7)	N(1)—C(15)—C(14)	175.7 (8)
N(2)—C(16)—C(14)	176.8 (11)		

Symmetry code: (i) x, $1 - y$, $1 - z$; (ii) x, $-y$, $-z$.

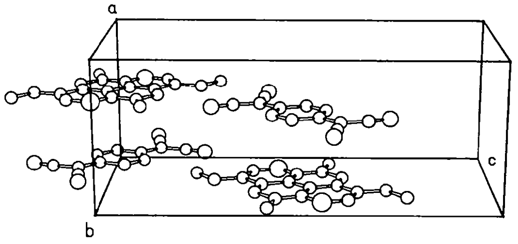

Fig. 2. Side view showing the mixed stacking along **a**.

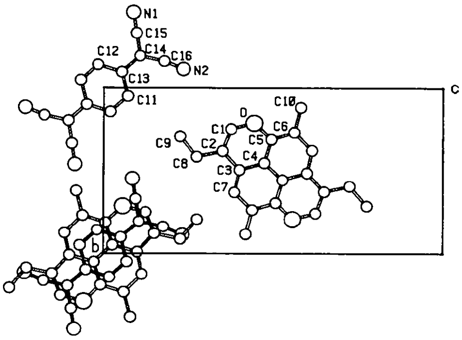

Fig. 1. Projection along **a** showing the atomic numbering and molecular overlap.

The molecular overlap between DEDMDOP and TCNQ is depicted in Fig. 1. The central C(4)—C(4′) bond of DEDMDOP is right above (and below) the central quinonoid ring of TCNQ. This is a more 'symmetric' overlap than that found in the mixed-stack TCNQ complex of 2,7-bis(methylthio)-DTP (Nakasuji *et al.*, 1987).

The packing arrangement is shown in Fig. 2. No intermolecular distances shorter than the sum of the van der Waals radii are observed for non-H atoms, neither within stacks nor between stacks. Weak C—H···N interactions may be present but the rather inaccurate H-atom coordinates did not allow a detailed analysis. As normally found for a mixed-stack structure, the observed electrical conductivity is very low ($\sigma = 3 \times 10^{-6}$ S m^{-1}).

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References

CHRISTENSEN, J. B., JOHANNSEN, I. & BECHGAARD, K. (1991). *J. Org. Chem.* Submitted.

FLANDROIS, S. & CHASSEAU, D. (1977). *Acta Cryst.* **B33**, 2744–2750.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

LONGO, J. & RICHARDSON, M. F. (1982). *Acta Cryst.* **B38**, 2724–2726.

NAKASUJI, K., SASAKI, M., KOTANI, T., MURATA, I. ENOKI, T., IMAEDA, K., INOKUCHI, H., KAWAMOTO, A. & TANAKA, J. (1987). *J. Am. Chem. Soc.* **109**, 6970–6975.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

SPEK, A. L. (1990). *Acta Cryst.* **A46**, C-31.

THORUP, N., RINDORF, G., JACOBSEN, C. S., BECHGAARD, K., JOHANNSEN, I. & MORTENSEN, K. (1985). *Mol. Cryst. Liq. Cryst.* **120**, 349–352.

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Molecular Co-Crystals of Carboxylic Acids. 3.* Structures of the 1:1 Adducts of 2,4,6-Trinitrobenzoic Acid with 4-Aminobenzoic Acid and 3-Hydroxypyridine

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Abstract. (1) $C_7H_8NO_2^+.C_7H_2N_3O_8^-.H_2O$, $M_r = 412.3$, orthorhombic, $Pbcn$, $a = 29.528$ (4), $b = 11.306$ (2), $c = 10.603$ (1) Å, $V = 3539.9$ (8) Å^3, $Z = 8$, $D_m = 1.55$, $D_x = 1.546$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.15$ mm^{-1}, $F(000) = 1696$, $T = 295$ K, $R = 0.039$ for 958 observed reflections. (2) $C_5H_6NO^+.C_7H_2N_3O_8^-$, $M_r = 352.2$, monoclinic, $P2_1/c$, $a = 7.276$ (3), $b = 8.310$ (1), $c = 24.130$ (7) Å, $\beta = 92.48$ (2)°, $V = 1457.6$ (7) Å^3, $Z = 4$, $D_m = 1.60$, $D_x = 1.604$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.15$ mm^{-1}, $F(000) = 720$, $T = 295$ K, $R = 0.032$ for 1368 observed reflections. Compound (1) may be prepared by both solid-state and solution reactions. Crystals were obtained from water. Extensive hydrogen bonding between amino groups, carboxylic acids and waters exists. The two acids are uniquely hydrogen bonded across one carboxylic acid oxygen pair, with no interactions between the other two oxygens. Compound (2) was prepared in aqueous solution and crystallized from water. In this adduct, hydrogen bonding exists between the deprotonated carboxylic acid groups and the protonated pyridine nitrogens.

Introduction. 4-Aminobenzoic acid (4-ABA) is recognized as an important acid for molecular adduct formation. Prior to 1989 only two molecular co-crystals with 4-ABA were known, 4-nitropyridine *N*-oxide (Lechat, 1984) and 1,3-dimethyl-2-imidazolidinone (Ueda, Onishi & Nagai, 1986). Both the carboxylic acid and amino groups on 4-ABA have potential for hydrogen-bonding interactions. This property, together with the linearity of the molecule, was used in the synthesis of co-crystals with other carboxylic acids, particularly nitrobenzoic acids (Etter, Frankenbach & Bernstein, 1989; Etter & Frankenbach, 1989). Adduct formation may also result from a solid-state reaction, simply by grinding two acids together. In the structure of the 4-ABA–3,5-dinitrobenzoic acid adduct (Etter, Frankenbach & Bernstein, 1989) the carboxylic acids form hydrogen-bonded cyclic dimers while the amino and nitro groups also interact. 2,4,6-Trinitrobenzoic acid (TNBA) is an acid not previously reported in molecular adduct formation, possibly because it readily decarboxylates when boiled in water, forming 1,3,5-trinitrobenzene (TNB) (Coffey, 1977). This was observed in attempted co-crystal preparation of TNBA with indole-3-acetic acid (IAA), giving

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* Part 2: Lynch, Smith, Byriel & Kennard (1991*a*).

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