

Structure of 2-Acetoxyethoxy-7,7,8,8-tetracyanoquinodimethane, AETCNQ*

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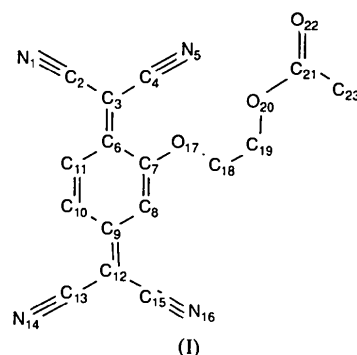
Abstract. IUPAC name: 2-[2,5-bis(dicyanomethylene)cyclohexadienyloxy]ethyl acetate, $C_{16}H_{10}N_4O_3$, $M_r = 306.28$, triclinic, $P\bar{1}$, $a = 7.165$ (3), $b = 9.058$ (8), $c = 13.244$ (4) Å, $\alpha = 70.06$ (7), $\beta = 87.14$ (3), $\gamma = 68.22$ (6)°, $V = 747.4$ Å³, $Z = 2$, $D_x = 1.36$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.06$ cm⁻¹, $F(000) = 316.0$, $T = 295$ (3) K, $R = 3.4\%$ for 1143 observed reflections. The TCNQ part of the AETCNQ molecule has an almost quinoid geometry with *mmm* symmetry, but the acetoxy tail curls over and points to the next AETCNQ molecule. The structure consists of 'dimers' stacked along [332], in which the carbonyl group of one AETCNQ approaches a ring H atom of the next AETCNQ molecule, but there is a low degree of π - π overlap (intra-'dimer' distance 3.518 Å, inter-'dimer' distance 3.385 Å). The lattice energy (Madelung plus dispersion plus repulsion) is -114.291 kJ mol⁻¹.

Introduction. The molecule $C_{12}H_3N_4OCH_2CH_2OC(=O)CH_3$ [AETCNQ, (1)] is the synthetic precursor (Metzger, Panetta, Miura & Torres, 1987) to the novel powerful monofunctionalized one-electron acceptor (A) $C_{12}H_3N_4OCH_2CH_2OH$ (HETCNQ) (Miura, Torres, Panetta & Metzger, 1988), which, when coupled covalently to strong electron donors *D*, should yield unimolecular electrical rectifiers $D-\sigma-A$ (because $D^+-\sigma-A^-$ is much lower in energy than $D^--\sigma-A^+$) (Metzger, Panetta, Heimer, Bhatti, Torres, Blackburn, Tripathy & Samuelson, 1986; Metzger & Panetta, 1987).

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Experimental. The synthesis of 2-acetoxyethoxy-7,7,8,8-tetracyanoquinodimethane (m.p. 416 K, uncorr.) has been described briefly (Metzger, Panetta, Miura & Torres, 1987); synthetic details are given elsewhere (Miura, Torres, Panetta & Metzger, 1988).

A red crystal of dimensions 0.10 × 0.15 × 0.20 mm was examined on an Enraf-Nonius CAD-4F automated four-circle diffractometer at the University of Alabama, using graphite-monochromatized Mo *K* α radiation. The orientation matrix was obtained by a least-squares fit to 24 medium reflections ($\theta = 1.6$ – 18.5°). Unique data ($h = 0$ to 11, $k = 0$ to 10, $l = -14$ to 14, $\theta = 1.00$ to 22.00°) were collected in the ω - 2θ scan mode at 0.8 to 21° min⁻¹: of 1861 reflections collected, 1143 were measured above background [$F_{\text{obs}} > 1.67\sigma(F_{\text{obs}})$]. The data were corrected for Lorentz and polarization factors, but not for absorption. The structure was solved by direct methods and refined by full-matrix least squares, using anisotropic thermal parameters for all non-H atoms, riding positions and variable isotropic thermal parameters for the H atoms, and unit weights, to a final unweighted *R* index of 3.4% (1143 observations, 218 parameters). The largest shift/e.s.d. was -0.157 . The largest peak in the final difference Fourier map, surprisingly, had a density of 0.072 e Å⁻³. Atomic scattering factors from *SHELX76*. The programs used were *DATRDN*

(Hunter, 1982), *MULTAN80* (Main *et al.*, 1980), *SHELX76* (Sheldrick, 1976), *ORTEPII* (Johnson, 1976), *SYBYL* (Tripos Associates, 1986), *CELMAP* (Metzger, 1976) and *EWALD* (Metzger, 1976).

Discussion. The final atom coordinates are given in Table 1, the bond distances and bond angles within the molecule are given in Table 2.* The unit-cell packing, with the intra-‘dimer’ perpendicular overlap, can be seen in Fig. 1.

The TCNQ ring system of AETCNQ is very flat, but the acetoxyethoxy substituent is folded and hydrogen

* Lists of H-atom positions, least-squares planes, INDO charges, anisotropic temperature factors, and calculated and observed structure amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44391 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonded to the next AETCNQ molecule. The TCNQ part of AETCNQ almost has the ideal *mmm* ($=D_{2h}$) quinoid symmetry of TCNQ itself; the bond distances of Table 2 are very close to the bond distances in TCNQ (Long, Sparks & Trueblood, 1965). The malononitrile group N1–C2–C3–C4–N5 is bent slightly upward, in the direction of the acetoxyethoxy group. The molecules related by the inversion center at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ have some perpendicular overlap between the six-membered rings, but the molecules are shifted sideways away from eclipsed overlap. The acetoxyethoxy group of one molecule curls over and approaches (O22...H10) the next molecule along the stack. There is one short non-bonded contact, N1...N16 (3.070 Å). The structure consists of a chain of AETCNQ molecules stacked as weak ‘dimers’ along

Table 2. Bond distances (Å) and bond angles (°) within the AETCNQ molecule

N1–C2	1.141 (4)	C12–C13	1.428 (5)
C2–C3	1.443 (5)	C12–C15	1.435 (5)
C3–C4	1.442 (5)	N14–C13	1.137 (4)
C3–C6	1.363 (4)	N16–C15	1.142 (4)
N5–C4	1.140 (4)	C7–O17	1.340 (4)
C6–C7	1.466 (4)	O17–C18	1.448 (4)
C6–C11	1.446 (4)	C18–C19	1.501 (5)
C7–C8	1.354 (4)	C19–O20	1.443 (4)
C8–C9	1.428 (4)	C21–C23	1.498 (5)
C9–C10	1.456 (5)	C21–O20	1.349 (5)
C9–C12	1.377 (4)	C21–O22	1.191 (5)
C10–C11	1.342 (4)		
N1–C2–C3	178.5 (4)	C9–C10–C11	120.6 (3)
C2–C3–C4	112.0 (3)	C6–C11–C10	121.3 (3)
C2–C3–C6	120.4 (3)	C9–C12–C13	122.6 (3)
C4–C3–C6	127.5 (3)	C9–C12–C15	123.3 (3)
N5–C4–C3	173.5 (4)	C13–C12–C15	114.1 (3)
C3–C6–C7	121.9 (3)	C12–C13–N14	177.6 (4)
C3–C6–C11	120.8 (3)	C12–C15–N16	177.0 (4)
C7–C6–C11	117.2 (3)	C7–O17–C18	121.1 (3)
C6–C7–O17	112.2 (3)	O17–C18–C19	111.0 (3)
C6–C7–C8	121.3 (3)	C18–C19–O20	108.6 (3)
C8–C7–O17	126.5 (3)	C19–O20–C23	117.7 (3)
C7–C8–C9	120.2 (3)	O20–C21–O22	123.1 (4)
C8–C9–C10	119.1 (3)	O20–C21–C23	110.6 (4)
C8–C9–C12	121.2 (3)	O22–C21–C23	126.2 (5)
C10–C9–C12	119.7 (6)		

Table 1. Atomic coordinates and equivalent isotropic thermal parameters for non-H atoms (Å²)

$U_{eq} = \frac{1}{3}$ (trace of the orthogonalized U tensor).

	x	y	z	U_{eq}
N1	1.0971 (5)	0.0897 (4)	0.6903 (3)	0.064 (10)
C2	0.9734 (6)	0.1963 (5)	0.7101 (3)	0.048 (5)
C3	0.8177 (5)	0.3283 (4)	0.7380 (3)	0.042 (3)
C4	0.7916 (6)	0.2760 (5)	0.8518 (3)	0.049 (5)
N5	0.7838 (5)	0.2197 (4)	0.9424 (3)	0.067 (14)
C6	0.7097 (5)	0.4786 (4)	0.6601 (3)	0.039 (2)
C7	0.5544 (5)	0.6174 (4)	0.6857 (3)	0.041 (1)
C8	0.4376 (5)	0.7610 (4)	0.6070 (3)	0.039 (4)
C9	0.4698 (5)	0.7834 (4)	0.4963 (3)	0.041 (2)
C10	0.6295 (5)	0.6501 (4)	0.4696 (3)	0.044 (3)
C11	0.7433 (5)	0.5067 (4)	0.5476 (3)	0.044 (3)
C12	0.3528 (5)	0.9284 (4)	0.4150 (3)	0.043 (2)
C13	0.3807 (6)	0.9543 (5)	0.3037 (3)	0.051 (8)
N14	0.3968 (6)	0.9798 (5)	0.2141 (3)	0.079 (25)
C15	0.1931 (6)	1.0662 (5)	0.4342 (3)	0.046 (4)
N16	0.0645 (5)	1.1794 (4)	0.4447 (3)	0.060 (8)
O17	0.5480 (3)	0.5838 (3)	0.7922 (2)	0.046 (7)
C18	0.3925 (5)	0.6967 (5)	0.8351 (3)	0.048 (7)
C19	0.1971 (6)	0.6719 (5)	0.8326 (3)	0.052 (6)
O20	0.2240 (4)	0.5037 (4)	0.9050 (2)	0.063 (15)
C21	0.2367 (6)	0.3863 (6)	0.8612 (4)	0.066 (4)
O22	0.2217 (6)	0.4165 (4)	0.7664 (3)	0.100 (53)
C23	0.2770 (8)	0.2173 (6)	0.9473 (4)	0.075 (13)

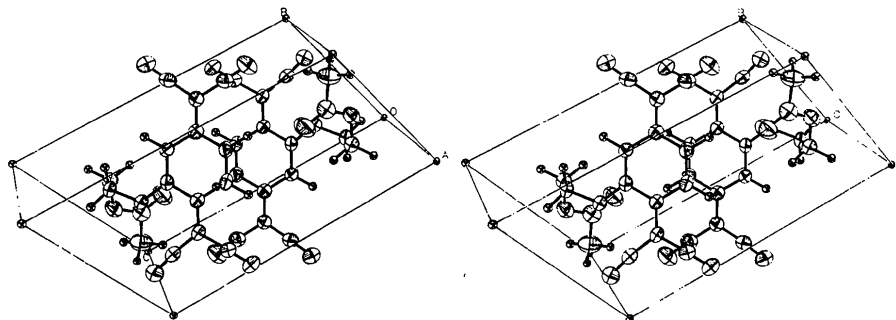


Fig. 1. Stereoscopic *ORTEPII* drawing (Johnson, 1971) of the unit cell, showing the perpendicular overlap between the AETCNQ molecules involved in the ‘dimer’. The thermal ellipsoids of vibration are depicted at the 90% probability level.

[332]; the normal to the least-squares plane of the central ring has Miller indices 2·006, 2·189, 1·000; the six-membered rings have two alternating perpendicular distances: 3·518 Å (intra-'dimer' distance, *i.e.* distance between the two molecules which are related by the inversion center at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and 3·385 Å (inter-'dimer' distance). Oddly, the inter-'dimer' distance is shorter than the intra-'dimer' distance.

Using the INDO atom-in-molecule charges (Pople & Beveridge, 1970),* the Madelung energy (Metzger, 1981) for AETCNQ, obtained by Ewald's method, is $E_M = -10·765 \text{ kJ mol}^{-1}$. Using the non-bonded van der Waals and repulsion parameters of Williams and co-workers (Williams, 1981; Williams & Cox, 1984; Cox, Hsu & Williams, 1981), the dispersion and repulsion energies for AETCNQ are $E_d = -199·260$ and $E_r = 95·734 \text{ kJ mol}^{-1}$, respectively, so that $E_M + E_d + E_r = -114·291 \text{ kJ mol}^{-1}$, a value that should correlate with enthalpies of sublimation.

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* See deposition footnote.

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Structure of Methyl 4-(*N,N*-Dimethylamino)phenylcarbamate, DMAPCMe*

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Abstract. *Chemical Abstracts* name [4-(dimethylamino)phenyl]carbamic acid, methyl ester; registry number 78823-56-0; $C_{10}H_{14}N_2O_2$, $M_r = 194·23$, orthorhombic, *Pbca* (space group number 61), $a =$

$13·926(4)$, $b = 9·999(4)$, $c = 14·854(7) \text{ Å}$, $V = 2068·3 \text{ Å}^3$, $Z = 8$, $D_x = 1·25 \text{ Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0·71069 \text{ Å}$, $\mu = 0·53 \text{ mm}^{-1}$, $F(000) = 832$, $T = 295(3) \text{ K}$, $R = 5·9\%$ for 786 observed reflections. The structure consists of flat molecules stacked along [001], with a large tilt, but no π - π perpendicular overlap. There is a significant quinoid distortion. The packing is controlled by intermolecular hydrogen bonding along [010]. This is supported by the infrared spectrum of the solid (N—H band at 3330 cm^{-1}). INDO and MINDO/3 calculations, and also the partial quinoid structure, suggest that DMAPCMe is a fairly strong electron

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References

- COX, S. R., HSU, L.-Y. & WILLIAMS, D. E. (1981). *Acta Cryst.* A37, 293–301.
- HUNTER, W. E. (1982). *DATRDN*. Univ. of Alabama, AL, USA.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138, revised. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
- LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* 18, 932–939.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- METZGER, R. M. (1976). *J. Chem. Phys.* 64, 2069–2075.
- METZGER, R. M. (1981). *Top. Curr. Phys.* 26, 80–107.
- METZGER, R. M. & PANETTA, C. A. (1987). Proc. Eighth Winter Conf. on Low-Temp. Physics, Cuernavaca, Mexico. In the press.
- METZGER, R. M., PANETTA, C. A., HEIMER, N. E., BHATTI, A. M., TORRES, E., BLACKBURN, G. F., TRIPATHY, S. K. & SAMUELSON, L. A. (1986). *J. Mol. Electronics*, 2, 119–124.
- METZGER, R. M., PANETTA, C. A., MIURA, Y. & TORRES, E. (1987). *Synth. Met.* 18, 797–802.
- MIURA, Y., TORRES, E., PANETTA, C. A. & METZGER, R. M. (1988). *J. Org. Chem.* 53, 439–440.
- POPLE, J. A. & BEVERIDGE, D. L. (1970). *Approximate Molecular Orbital Theory*. New York: McGraw-Hill.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- Tripos Associates (1986). *SYBYL*. Molecular modeling software. St Louis, MO, USA.
- WILLIAMS, D. E. (1981). *Top. Curr. Phys.* 26, 3–40.
- WILLIAMS, D. E. & COX, S. R. (1984). *Acta Cryst.* B40, 404–417.