

7,7,8,8-Tetracyanoquinodimethane(perylene)₂-Perylene*

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Abstract. $3C_{20}H_{12} \cdot C_{12}H_4N_4$, FW 961.15, triclinic, $P\bar{1}$, $a = 10.8750$ (3), $b = 12.6993$ (4), $c = 10.4217$ (3) Å, $\alpha = 114.905$ (2), $\beta = 90.797$ (2), $\gamma = 112.615$ (2)° at 20°C, $\lambda(\text{Cu } K\alpha_1) = 1.54051$ Å, $V = 1178.2$ Å³, $D_m = 1.36$, $Z = 1$, $D_x = 1.354$ g cm⁻³. Each molecule of $C_{12}H_4N_4$ (TCNQ) is sandwiched between two perylene molecules, with a mean interplanar spacing of 3.29 Å. The overlap configuration is favourable for charge transfer, and the distribution of bond lengths in TCNQ is consistent with the acquisition of 0.2 units of charge. Intermolecular distances suggest that the structure comprises discrete perylene molecules and units of TCNQ(perylene)₂.

Introduction. The crystals, prepared by Truong & Bandrauk (1976), are dark blue, shiny, and of compact habit. The specimen used for all X-ray measurements had extreme dimensions of 0.3 and 0.6 mm. The unit-cell constants were derived by least-squares refinement from the measured 2θ values (none less than 159°) of 30 independent reflexions. The intensities of the 4006 independent reflexions within the limiting sphere $2\theta = 130^\circ$ were measured with a Picker automatic diffractometer, using Ni-filtered Cu $K\alpha$ radiation and a scintillation counter. The $\theta-2\theta$ scan mode was used, with scans of 2° for $2\theta < 100^\circ$, and 3° otherwise. In addition, the intensities of the 1258 independent reflexions in the range $130 < 2\theta < 165^\circ$ were measured with a manually set General Electric XRD5 diffractometer, using a broad source and stationary specimen and detector (Furnas, 1957). For scaling and correlation purposes the 116 most intense reflexions in this range (and some at lower angles) were measured also by $\theta-2\theta$ scanning. Background intensities were estimated from an experimentally derived function of θ . Of the 5264 accessible reflexions, 417 were considered to be unobserved, as their net intensities were less than either 50 counts or 10% of the corresponding background intensity. No correction was made for absorption ($\mu = 6.2$ cm⁻¹).

A trial structure was deduced from inspection of the sharpened F_o^2 synthesis, and refined by block-diagonal

Table 1. Atomic coordinates with their e.s.d.'s ($\times 10^3$ for H; $\times 10^4$ otherwise)

	x	y	z
Perylene 1			
C (1)	-2983 (1)	664 (2)	4406 (2)
C (2)	-2134 (2)	1929 (2)	5233 (2)
C (3)	-730 (2)	2377 (1)	5296 (2)
C (4)	2219 (2)	3311 (1)	5373 (2)
C (5)	3619 (2)	3745 (2)	5401 (2)
C (6)	4131 (1)	2902 (2)	4637 (2)
C (7)	3267 (1)	1578 (2)	3811 (1)
C (8)	1838 (1)	1126 (1)	3771 (1)
C (9)	1315 (1)	2024 (1)	4573 (1)
C (10)	-159 (1)	1559 (1)	4525 (1)
C (11)	3790 (1)	691 (2)	3017 (2)
C (12)	2950 (2)	-584 (2)	2234 (2)
C (13)	1545 (1)	-1041 (1)	2181 (2)
C (14)	-1406 (1)	-1955 (1)	2032 (1)
C (15)	-2807 (1)	-2378 (1)	1979 (2)
C (16)	-3328 (1)	-1538 (1)	2737 (2)
C (17)	-2460 (1)	-219 (1)	3600 (1)
C (18)	-1027 (1)	227 (1)	3660 (1)
C (19)	-502 (1)	-669 (1)	2860 (1)
C (20)	970 (1)	-212 (1)	2924 (1)
H (1)	-395 (2)	32 (2)	432 (2)
H (2)	-253 (2)	251 (2)	582 (2)
H (3)	-15 (2)	334 (2)	596 (2)
H (4)	185 (2)	392 (2)	599 (2)
H (5)	421 (3)	468 (2)	600 (3)
H (6)	512 (3)	317 (3)	463 (3)
H (11)	479 (2)	101 (2)	305 (2)
H (12)	334 (2)	-119 (2)	173 (3)
H (13)	93 (2)	-199 (2)	161 (2)
H (14)	-103 (2)	-259 (2)	147 (2)
H (15)	-341 (2)	-325 (2)	138 (2)
H (16)	-432 (2)	-186 (2)	271 (2)
Perylene 2			
C (1)	-2497 (2)	5062 (1)	-2474 (2)
C (2)	-3324 (1)	4596 (2)	-1687 (2)
C (3)	-2806 (1)	4398 (1)	-619 (2)
C (4)	-1680 (1)	4004 (1)	1648 (2)
C (5)	-1134 (2)	3853 (1)	2747 (2)
C (6)	224 (2)	4168 (1)	3035 (2)
C (7)	1094 (1)	4644 (1)	2219 (1)
C (8)	551 (1)	4826 (1)	1115 (1)
C (9)	-878 (1)	4494 (1)	836 (1)
C (10)	-1435 (1)	4680 (1)	-307 (1)
H (1)	-285 (3)	519 (2)	-325 (3)
H (2)	-431 (2)	437 (2)	-188 (2)
H (3)	-338 (2)	408 (2)	-7 (2)
H (4)	-266 (2)	378 (2)	140 (2)
H (5)	-173 (3)	353 (2)	331 (3)
H (6)	64 (2)	408 (2)	383 (2)
TCNQ			
C (1)	1413 (1)	379 (1)	29 (1)
C (2)	443 (1)	-948 (1)	-774 (1)
C (3)	-902 (1)	-1312 (1)	-807 (1)
C (7)	2787 (1)	738 (1)	54 (1)
C (9)	3276 (1)	-203 (1)	-716 (1)
N (9)	3635 (1)	-976 (1)	-1343 (2)
C (10)	3788 (1)	2043 (1)	821 (1)
N (10)	4597 (1)	3087 (1)	1424 (2)
H (9)	-153 (2)	-218 (2)	-132 (2)
H (10)	77 (2)	-160 (2)	-127 (2)

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least squares, minimizing $\sum w(\Delta F)^2$. The weighting scheme, adopted to reduce systematic dependence of the weighted residual on $|F_o|$ and θ , was $w = F_o \sin \theta/2$ for $F_o < 2$, $= 2 \sin \theta/F_o$ otherwise. The 146 most intense reflexions were corrected for extinction using the method of Pinnock, Taylor & Lipson (1956). The largest correction was 60% of $|F_o|$. In the final stages of refinement 12 weak reflexions for which the calculated amplitudes were inexplicably small were assigned zero weight. The refinement converged at $R = 0.047$ (observed reflexions only). In the final cycle no parameter shift exceeded $\frac{1}{3}$ of the corresponding e.s.d. The final atomic coordinates are given in Table 1.*

In order to assess the probable effect on bond lengths, the thermal motion has been analysed by the method of Schomaker & Trueblood (1968). The results are in good accord with the assumption that each of the perylene molecules and the group of eight innermost C atoms of TCNQ behave as rigid bodies. For TCNQ the libration is severely anisotropic, and the axis of greatest libration (r.m.s. amplitude 4.6°) lies 11° from the long axis of the molecule. For the perylene molecules the librations are smaller, and more nearly isotropic (maximum amplitudes 3.6 and 3.7°). Appropriate bond-length corrections have been applied (Busing & Levy, 1964). They range from 0.002 to 0.005 Å for TCNQ and from 0.003 to 0.004 Å for perylene. (It is to be noted that the corrections are probably underestimated for the C—N bonds of TCNQ.)

The bond lengths have been determined to a nominal accuracy of 0.002 to 0.003 Å. There are no significant differences between the bond-length distributions in the two perylene molecules, and it must be assumed that they are identical. There are therefore groups of as many as six chemically equivalent bonds for comparison. The greatest range of values in any of these is 0.009 Å ($t = 3.2$).

Computer programs used were those of P. K. Gantzel and K. N. Trueblood (MGTLS, thermal-motion analysis) and Ahmed, Hall, Pippy & Huber (1973). Atomic scattering factors were taken from Stewart, Davidson & Simpson (1965) for H, and from Hanson, Herman, Lea & Skillman (1964).

Discussion. All molecules in the structure are approximately planar, as no C or N atom lies more than 0.04 Å from the appropriate molecular plane. Mean bond lengths are given in Fig. 1. For perylene these appear normal, although no very precise comparison values are available. For TCNQ the bond lengths are inter-

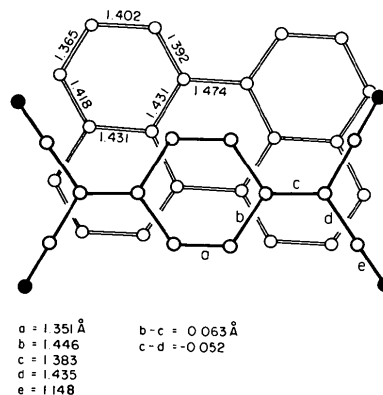


Fig. 1. Overlapping molecules, viewed normal to the mean plane of the perylene molecule. The e.s.d.'s of the interatomic distances shown are 0.002 to 0.003 Å.

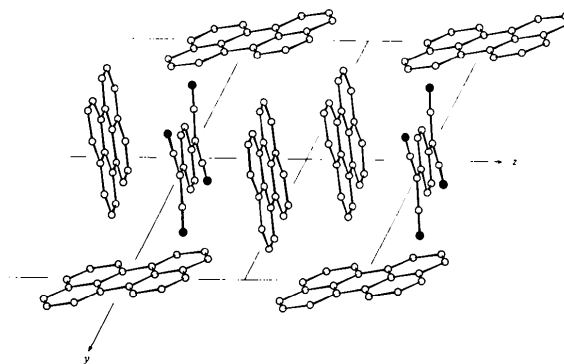


Fig. 2. The structure viewed along a.

mediate between those observed for neutral TCNQ (Long, Sparks & Trueblood, 1965) and for $R^+(\text{TCNQ})_2^-$ (Goldstein, Seff & Trueblood, 1968; Hanson, 1968). Recently, Flandrois & Chasseau (1977) have demonstrated that the amount of charge transfer in salts of TCNQ can be estimated from the bond-length distribution (or, more precisely, from the differences $b-c$ and $c-d$, Fig. 1). The distribution observed here is consistent with the acquisition of about $0.2 e$ by the (average) TCNQ molecule. A view of the structure is given in Fig. 2. Each TCNQ molecule is sandwiched between two perylene molecules, overlapped as shown in Fig. 1, with a mean separation of 3.29 Å. The overlap configuration is essentially that proposed by Mayoh & Prout (1972) for maximum charge-transfer interaction, and observed (with a separation of 3.44 Å) for the 1:1 complex of these molecules (Tickle & Prout, 1973). There is therefore consistent evidence for appreciable charge transfer in this compound. Adjacent overlapping perylene molecules are separated by 3.48 Å, a distance indicative of no interaction stronger than van der Waals. The second perylene molecule lies almost at

* Lists of structure factors, thermal parameters, details of the thermal-motion analysis, bond lengths and angles and details of molecular planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33455 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

right angles to the first, and does not appear to interact with adjacent molecules. It seems appropriate therefore to describe the structure as resulting from the co-crystallization of perylene molecules and units of TCNQ(perylenes)₂.

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Structure of 1-Benzyl(methyl)amino-1-deoxy- α -D-lyxo-hexulopyranose

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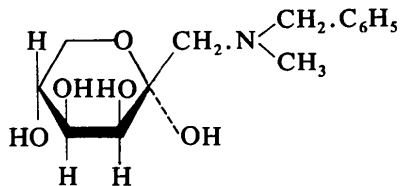
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Abstract. C₁₄H₂₁NO₅, orthorhombic, *P*2₁2₁2₁, *a* = 25.194 (2), *b* = 7.881 (1), *c* = 6.974 (1) Å, *Z* = 4, *D*_c = 1.36, *D*_m = 1.37 g cm⁻³; single-crystal X-ray analysis from diffractometer data [$\lambda(\text{Mo } K\alpha) = 0.7107$ Å]. The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final *R* of 0.047. The molecular packing is clearly dominated by the formation of hydrogen bonds.

Introduction. The structure determination of the title compound was undertaken as part of a series of structural studies of compounds (of the 1-alkylamino-1-deoxyketose type) obtained by the reaction of aldoses and aliphatic amines and Amadori transposition (Michael & Hagmann, 1959; Schneider & Geyer, 1964; Fernández Bolaños & Jimenez-Gracia, 1977). These highly reactive compounds are intermediate products in the synthesis of a large number of heterocyclic N compounds.

Studies based on infrared spectroscopy proposed pyranose and hemiacetal structures for these compounds. The present paper confirms that the ketose chain is pyranose and that the hemiacetal hydroxyl is in the α position.



The crystals of C₁₄H₂₁NO₅ were colourless prisms elongated along the *c* axis. Weissenberg and rotation photographs established that the crystals were orthorhombic, space group *P*2₁2₁2₁.

Intensity data were collected by the ω -2 θ scan method on a Philips automated four-circle diffractometer with graphite-monochromated Mo *K* α radiation.