

(Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Tetracyano-*p*-xylene†

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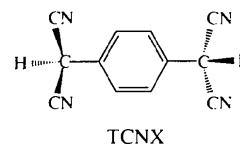
Abstract

The title compound, C₁₂H₆N₄, may be considered as the hydrogenated form of tetracyanoquinodimethane. The main property shown in the solid state is luminescence (blue–green emission) and it is due to the stacking interaction established between molecules along the *z* axis related by a *c* glide plane.

† IUPAC name: 2,2'-(*p*-phenylene)bis(propanedinitrile).

Comment

Over the last decade, organic semiconductors have attracted renewed interest owing to their potential applications as active layers in electronic and optoelectronic devices such as light-emitting diodes (Cimrova & Neher, 1996; Kalinowski *et al.*, 1996; Burrows *et al.*, 1996). Since its discovery in 1960, tetracyanoquinodimethane (TCNQ) has been among the most extensively studied semiconductors, owing to its ability to form small-band-gap charge-transfer complexes and organic metals suitable for technological uses (Epstein & Reiff, 1988; Bozio & Pecile, 1991; Miller, 1981–1983; Ferraro & Williams, 1987; Marks, 1990). Here we report the synthesis and the crystal structure of the hydrogenated form of TCNQ, namely the tetracyano-*p*-xylene (TCNX) obtained for the first time as a single crystal. As indicated by optical studies, TCNX seems to be a promising candidate for the realization of optoelectronic devices. The results of absorption measurements indicate that TCNX is a semiconductor with a direct optical absorption threshold below 450 nm, comparable to that of TCNQ. The most striking difference between the optical behaviour of TCNQ and TCNX is that TCNX shows an intense photoluminescence spectrum when excited with light of wavelength lower than 450 nm. Preliminary measurements of luminescence *versus* temperature show the presence of at least two emission bands, centred at approximately 480 nm and 530 nm, characterized by different mean lifetimes.



It is well known (Melby *et al.*, 1962) that AgTCNQ microcrystals can be easily obtained by dipping a metallic plate into a saturated solution of TCNQ. According to the literature (Duan *et al.*, 1993), the microcrystals form as a result of a corrosion process that the metal undergoes in the presence of the highly oxidizing TCNQ. We have noticed that when a silver plate is immersed in a TCNQ solution in ethanol in the presence of 1 mM 1,8-octanedithiol, AgTCNQ does not form and needle-shaped TCNX single crystals (mean dimension 0.1 × 0.3 × 5 mm) grow in a few days. This result can be explained as a consequence of the presence of self-assembled dithiol layers that, according to the literature (Ulman, 1996), grow on silver when it is dipped in alcoholic solutions containing alkane dithiols. The dithiol layers act as an anti-corrosion film, preventing the metal oxidation and thus preventing the formation of the AgTCNQ complex. At the same time, the dithiol layers behave as a substrate for the spontaneous growth of the TCNX crystals.

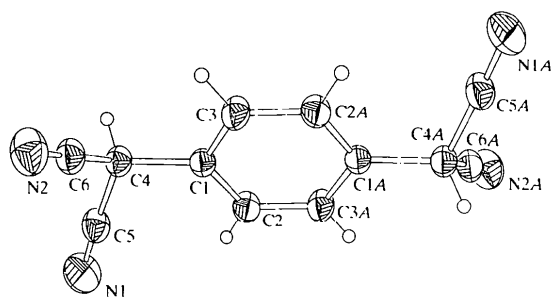


Fig. 1. A view of the title compound showing the atomic numbering scheme and displacement ellipsoids at the 50% probability level for non-H atoms.

The molecule lies on an inversion centre so there is only half a molecule in the asymmetric unit. It was expected that an sp^2 -C atom would join the cyano groups to the phenyl ring. The hydrogen at C4 may show some tendency to be lost. Geometrical parameters show such a situation [C4—C5 1.475 (1), C4—C6 1.476 (1), C4—C1 1.531 (1) Å, C5—C4—C6 108.89 (8), C6—C4—C1 111.99 (7), C5—C4—C1 112.28 (8)°]. They also testify to a slight electronic delocalization involving the C—C single bonds close to the cyano groups and the C—C single-bond character for C4—C1, in contrast to the bond lengths measured for all the TCNQ molecules where a wide electronic delocalization has been observed (Viossat *et al.*, 1995; Corfield & La Placa, 1996).

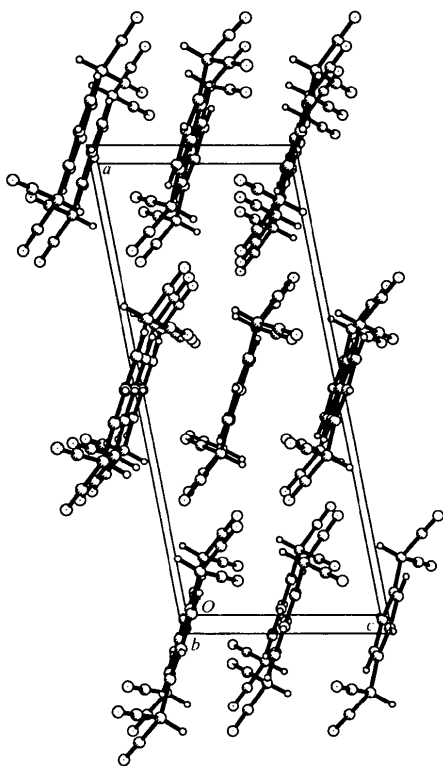


Fig. 2. A view of the crystal packing along the b axis.

C4 is only 0.057 (1) Å out of the plane of the aryl ring and C5 and C6 are on the opposite side of the same plane by 0.316 (1) and 0.807 (1) Å with respect to C4, respectively. The CN triple bond assumes its typical value [C5—N1 1.137 (1), C6—N2 1.133 (1) Å]. The most interesting feature found is the crystal packing which may justify the physical properties of the compound. The crystal may be viewed as a stack of (001) planes with a stacking distance of 3.823 (1) Å. Such graphitic interaction between the molecules that form piles along the z axis may be the reason why, unlike the most common organic materials, the optical spectrum of the crystal phase of TCNQ is substantially different from that of the constituting individual molecule (Rinaldi *et al.*, 1998).

Experimental

Crystals suitable for X-ray diffractometric analysis were obtained as described in a recent paper (Rinaldi *et al.*, 1998).

Crystal data

C₁₂H₆N₄
 $M_r = 206.21$
 Monoclinic
 $C2/c$
 $a = 18.4255 (16)$ Å
 $b = 7.2396 (6)$ Å
 $c = 7.6466 (5)$ Å
 $\beta = 101.126 (6)^\circ$
 $V = 1000.83 (14)$ Å³
 $Z = 4$
 $D_x = 1.369$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 48 reflections
 $\theta = 5.5\text{--}13.5^\circ$
 $\mu = 0.088$ mm⁻¹
 $T = 293 (2)$ K
 Prismatic
 $0.8 \times 0.8 \times 0.4$ mm
 Yellow

Data collection

Siemens $R3m/V$ diffractometer
 ω - 2θ scans
 Absorption correction:
 ψ scan (Kopfmann & Huber, 1968)
 $T_{\min} = 0.902$, $T_{\max} = 0.965$
 1936 measured reflections
 1467 independent reflections

1073 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.010$
 $\theta_{\max} = 30.06^\circ$
 $h = 0 \rightarrow 25$
 $k = -2 \rightarrow 10$
 $l = -10 \rightarrow 10$
 3 standard reflections
 every 197 reflections
 intensity decay: 0.43%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.107$
 $S = 0.966$
 1467 reflections
 86 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0713P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.337$ e Å⁻³
 $\Delta\rho_{\min} = -0.201$ e Å⁻³
 Extinction correction:
 SHELXL97 (Sheldrick, 1997a)
 Extinction coefficient:
 0.004 (3)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

C1—C4	1.531 (1)	C5—N1	1.136 (1)
C4—C5	1.475 (1)	C6—N2	1.133 (1)
C4—C6	1.476 (1)		
C5—C4—C6	108.9 (8)	N1—C5—C4	177.2 (1)
C5—C4—C1	112.3 (8)	N2—C6—C4	179.5 (1)
C6—C4—C1	112.0 (7)		

Reflection intensities were evaluated by profile fitting of a 96-step peak scan using a 2θ shell procedure (Diamond, 1969) and then corrected for Lorentz–polarization effects. Standard uncertainties, $\sigma(I)$, were estimated from counting statistics. H atoms have been treated isotropically [U_{iso} varies from 0.035 (3) to 0.061 (4) \AA^2]. C—H bond lengths range from 0.95 (1) for C4—H4 to 1.01 (2) \AA for C3—H3. All calculations were performed on a μ -VAX 3400 and on an AXP DecStation 3000/400.

Data collection: *P3/V* (Siemens, 1989). Cell refinement: *P3/V*. Data reduction: *XDISK* (Siemens, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *XPW* (Siemens, 1996). Software used to prepare material for publication: *PARST95* (Nardelli, 1995) and *SHELXL97*.

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2'-(1,3-Dithiolan-2-ylidene)-4'-(1,3-dithiol-2-ylidene)spiro[1,3-dithiole-2,5'-(4*H*-5',6'-dihydro-1',3'-dithiapentalene)], the Self-Condensation Product of an Extended Tetrathiafulvalene Derivative

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Abstract

Silica-gel treatment of the extended tetrathiafulvalene derivative 2,3-bis(1,4-dithiafulven-6-yl)-6,7-dihydro-tetrathiafulvalene, bearing two 1,4-dithiafulven-6-yl groups in vicinal positions, afforded the title compound, $\text{C}_{14}\text{H}_{10}\text{S}_8$, as a cyclization product. While one dithiafulvenyl group is still conjugated with the tetrathiafulvalene moiety, the other one gives rise to a strongly folded 1,3-dithiole group linked to the molecule through a spiro-C atom. Two short non-bonding intramolecular 1,5-S...S contacts are also identified in the title compound.

Comment

Extended tetrathiafulvalene derivatives such as (1) (see scheme below) have proved to be interesting candidates as precursors for the synthesis of novel organic conducting materials (Sallé *et al.*, 1996). We recently reported that the electrocrystallization of (1) in the presence of $n\text{-Bu}_4\text{NClO}_4$ affords a 1:1 salt with ClO_4^- (Sallé *et al.*, 1993). This salt exhibits a novel mode of overlap, which allows the outer dithiafulvenyl groups of (1) to interleave in a direction perpendicular to the stacking axis.