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## Key indicators

Single-crystal X-ray study  
 $T = 173$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å  
 $R$  factor = 0.048  
 $wR$  factor = 0.157  
Data-to-parameter ratio = 12.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.9-Methylene-10,10-bis(phenylethynyl)fluorene–  
tetracyano-*para*-quinodimethane (2/3)In the title compound,  $2\text{C}_{30}\text{H}_{18}\cdot 3\text{C}_{12}\text{H}_4\text{N}_4$ , the asymmetric unit  
consists of half a formula unit (one quinodimethane molecule  
displays inversion symmetry). There is no ring stacking;  
instead, the residues associate by weak  $\text{C}-\text{H}\cdots\text{N}$  contacts in  
planes parallel to  $(2\bar{1}\bar{1})$ .

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## Comment

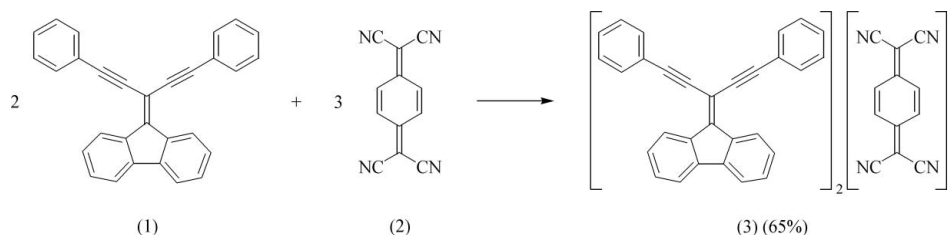
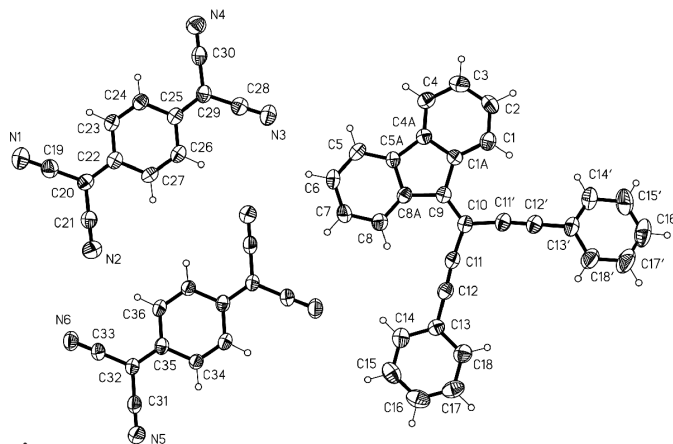
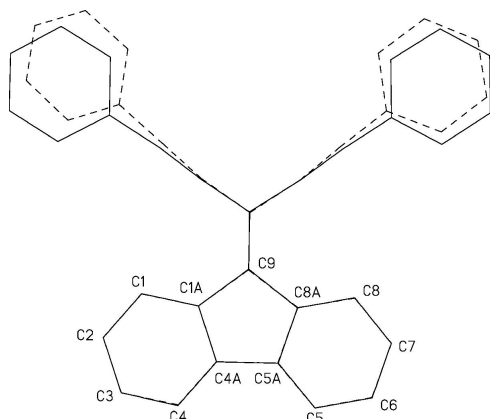
In a previous paper (Jones *et al.*, 2005), we have described the  
structure of the cross-conjugated fluorene derivative (1). We  
expected that this very electron-rich compound would form a  
charge-transfer complex with a suitable acceptor molecule  
such as tetracyano-*para*-quinodimethane (TCNQ), (2) [for a  
similar example, see Jones *et al.* (2004)]; the 2:3 adduct from  
these components, (3), was prepared (see *Experimental*), and  
its structure is described here.The asymmetric unit of (3) is shown in Fig. 1. It consists of  
one molecule of the fluorene (1) and one and a half molecules  
of TCNQ, corresponding to a 2:3 stoichiometry. The half  
molecule is completed by inversion symmetry. Bond lengths

Figure 1

The asymmetric unit of (3), together with the second half of the  
centrosymmetric TCNQ molecule. Displacement ellipsoids are shown at  
the 50% probability level. H atom radii are arbitrary. Only the  
asymmetric unit is numbered. Unlabelled atoms are related to labelled  
atoms by the inversion symmetry operator  $1-x, 2-y, 1-z$

**Figure 2**

Least-squares fit of the fluorene component (1) in complex (3) (dashed lines) with uncomplexed (1) (Jones *et al.*, 2005).

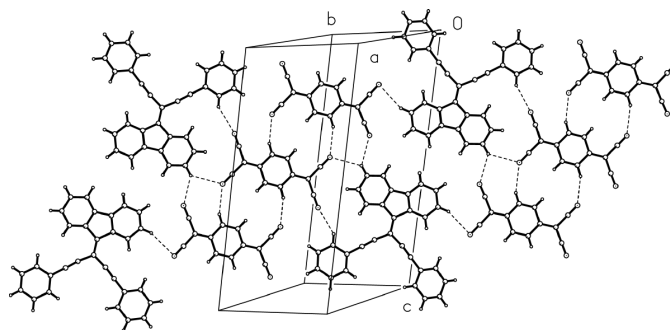
and angles (*e.g.* the necessarily distorted, formally  $sp^2$  angles at C9) may be regarded as normal (Table 1). The dimensions of the fluorene component (1) are similar to those of uncomplexed (1) (Jones *et al.*, 2005); a least-squares fit of the 13 atoms of the fluorene ring system, which is essentially planar [r.m.s. deviation from best plane 0.026 Å in (3)], gave an r.m.s. deviation between both structures of 0.022 Å. Slight differences between (3) and uncomplexed (1) in the angles at C10, C11, C11', C12 and C12', coupled with differences in the interplanar angles between the phenyl rings and the fluorene plane [in (3); 3.1 (2) and 19.2 (2)°], lead to small but significant differences in the relative position of the rings (Fig. 2).

A common feature of complexes of TCNQ is ring stacking, albeit sometimes of limited extent (*e.g.* Jones *et al.*, 2004). The molecular packing of (3) (Fig. 3), however, shows no stacking. Instead, the residues lie in planes parallel to (211), and are associated by weak C—H...N interactions (Table 2) to form a broad band in which groups of two molecules of (1) alternate with groups of three molecules of TCNQ. The distance between neighbouring planes is only 3.19 Å; the TCNQ residues of one plane lie above the fluorene residues of the neighbouring plane and *vice versa*. Despite this short distance, any apparent ring stacking proved to be an artifact of view direction; the least unconvincing stacking is C22—C27 of one layer to C13—C18 of the next, with interplanar angle 5.2 (2)°, intercentroid distance 3.66 Å, vertical displacement 3.39 Å and lateral displacement 1.38 Å. All other pairs of rings have larger lateral displacements (> 1.7 Å).

Although such complexes of TCNQ are generally labelled 'charge transfer complexes', the actual extent of charge transfer can vary appreciably. The bond lengths of the TCNQ residues of (3), of which a representative selection is given in Table 1, are such as to indicate very little charge transfer according to the criteria of Kistenmacher *et al.* (1982).

## Experimental

An acetonitrile solution of 10,10-bis(phenylethynyl)-9-methylnene-fluorene, (1), was treated with an equimolar amount of tetracyano-*para*-quinodimethane, (2) (Berger, 2005). Crystals of the title

**Figure 3**

Crystal packing of compound (3), viewed perpendicular to (211). Radii are arbitrary. Weak hydrogen bonds are indicated by dashed lines.

adduct precipitated after a short time and proved to be suitable for structure determination. Consistent analytical and spectroscopic data (Berger, 2005) were recorded.

### Crystal data

$2C_{30}H_{18} \cdot 3C_{12}H_4N_4$   
 $M_r = 1369.46$   
 Triclinic,  $P\bar{1}$   
 $a = 9.589$  (5) Å  
 $b = 9.617$  (5) Å  
 $c = 21.952$  (12) Å  
 $\alpha = 80.81$  (3)°  
 $\beta = 80.64$  (4)°  
 $\gamma = 62.50$  (4)°  
 $V = 1763.4$  (16) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.290$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 10$ –11.5°  
 $\mu = 0.08$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 Plate, dark blue–violet  
 $0.7 \times 0.7 \times 0.1$  mm

### Data collection

Siemens R3 diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 9928 measured reflections  
 6211 independent reflections  
 2764 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.050$

$\theta_{max} = 25.0^\circ$   
 $h = -11 \rightarrow 9$   
 $k = -11 \rightarrow 9$   
 $l = -26 \rightarrow 26$   
 3 standard reflections  
 every 147 reflections  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.157$   
 $S = 1.01$   
 6211 reflections  
 487 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0588P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.22$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.25$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

C9—C10	1.369 (4)	C24—C25	1.445 (4)
C11—C12	1.203 (4)	C25—C29	1.374 (4)
C11'—C12'	1.195 (4)	C29—C30	1.438 (4)
C23—C24	1.339 (4)		
C1—C1A—C9	132.1 (3)	C9—C10—C11'	123.5 (3)
C4—C4A—C5A	130.2 (3)	C9—C10—C11	124.4 (3)
C5—C5A—C4A	130.9 (3)	C11'—C10—C11	112.0 (3)
C8—C8A—C9	133.2 (3)	C12—C11—C10	173.3 (3)
C10—C9—C1A	127.2 (3)	C11—C12—C13	177.1 (3)
C10—C9—C8A	125.8 (3)	C12'—C11'—C10	172.8 (3)
C1A—C9—C8A	106.9 (2)	C11'—C12'—C13'	178.8 (4)
C1A—C9—C10—C11'	0.4 (5)	C1A—C9—C10—C11	-178.3 (3)
C8A—C9—C10—C11'	177.2 (3)	C8A—C9—C10—C11	-1.5 (5)

**Table 2**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C36—H36 $\cdots$ N2 <sup>i</sup>	0.95	2.49	3.389 (4)	159
C6—H6 $\cdots$ N3	0.95	2.71	3.436 (4)	134
C6—H6 $\cdots$ N5	0.95	2.78	3.501 (5)	134
C26—H26 $\cdots$ N5	0.95	2.58	3.480 (4)	157
C14—H14 $\cdots$ N6	0.95	2.67	3.464 (4)	141
C2—H2 $\cdots$ N4 <sup>ii</sup>	0.95	2.78	3.651 (5)	152

Symmetry codes: (i)  $-x + 1, -y + 2, -z + 1$ ; (ii)  $-x, -y, -z + 1$ .

H atoms were included using a riding model, starting from calculated positions, with  $C-H = 0.95 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . To improve stability of refinement in view of the weak data, displacement parameters of C and N atoms were subject to rigid bond restraints.

Data collection: *P3/PC* (Siemens, 1989); cell refinement: *P3/PC*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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