organic papers

10,10-Bis(trimethylsilylethynyl)-9-methylene-fluorene–tetracyano-*para*-quinodimethane (2/1)

Peter G. Jones,[a]* Harald Berger,[b] Peter Bubenitschek[b] and Henning Hopf[b]

[a]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and [b]Institut für Organische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Correspondence e-mail: p.jones@tu-bs.de

The title compound {systematic name: 9-[bis(trimethyl-silylethynyl)methylene]fluorene–tetracyano-*para*-quinodi-methane (2/1)}, 2 $C_{24}H_{26}Si_2 \cdot C_{12}H_4N_4$, consists of sandwich-like fluorene–TCNQ–fluorene units with inversion symmetry. The ring systems of the sandwich are parallel; the interplanar separation is 3.3–3.4 Å. The packing of the sandwich units is a herringbone pattern.

Comment

In a previous paper (Jones *et al.*, 2004), we have described the cross-conjugated fulvene derivative, (1). We suspected that this very electron-rich compound would react with a suitable acceptor molecule, such as tetracyano-*para*-quinodimethane (TCNQ), (2); the 2:1 adduct, (3), was prepared (see *Experimental*), and its structure is described here. Consistent analytical and spectroscopic data (unpublished) were recorded.
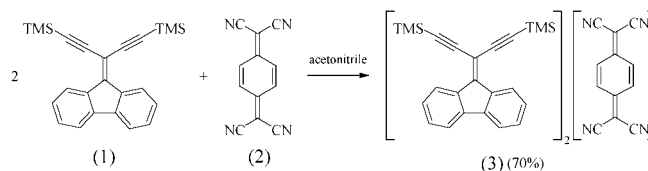
The asymmetric unit consists of one molecule of (1) and half a molecule of TCNQ, which is extended to a complete TCNQ molecule by crystallographic inversion symmetry (Fig. 1). The dimensions of the TCNQ molecule suggest little charge
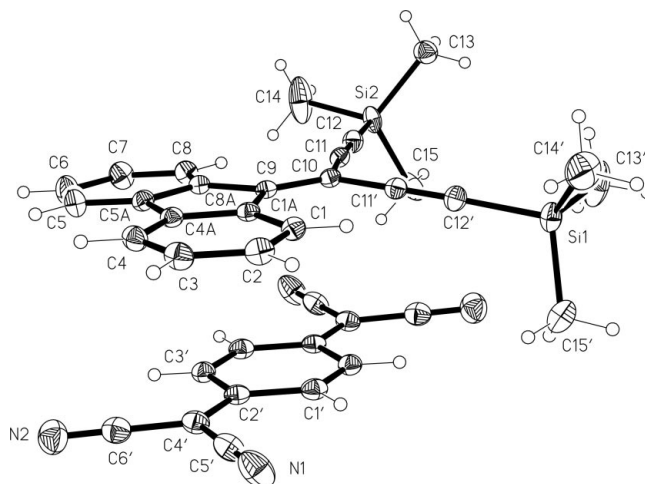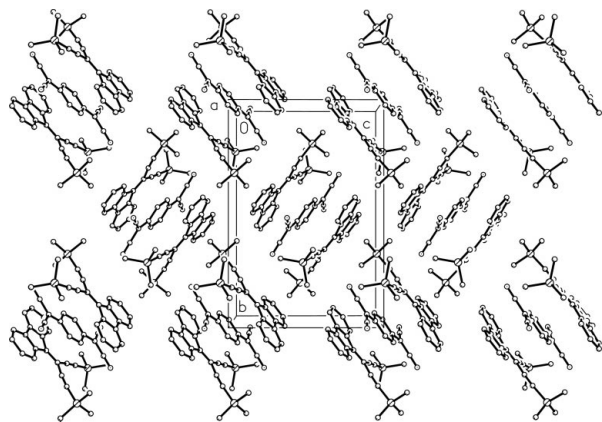

Figure 1
The title compound in the crystal structure; only one molecule of the fluorene component is shown. The half TCNQ molecule of the asymmetric unit (labelled) is shown here completed by inversion symmetry. Displacement ellipsoids are drawn at the 30% probability level. H-atom radii are arbitrary.

Figure 2
Packing diagram of (3), viewed parallel to the *a* axis. H atoms have been omitted for clarity; radii are arbitrary.

transfer from the fluorene group (Kistenmacher *et al.*, 1982). The fluorene component is appreciably less planar than it is in the non-complexed structure; the r.m.s. deviation for the fluorene ring system plus atoms C10 and C11 is 0.05 Å, but the atoms of the linear chains deviate from this plane by up to 0.611 (2) Å for atom Si1. The interplanar angle between the fluorene and TCNQ planes is 1.0 (1)°, and the interplanar distance is 3.3–3.4 Å.

The molecules form sandwich-like fluorene–TCNQ–fluorene units with inversion symmetry (Fig. 2). Neighbouring units pack in a manner reminiscent of the 'sandwich herringbone' packing of aromatic hydrocarbons (Desiraju & Gavezzotti, 1989). Some long C—H···N contacts might be regarded as weak hydrogen bonds (Table 2). In addition, there is a C13—H13B···$Cg1^{iv}$ contact [$Cg1$ is the centroid of the C1—C4/C1A/C4A ring; H···$Cg1^{iv}$ = 2.79 Å and C—H···$Cg1^{iv}$ = 138°; symmetry code: (iv) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; C—H normalized to 1.08 Å].

Experimental

An acetonitrile solution of 10,10-bis(trimethylsilylethynyl)-9-methylenefluorene, (1), was treated with TCNQ, (2) (Berger, 2004). Crystals of the title adduct formed after a short time and proved to be suitable for structure determination.

Crystal data

$2C_{24}H_{26}Si_2 \cdot C_{12}H_4N_4$	$D_x = 1.143$ Mg m^{-3}
$M_r = 945.44$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 46
$a = 11.933$ (2) Å	reflections
$b = 18.398$ (4) Å	$\theta = 10–11.5°$
$c = 12.509$ (3) Å	$\mu = 0.15$ mm^{-1}
$\beta = 90.85$ (3)°	$T = 143$ (2) K
$V = 2746.0$ (10) Å^3	Block, violet–black
$Z = 2$	$0.6 \times 0.5 \times 0.4$ mm

Data collection

Stoe Stadi-4 diffractometer	$\theta_{max} = 25.0°$
ω/θ scans	$h = -14 \rightarrow 14$
Absorption correction: none	$k = -21 \rightarrow 13$
8921 measured reflections	$l = -14 \rightarrow 0$
4831 independent reflections	3 standard reflections
3827 reflections with $I > 2\sigma(I)$	frequency: 60 min
$R_{int} = 0.029$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$+ 1.3032P]$
$wR(F^2) = 0.111$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
4831 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
313 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C11—C12	1.203 (3)	C2′—C3′	1.445 (3)
C11′—C12′	1.201 (3)	C4′—C6′	1.432 (3)
C1′—C3′^{i}	1.343 (3)	C4′—C5′	1.437 (3)
C1′—C2′	1.436 (3)	C5′—N1	1.141 (3)
C2′—C4′	1.371 (3)	C6′—N2	1.143 (3)
C12—C11—C10	174.3 (2)	C12′—C11′—C10	173.4 (2)
C11—C12—Si2	179.4 (2)	C11′—C12′—Si1	173.70 (18)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···N1^{ii}	0.95	2.71	3.573 (3)	151
C14—H14C···N1^{ii}	0.98	2.64	3.415 (4)	137
C15—H15B···N1^i	0.98	2.66	3.539 (3)	150
C13—H13C···N2^{iii}	0.98	2.73	3.619 (3)	152

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x - 1, y, z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Methyl H atoms were located in difference syntheses, idealized (C—H = 0.98 Å and H—C—H = 109.5°) and treated as rigid groups allowed to rotate but not tip. Other H atoms were placed at calculated positions and included in the refinement as riding, with C—H bond lengths of 0.95 Å; U_{iso}(H) values were fixed at $1.2U_{eq}$ of the parent atom.

Data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

References

Berger, H. (2004). PhD thesis. Technical University of Braunschweig, Germany.
Desiraju, G. R. & Gavezzotti, A. (1989). *Acta Cryst.* B**45**, 473–482.
Jones, P. G., Berger, H., Bubenitschek, P. & Hopf, H. (2004). *Acta Cryst.* E**60**, o490–o491.
Kistenmacher, T. J., Emge, T. J., Bloch, A. N. & Cowan, D. O. (1982). *Acta Cryst.* B**38**, 1193–1199.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.
Stoe & Cie (1992). *DIF*4 and *REDU*4. Stoe & Cie, Darmstadt, Germany.