

The charge-transfer complex *trans*-STB–TCNQF₄

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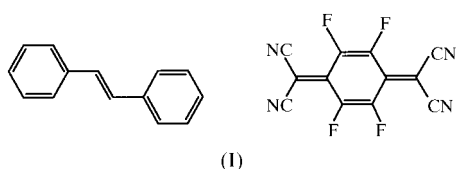
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In the crystal structure of the title charge-transfer complex, namely *trans*-stilbene–2,2'-(2,3,5,6-tetrafluorobenzene-1,4-diyldene)propanedinitrile (1/1) (*trans*-STB–TCNQF₄), C₁₄H₁₂–C₁₂F₄N₄, the planar STB and TCNQF₄ molecules are stacked alternately. The structure is not isostructural with that of STB–TCNQ. No anomaly was found in the displacement parameters of any atoms, while the bond length of the central C=C moiety was shorter than the corresponding bond in ethylene. This suggests that the central C=C moiety of the STB molecule vibrates with a large amplitude, similar to the case in free STB and STB–TCNQ.

Comment

The dynamic co-operation between molecular (atomic) dynamics and change in electronic state is of current interest (Mitani *et al.*, 1988; Nakasuji *et al.*, 1991). Although most studies in the field have been performed on systems with hydrogen bonds, recently, the authors have demonstrated the interplay in a high-*T_c* organic superconductor, *i.e.* *κ*-(BEDT–TTF)₂Cu[N(CN)₂]Br [BEDT–TTF is bis(ethylenedithio)-tetrathiafulvalene; Saito *et al.*, 1999; Akutsu *et al.*, 2000]. As another approach, the authors have shown that reorientation of the molecule involved in the charge transfer (CT) occurs in the crystalline lattice of the CT complex *trans*-stilbene–TCNQ (STB–TCNQ, where TCNQ is 7,7,8,8-tetracyano-*p*-quinodimethane; Saito *et al.*, 2000). We report here the crystal structure of STB–TCNQF₄ (TCNQF₄ is 7,7,8,8-tetracyano-2,3,5,6-tetrafluoro-*p*-quinodimethane), (I), which is a halogenated derivative of STB–TCNQ.



A view of the two molecules in the asymmetric unit is shown in Fig. 1 and the packing is shown in Fig. 2. The STB molecule lies about an inversion center at (0,0,0) and the TCNQF₄

molecule lies about an inversion center at ($\frac{1}{2}$,0,0) at room temperature, and these are ordered in space group *P2₁/n*, in contrast to what was found in the structure of STB–TCNQ in space group *C2/m* (Zobel & Ruban, 1983). Thus, the crystal structure of the present complex is not isostructural with that of STB–TCNQ. Molecules of STB and TCNQF₄ stack alternately to form a column along the *a* direction. The STB and TCNQF₄ molecules overlap with a slip of half the molecular length (Fig. 2). This is different from the exact overlapping and ring-over-ring arrangement in STB–TCNQ. In STB–TCNQF₄, the interplanar angle between the unique ring of the STB

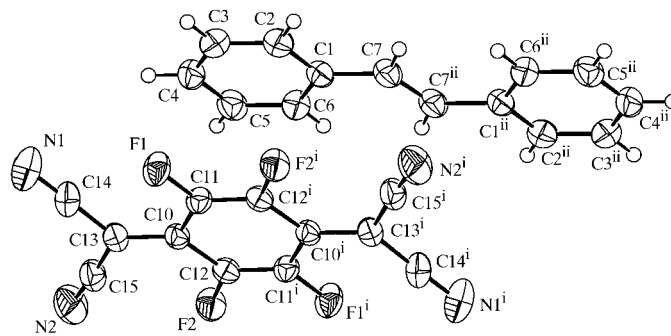


Figure 1
The two molecules in the asymmetric unit of the STB–TCNQF₄ complex. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, -y, -z$.]

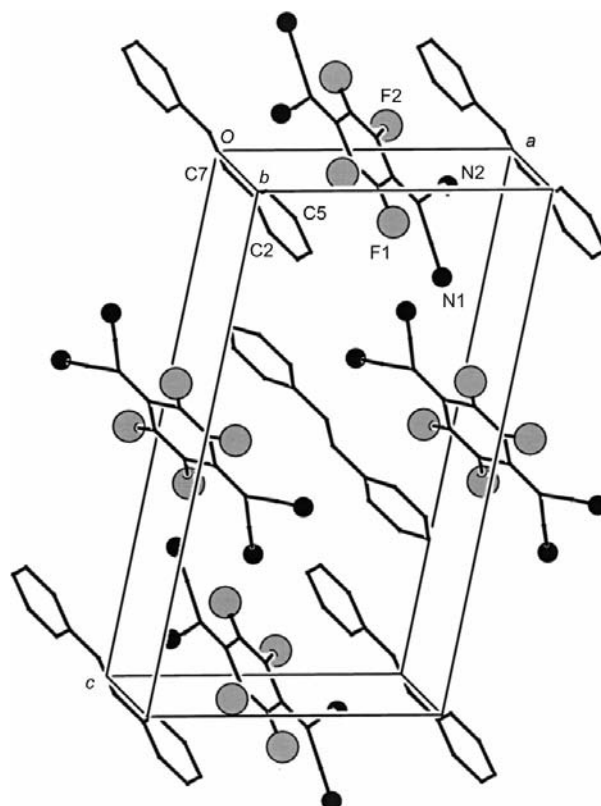


Figure 2
A view showing the molecular arrangement in the unit cell of the STB–TCNQF₄ complex.

molecule and that of the TCNQF₄ molecule is 5.59 (11)°. The separations of the ring centroids from the plane of the adjacent overlapped rings are 3.255 (unique STB ring plane centroid to TCNQF₄ plane) and 3.355 Å (TCNQF₄ centroid to unique STB ring plane). No unusual displacement parameters were found for any atoms.

The central C=C bond length in the STB molecule is 1.315 (4) Å, which is equal to the corresponding length in STB-TCNQ [1.318 (6) Å; Zobel & Ruban, 1983], within experimental error. The angle of the central Ph-C=C moiety is 126.9 (2)°. While the bond length suggests a localization of electron density on the central C=C moiety, the Ph-C=C angle indicates delocalization on the central C=C moiety. Since the degree of CT of (I) was estimated to be *ca* 0.2 e by IR measurement, the central C=C bond in (I) should be longer than the bond of 1.337 (6) Å in ethylene (*International Tables for X-ray Crystallography*, Vol. III, 1968). Short central C=C bonds have been widely observed in the structures of free STB and its derivatives (Finder *et al.*, 1974; Bernstein, 1975; Bouwstra *et al.*, 1984). Ogawa *et al.* (1992) proposed a possible cause for this anomalously short C=C bond, *i.e.* that molecules oscillate in a shallow potential with a large amplitude while maintaining the orientation of the phenyl rings. The existence of this type of molecular vibration in STB was supported by a lattice dynamical calculation (Saito & Ikemoto, 1996). The observed short C=C bond implies that the STB molecule vibrates in the assumed manner with a large amplitude, as proposed by Ogawa *et al.* (1992), even in (I).

Experimental

Crystals of STB-TCNQF₄ were prepared by slow cooling of a concentrated acetone solution containing STB and TCNQF₄. The complex was obtained as needle-like dark-green crystals. The molar ratio was found to be 1:1 by chemical analysis, *i.e.* the complex was STB-TCNQF₄. Crystals were slightly air sensitive.

Crystal data

C₁₄H₁₂·C₁₂F₄N₄
M_r = 456.40
 Monoclinic, *P*2₁/*n*
a = 9.555 (2) Å
b = 6.287 (2) Å
c = 17.295 (2) Å
 β = 99.990 (10)°
V = 1023.2 (4) Å³
Z = 2

D_x = 1.481 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 29.4–30.0°
 μ = 0.12 mm⁻¹
T = 293 K
 Needle, green
 0.2 × 0.2 × 0.2 mm

Data collection

Rigaku AFC-7R diffractometer
 ω -2 θ scans
 2716 measured reflections
 2347 independent reflections
 1463 reflections with *I* > 2 σ (*I*)
R_{int} = 0.015
 θ_{\max} = 27.5°

h = -12 → 0
k = 0 → 8
l = -21 → 22
 3 standard reflections
 every 150 reflections
 intensity decay: 1.6%

Table 1

Selected bond lengths (Å).

C1—C2	1.389 (3)	N1—C14	1.144 (2)
C1—C6	1.397 (3)	N2—C15	1.140 (2)
C1—C7	1.474 (2)	C10—C13	1.377 (2)
C2—C3	1.383 (3)	C10—C12	1.436 (2)
C3—C4	1.376 (3)	C10—C11	1.440 (2)
C4—C5	1.382 (3)	C11—C12 ⁱⁱ	1.341 (2)
C5—C6	1.386 (2)	C12—C11 ⁱⁱ	1.341 (2)
C7—C7 ⁱ	1.315 (4)	C13—C14	1.431 (3)
F1—C11	1.3324 (17)	C13—C15	1.432 (3)
F2—C12	1.3356 (18)		

Symmetry codes: (i) -*x*, -*y*, -*z*; (ii) 1 - *x*, -*y*, -*z*.

Refinement

Refinement on *F*²

R(*F*) = 0.040

wR(*F*²) = 0.124

S = 1.03

2347 reflections

154 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 0.1154P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.20 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.18 \text{ e } \text{Å}^{-3}$$

H atoms were treated as riding with a C—H distance of 0.93 Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1110). Services for accessing these data are described at the back of the journal.

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