X-Ray Crystal Structure of the Organic Conductor from 2,2′-Bi-(2,4-diselenabicyclo[3.3.0]octylidene) and 7,7,8,8-Tetracyano-*p*-quinodimethane (HMTSF–TCNQ)

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Summary The *X*-ray crystal structure of the organic conductor HMTSF–TCNQ consists of separate stacks of radical cations and radical anions coupled so as to make this the most two-dimensional member of the TTF–TCNQ family of organic metals.

ORGANIC conductors based upon the prototype TTF–TCNQ[1] typically undergo transitions from metallic to insulating phases as the temperature is lowered.[1–4] The exception is the molecular charge-transfer salt HMTSF–TCNQ,[5] the first organic substance the conductivity of which remains metallic in magnitude to very low temperature (0·045 K).

Since the difference between HMTSF and the normally behaving selenium analogues[2,4] of TTF is largely steric rather than electronic, the crystal structure of HMTSF–TCNQ is of special interest.

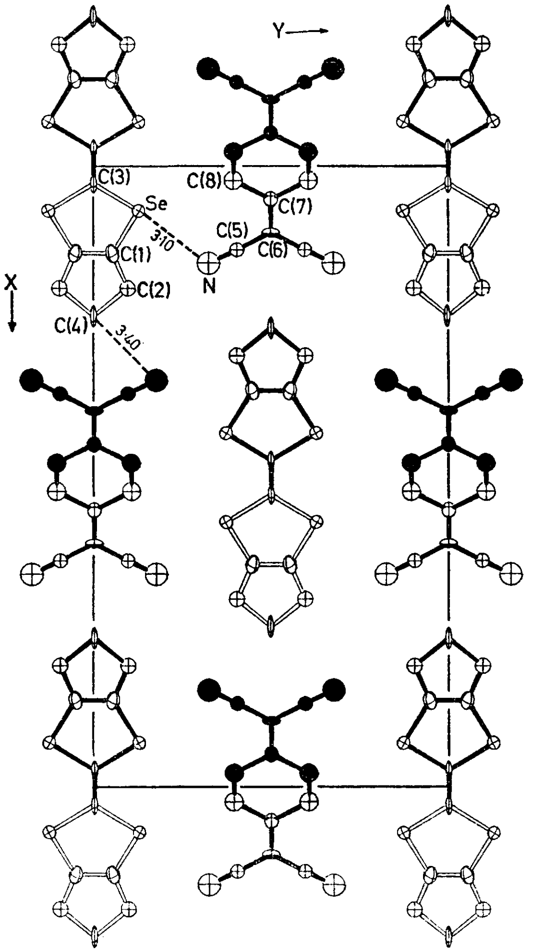

Figure. A projection of the structure of HMTSF–TCNQ onto the *ab* plane. The HMTSF radical cations are centred about the 1 symmetry element at 0,0,0 and the TCNQ radical anions are centred about the 1 at 0, ½, ½.

The diffraction symmetry of the intensity-weighted reciprocal lattice of HMTSF–TCNQ is monoclinic, though nearly orthorhombic. *Crystal data*: $a = 21{\cdot}999(14)$, $b = 12{\cdot}573(8)$, $c = 3{\cdot}890(1)$ Å; $\beta = 90{\cdot}29(4)^\circ$; $D_m = 2{\cdot}09(1)$, $D_c = 2{\cdot}09$ g cm^{-3}, $Z = 2$, space group $C2/m$. A total of 1304 independent intensities were collected on a Syntex P-1 automated diffractomer, employing graphite-monochromatized Mo-K_α radiation. Diffraction phorographs showed strong diffuse streaking superimposed on the specular pattern and implied incomplete long-range ordering along the *a*-axis. When the structure was modelled by heavy-atom Patterson and Fourier methods and refined by full-matrix least-squares, the disorder limited the refinement to a final R value of 0·18.

About 80% of the heavy-atom electron density in the (averaged) unit cell is projected onto the *ab* plane in the Figure. The planes of the molecules in the Figure are tilted relative to the *ab* plane by 22(1)° (HMTSF) and 34(1)° (TCNQ), but the remaining heavy-atom electron density apparently corresponds to *bc* layers in which the tilts are different. Each of the molecular ions is required to have crystallographic symmetry $C_{2h}(2/m)$. The structure consists of columns of separately stacked HMTSF cations and TCNQ anions, with intrachain molecular overlaps and interplanar spacings [3·6(1) for HMTSF and 3·2(1) Å for TCNQ] typical of such materials.[1–4]

It is in the interchain coupling that HMTSF–TCNQ contrasts sharply with other members of the class.[1–4] Along the *a* axis, the coupling appears to be exceptionally weak, consistent with the observed disorder. Here the saturated methylene rings separate the π-conduction electron systems of the cation and anion columns, and the only significant contact, N · · · C(4) = 3·40(6) Å, is undoubtedly dispersive in character. The *b* axis coupling, on the other hand, is strong and dominated by the very short Se · · · N contact of 3·10(3) Å. This contact is considerably shorter than the S · · · N contacts in TTF–TCNQ,[1] and the geometry is such that substantial direct π-bonding, as well as the expected coulombic interaction, is possible.

In summary, we find that contrary to our original expectations[5] HMTSF–TCNQ is probably the most nearly two-dimensional conductor of the TTF–TCNQ family. To what degree the low-temperature metallic behaviour of HMTSF–TCNQ arises from two-dimentional suppression[6] of the Peierls instability, and to what degree from the lack of long-range order along the weakly-coupled *a* axis,[5] must await further study.

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[1] J. Ferraris, D. O. Cowan, V. Walatka, and J. H. Perlstein, *J. Amer. Chem. Soc.*, **1973, 95,** 948; T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *Acta Cryst.*, 1974, **B30**, 763.

[2] E. M. Engler and V. V. Patel, *J. Amer. Chem. Soc.*, 1974, **96**, 7376.

[3] J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, *Tetrahedron Letters*, **1973, 27,** 2553.

[4] K. Bechgaard, D. O. Cowan, and A. N. Bloch, *J.C.S. Chem. Comm.*, 1974, 937.

[5] A. N. Bloch, D. O. Cowan, K. Bechgaard, R. E. Pyle, R. H. Banks, and T. O. Poehler, *Phys. Rev. Letters*, **1975, 34,** 1561.

[6] G. Beni, *Solid State Comm.*, 1974, **15**, 269.