Crystal Structure of the Radical-cation Radical-anion Salt from 2,2′-Bi-1,3-dithiole and 7,7,8,8-Tetracyanoquinodimethane

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Summary The three-dimensional structure of the radical-cation radical-anion salt from 2,2′-bi-1,3-dithiole (**1**) and 7,7,8,8-tetracyanoquinodimethane (**2**) has been determined by *X*-ray diffraction methods; the structure is composed of segregated columnar stacks of cations and anions.

Recent interest[1,2] in the electrical and magnetic properties of the salt of the radical-cation of 2,2′-bi-1,3-dithiole, (**1**) and the radical-anion of 7,7,8,8-tetracyanoquinodimethane, (**2**), has led us to determine its three-dimensional structure by *X*-ray diffraction methods.

The salt crystallises in the monoclinic system, space group $P2_1/c$, with cell constants: $a = 12{\cdot}298(6)$ Å, $b = 3{\cdot}819(2)$ Å, $c = 18{\cdot}468(8)$ Å, $\beta = 104{\cdot}46(4)^\circ$, $D_m = 1{\cdot}618$, $D_c = 1{\cdot}615$ g cm^{-3}, $Z = 2$. A total of 1373 independent intensities (*hkl* and $hk\bar{l}$) were collected on an automated Syntex $P\bar{1}$ diffractometer with monochromatized Mo-K_α ($\lambda = 0{\cdot}71069$Å) radiation. The structure was solved by standard heavy-atom methods.† Each of the molecular

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† The results of a two-dimensional study of the structure of (**1**)–(**2**) were communicated to us by J. D. Wilson, F. Sanz, and J. J. Daly of Monsanto Research. The two-dimensional results were helpful in the interpretation of the three-dimensional Patterson function.

ions is crystallographically required to be centrosymmetric. Full-matrix least-squares refinement, with the sulphur atoms anisotropic and the hydrogen atom contributions included in the calculated structure factors but their parameters not refined, has led to a final R-value of 0·046.

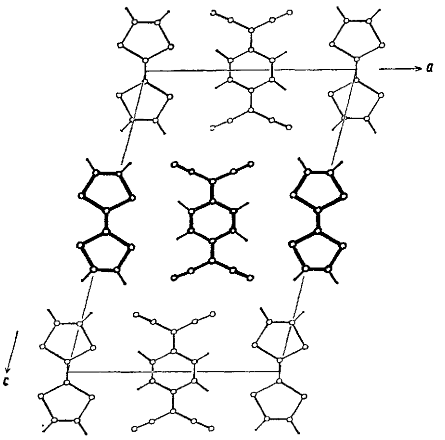

FIGURE 1. *A projection of the structure of* (**1**) : (**2**) *down* [010].

The crystal structure is illustrated in Figure 1 which is a projection down [010]. The structure is made up of *segregated* columnar stacks of radical cations ($\cdots D^+D^+D^+D^+\cdots$) and radical anions ($\cdots A^-A^-A^-A^-\cdots$) along the short b-axis. The molecular planes of the cations and anions are tilted in opposite directions relative to [010] such that their normals describe a dihedral angle of 58·5° There are no short inter-stacking distances; the shortest contact being between one of the cyano nitrogens and a fulvalene hydrogen at 2·59 Å, only slightly shorter than the sum of the van der Waal radii, 2·70 Å.

The molecular overlap in the cationic and anionic columns is illustrated in Figure 2, which also contains molecular overlap drawings for the neutral species.[3,4] In each case the overlap is more "symmetric" in the charge species than the neutral molecules. The intra- and inter-columnar stacking, in this structure, is presumedly the minimum energy compromise between direct coulombic interactions and induced van der Waal interactions.[5]

The molecular dimensions of the anions (**2**) are in good agreement with those found in other crystal structure analyses,[6] but do not unequivocally indicate the transfer of a full electron. The dimensions of the cation (**1**), when compared to the dimensions of the neutral molecule,[5] are consistent with the removal, or partial removal, of a delocalized, bonding electron.

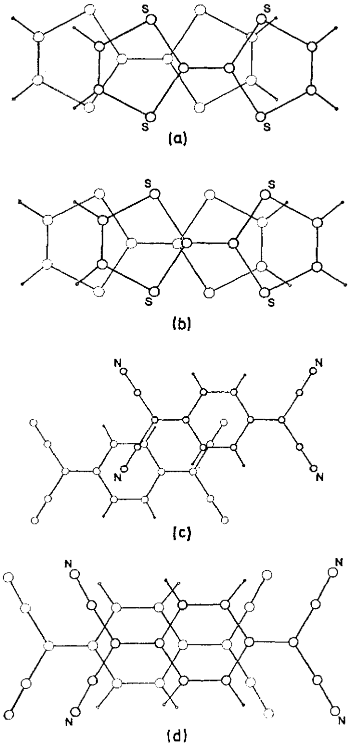

FIGURE 2. *Molecular overlap drawings:* (a) (**1**), [4] D (stacking distance) = 3·62 Å; (b) cation (**1**), D = 3·47 Å; (c) (**2**),[3] D = 3·45 Å, (d) anion (**2**), D = 3·17 Å. *This is the shortest stacking distance yet reported for columnar stacking of TCNQ molecules.*

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[1] J. Ferraris, D. O. Cowan, V. Walatka, jun., and J. H. Perlstein, *J. Amer. Chem. Soc.*, 1973, **95**, 949.

[2] L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Comm.*, submitted for publication.

[3] R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Cryst.*, 1965, **18**, 932.

[4] W. F. Cooper, N. C. Kenny, J. W. Edmonds, A. Nagel, F. Wudl, and P. Coppens, *Chem. Comm.*, 1971, 889, and personal communication.

[5] P. J. Strebel and Z. G. Soos, *J. Chem. Phys.*, 1970, **53**, 4077.

[6] F. H. Herbstein, in 'Perspectives in Structural Chemistry', eds. J. D. Dunitz and J. A. Ibers, vol. IV, 1971.