

Structure of a 'Doped' Diacetylene that is Polymerisable in the Solid State

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The crystal structure has been determined of a silver perchlorate-doped diacetylene derivative which yields upon γ -ray irradiation a semi-conducting polymer product; whereas the perchlorate ions are randomly distributed throughout the monomer structure, the silver ions are preferentially located close to the electron rich regions of the organic molecular framework.

Some so-called conducting polymers are not good conductors in their pristine states, and may even exhibit insulating behaviour when ultrapure. They can, however, be rendered conducting by incorporation of either donor or acceptor dopants.¹ To date, most of the conducting organic polymers that have been prepared are those that principally contain conjugated double bonds such as polyacetylene,² polypyrrole,³ and polyphenylene.⁴ By contrast, comparatively little is known about the conducting (as distinct from other) properties of organic polymers with triple-bond character. Many appropriately packed diacetylenes undergo topochemical solid-state polymerisation to give large single crystals of essentially insulating polymer^{5,6} (conductivity *ca.* 10^{-12} S cm^{-1}). However, because of the rather rigid structures of such polymeric crystals, doping is inefficient so that the polymers cannot be readily converted into their conducting state. Certain dopants, such as AgClO_4 , I_2 , SbF_5 , and SO_3 , can, however, be conveniently introduced prior to polymerisation,

and such 'mixed' monomeric crystals, after exposure to γ -rays, yield good semiconducting polymeric crystals⁷ (conductivity *ca.* 10^{-5} S cm^{-1}).

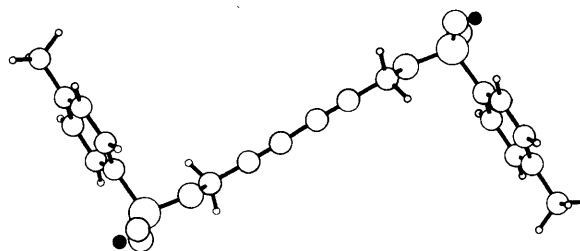


Figure 1. The molecular structure of the hexadiynylene toluene-*p*-sulphonate (TS) in the solid state. The filled circle represents the position of the Ag^+ ions. Such Ag^+ ions have an occupancy 2%, in agreement with the chemical analysis.

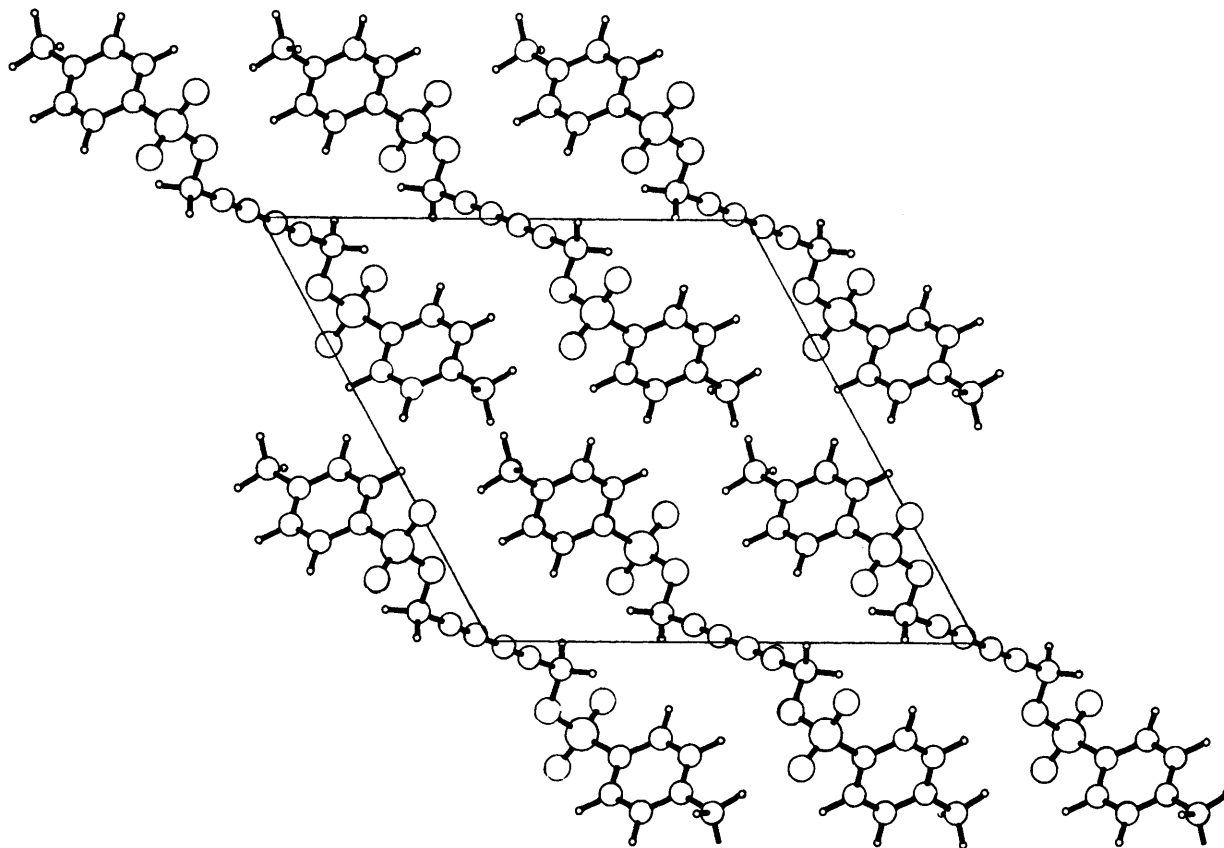


Figure 2. View of the crystal structure of AgClO_4 -doped TS viewed along the b axis. Dopant species are omitted for clarity (see text).

The aim of this crystallographic study of AgClO_4 -doped hexa-2,4-diyneleene bistoluene-*p*-sulphonate (TS) was to locate the dopant in the structure of the monomer and hence to probe further the nature of the dopant-organic interactions which govern the conductivity of the polymer. Such studies are not possible in other polymerisable systems, because the product, unlike the situation that prevails here, is polycrystalline. The tosyl derivative of diacetylene is an appropriate monomer to study for the following reasons: (i) relative ease with which it yields perfect crystals; (ii) it is sufficiently stable to X -ray irradiation that structural data may be obtained without excessive polymerisation; and (iii) incorporation of sufficient dopant does not result in the growth of a new polymorph. Previous studies have shown that AgClO_4 is an appropriate dopant,⁸ the resulting conductivity being *ca.* $3.3 \times 10^{-4} \text{ S cm}^{-1}$.

Full intensity data were obtained at room temperature on a Nicolet P3F 4-circle diffractometer, using a $\theta/2\theta$ scanning routine and $\text{Cu-K}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) graphite-monochromatised radiation. Since TS slowly polymerises on exposure to X -rays, three different crystals were used for data collection, such that no crystal was exposed to the X -ray beam for more than 20 h. Control reflections showed no significant drop in intensity, indicating that polymerisation did not proceed to any appreciable extent. Three sets of intensity data were merged using common reflections for scaling. For the three crystals used, elemental analysis showed the AgClO_4 content to be close to 2 mol %. Structure solution was achieved by the tangent refinement method, with the refinement of the structure carried out by full matrix least squares techniques. After the structure had converged the dopant was

located near the SO_2 moiety as the only significant peak in the ΔF map.[†]

The asymmetric unit constitutes half the molecule, with the middle of the central single bond lying on a centre of symmetry (see Figure 1 for the molecular structure of AgClO_4 -doped TS). The ΔF peak assigned to the dopant is believed to correspond to Ag^+ since it is located near an electron rich part of the TS framework. Furthermore, previous work on doped polyacetylene has shown that the ions in AgClO_4 , or other dopant species, are separated in the polymer matrix. It has been shown⁹ that, in the case of this dopant, it is the cation which reacts electrochemically with the substrate, whereas the perchlorate counterion is, presumably, randomly distributed among various sites in the structure. This peak was assigned to Ag^+ with a crystallographic occupancy factor of 2%, in agreement with chemical analysis. The structure converged

[†] *Crystal Data:* $\text{C}_{20}\text{H}_{18}\text{O}_6\text{S}_2$, $M_r = 418.5$, $D_c = 1.40 \text{ g cm}^{-3}$, space group $P2_1/c$, $a = 14.668(5)$, $b = 5.174(1)$, $c = 14.938(5) \text{ \AA}$, $\beta = 118.85(3)^\circ$, $U = 993.0(6) \text{ \AA}^3$, $Z = 2$, $F(000) = 441$, $\mu = 26.04 \text{ cm}^{-1}$, total data 1829 unique, 1513 observed with $F_o > 5\sigma(F_o)$. 140 Parameters refined, weighting scheme $(\sigma^2 F + 0.0001 F^2)^{-1}$, final $R = 0.0904$, $R_w = 0.0967$. The final difference Fourier map had no peaks higher than 0.32 e \AA^{-3} . Crystals used for data collection in the range $0 < 2\theta < 60^\circ$ had dimensions $0.35 \times 0.20 \times 0.15 \text{ mm}$. The second crystal was used in the range $55 < 2\theta < 105^\circ$ ($0.30 \times 0.18 \times 0.18 \text{ mm}$), and the third one for the range $95 < 2\theta < 145^\circ$. All three were fragments from the same single crystal. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

satisfactorily. The packing in doped TS (Figure 2) is similar to that reported¹⁰ for the undoped parent at 120 K. Stacks of molecules are packed with a repeat distance of 5.17 Å inclined at 45° to the *b* axis, this being the configuration generally accepted as being conducive to topochemical polymerisation in diacetylene.

Comparison of the cells of TS and doped-TS shows that the volume available for each TS molecule is very similar in the two structures. Therefore, wherever a dopant ion is present in the lattice (roughly in one out of every fifty unit cells) it may only be accommodated by distorting slightly its neighbouring organic molecules. These distortions may well be associated with solitons,¹¹ the inferred presence of which, along with the disordered perchlorate moieties, probably accounts for the high *R* value for this structure.

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