

Electroconductive Charge Transfer Complexes of 2,4,6-Tricyano-*s*-triazine and of 3,6-Dicyano-1,2,4,5-tetrazine with Tetrathiafulvalene

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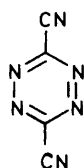
Tetrathiafulvalene afforded 1 : 1 charge transfer complexes with 3,6-dicyano-1,2,4,5-tetrazine and 2,4,6-tricyano-*s*-triazine: the former showed good electrical conductivity, thus proving that the attainment of aromaticity in the formed radical anion is not a necessary requisite for conductivity; the latter is a semi-conducting product which is converted by water into a new good electroconductive material.

The search for systems that can act as acceptors in electroconductive charge transfer (C.T.) complexes is a very active area of investigation.¹ Recipes for designing efficient electron acceptors require that the radical anion originated by mono-electron transfer from the donor be long-lived, the necessary stabilization being generally achieved by attainment of the aromatic character of the system.² We report herein on the synthesis and the electrical properties of two new C.T. complexes in which the neutral electron-accepting precursor moves instead from an aromatic to a non-aromatic arrangement. The systems on which we have focused our attention are the 3,6-dicyano-1,2,4,5-tetrazine (**1**) and the 2,4,6-tricyano-*s*-triazine (**2**), predicted by theoretical calculations to be good candidates for giving stable radical anions.^{3,4}

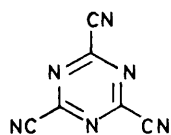
The dicyanotetrazine (**1**) has already been described in the literature,⁵ but its characterization was poor. This compound (orange coloured crystals with m.p. 91 °C, twice sublimed at 0.2 mm Hg) was prepared in analytically pure form according to the known procedure starting from analytically pure[†] 3,6-dicarboxamido-1,2,4,5-tetrazine. A black 1 : 1 C.T. complex with tetrathiafulvalene (TTF) was obtained starting from equimolar amounts of (**1**) and TTF in MeCN‡ solution; it was

[†] The yields and the purity of compound (**1**) were highly dependent upon the purity of the starting material.

[‡] The solvents were spectroscopic grade reagents, further distilled over P₂O₅ prior to use.



(1)



(2)

considerably stable in air at room temperature (m.p. 165 °C from MeCN; satisfactory C, H, N analysis). The conductivity of this C.T. complex was found to be 3 S cm^{-1} , a value which is very similar to that reported for the well known TTF TCNQ C.T. complex (TCNQ = tetracyanoquinodimethane),⁶ thus proving that the attainment of aromaticity in the formed radical anion is not a necessary requisite for conductivity. Upon concentration under reduced pressure of a CH_2Cl_2 solution of equimolar amounts of TTF and (2), a deep green C.T. complex was obtained (m.p. 110 °C; satisfactory C, H, N analysis). This compound showed semi-conducting properties and a non-ohmic behaviour ($\sigma \approx 2 \times 10^{-4} \text{ S cm}^{-1}$ at 10 μA), thus confirming that the stabilization of the radical anion is not the only requisite for good conductivity of a C.T. complex; the reduction potential of (2) may be outside the very narrow range compatible with the oxidation potential of TTF for giving an electroconducting C.T. complex.⁷

Interestingly however this C.T. complex was very rapidly transformed by exposure to air into a new dark brown electroconducting compound for which analytical data suggest the structure of a 1:1 TTF 1,3-dicyano-5-hydroxy-s-triazine

C.T. complex (m.p. 145 °C from MeCN; satisfactory C, H, N analysis). HCN was easily detected during the above solid state transformation and this new compound was the only product recovered from the reaction of TTF and (2) whenever the solvent was not properly dried.

The good conductivity observed for this material ($\sigma = 0.5 \text{ S cm}^{-1}$) possibly outlines a completely new class of acceptors.

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