Synthesis of *cis*- and *trans*-Diselenadithiafulvalene and its Highly Conducting Charge-transfer Salt with Tetracyano-*p*-quinodimethane

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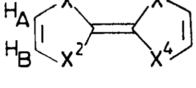
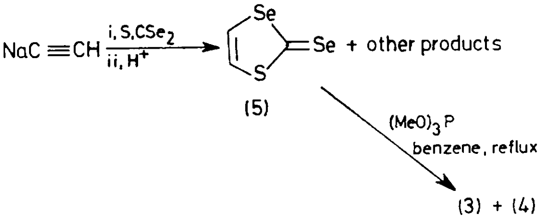
Summary *cis*- and *trans*-Diselenadithiafulvalene is synthesized in two steps, and its highly conducting, metallic-like charge-transfer salt with tetracyano-*p*-quinodimethane prepared.

CHARGE-TRANSFER salts containing the organic donor **tet**rathiafulvalene (**1**; TTF)[1] or its derivatives[2] have the highest electrical conduction of organic solids presently known. Recently, the preparation of tetraselenafulvalene (**2**; TSeF),[3] the selenium analogue of TTF, was found to lead to an improvement in the metallic-like properties of its charge-transfer salt with tetracyano-*p*-quinodimethane (TCNQ). Moreover, this modification still maintains the original TTF–TCNQ crystal structure, a factor which hopefully will facilitate attempts to understand the correlation of molecular properties with the resultant solid-state properties of the charge-transfer salt. In order to examine further the effect of perturbing the electronic properties of TTF under this common basis of isostructurality, we have synthesized *cis*- and *trans*-diselenadithiafulvalene (**3** and **4**, DSeDTF) and their charge-transfer salt with TCNQ.[4] The electrical properties of DSeDTF–TCNQ have already been published.[5]



(1) X^1–X^4 = S
(2) X^1–X^4 = Se
(3) X^1 = X^3 = S, X^2 = X^4 = Se
(4) X^1 = X^4 = S, X^2 = X^3 = Se

 (1)

DSeDTF was prepared in two steps as outlined in equation (1). The synthesis of the key intermediate, 1,3-thiaselenone-2-selone (**5**), has been described previously.[6] Attempts to couple (**5**) through the thiaselenolylium cation,[5] by analogy with the preparation of TTF,[6] were unsuccessful. However, (**5**) could be readily converted into DSeDTF by treatment with alkyl phosphorous bases.[3,9] The presence of the selenocarbonyl group in (**5**) was found to be crucial for the success of this synthesis. For example, treatment of the corresponding 1,3-thiaselenole-2-thione[6] with phosphorous bases under a variety of conditions failed to give the desired product. With the selenocarbonyl group, on the other hand, (**5**) is smoothly converted into DSeDTF in yields of 60—80% by treatment with a 2 molar excess of trimethyl phosphite in refluxing benzene for 4—5 h.

The product was isolated by chromatography over a short silica gel column with hexane as eluant. Recrystallization from hexane gave DSeDTF as red-orange prisms: m.p. 117—117·5 °C; δ ($CDCl_3$; relative to Me_4Si) 6·59 and 6·95 (AB, *J* 6·5 Hz) and 6·65 and 6·89 (A′B′, *J* 6·5 Hz); λ_{max} (hexane) 470 (ϵ 175), 375sh (1000), 322sh (6500), and 297 nm (11,000); *m/e* 396 (based on ^{80}Se). Cyclic voltammetry in acetonitrile gave two reversible one-electron oxidation peaks at 0·40 and 0·72 V.[10]

The coupling of (**5**) presents the possibility of forming *cis*- and *trans*-isomers (**3**) and (**4**). Surprisingly, the 220 MHz n.m.r. spectrum of DSeDTF resolves this question by showing two distinct AB coupling patterns in about equal intensities (major isomer 57%). On the basis of an earlier study on the 1,3-thiaselenole ring system,[7] the proton adjacent to sulphur (H_A in **3** and **4**) is assigned to the low field chemical shifts in DSeDTF. Initial attempts to separate the *cis*- and *trans*-isomers (**3**) and (**4**) by high pressure liquid chromatography have so far been unsuccessful.

Mixing of DSeDTF with TCNQ in acetonitrile instantly precipitated the 1:1 black charge-transfer salt which was found to have essentially the same crystal structure as TTF–TCNQ and TSeF–TCNQ.[5] Single-crystal electrical conductivity measurements on DSeDTF–TCNQ show a metallic-like temperature dependence similar to TTF–TCNQ and TSeF–TCNQ with a room temperature conductivity of *ca.* 550 Ω^{-1} cm^{-1}.[5]

DSeDTF–TCNQ provides an opportunity to study the effects of disorder[11] (introduced owing to the lower symmetry of the donor and the presence of *cis*- and *trans*-isomers) on the solid-state properties of these charge-transfer salts. In general, disorder seems to play a minor role, with the solid-state properties of DSeDTF–TCNQ being essentially intermediate between TTF–TCNQ and TSeF–TCNQ. Detailed physical studies on DSeDTF–TCNQ will be reported forthwith, as well as the formation of organic alloys with its isostructural relatives, TTF–TCNQ and TSeF–TCNQ.[12]

(*Received, 2nd June* 1975; *Com.* 622.)

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[4] An alternative synthesis of DSeDTF has recently been reported: M. V. Lakshmikantham, M. P. Cava, and A. F. Garito, *J.C.S. Chem. Comm.*, 1975, 383. In this synthesis, it was reported that only the *trans*-isomer was formed; however further examination by n.m.r. spectroscopy indicates that both *cis*- and *trans*-isomers are present in the same ratio as found in the present synthesis (M. P. Cava, personal communication).

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