Tetrathio-derivatives of Quinodimethane. Synthesis and Ion-radical Complex Formation of Cyclohexa-2,5-diene-1,4-diylidenebis-1,3-benzodithiole derivative

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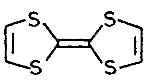
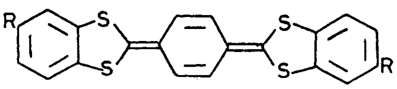
Summary The new 7,7,8,8-tetrathioquinodimethane-type organic sulphur electron-donor compound (**2**) and its charge transfer complex (**4**) with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone have been isolated.

There has been great interest recently in the 1 : 1 complex of tetrathiafulvalene (TTF) with tetracyanoquinodimethane (TCNQ) in view of its unusual electric and magnetic properties.[1] In connection with our studies on TTF derivatives,[2] we have investigated the preparation of derivatives of cyclohexa-2,5-diene-1,4-diylidenebis-1,3-benzodithiole (CBDT) (**1**).[3]



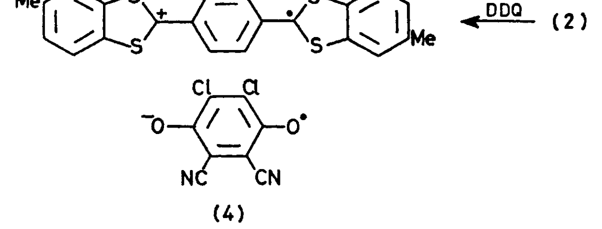
TTF



(1) R = H (CBDT)
(2) R = Me

The relationship between the conjugated system, of TTF and CBDT would be expected to be similar to that between tetracyanoethylene (TCNE) and TCNQ, although the former two compounds are donors and the latter are acceptors.

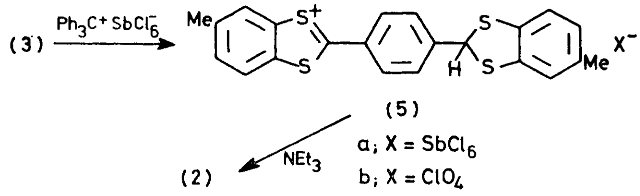
We now describe the preparation (Scheme) and charge-transfer complex formation of the dimethyl derivative (**2**) of CBDT.



Scheme

The bis-dithioacetal (**3**) was prepared (82% yield) by condensation of toluene-3,4-dithiol with terephthalaldehyde in methylene chloride at room temperature with HCl bubbling for 2 h, m.p. 172—174 °C, (from n-hexane–$CHCl_3$), δ ($CDCl_3$) 2·27 (6H, s, Me), 6·18 (2H, s, CH), 7·10 (6H, m), and 7·60 (4H).

The bis-dithioacetal (**3**) was converted into the mono-cation (**5a**) in 88% yield with 1 equiv. of trityl hexachloroantimonate in methylene chloride at room temperature for 1 h. 1 equiv. of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in 70% perchloric acid and acetic acid also caused the conversion of (**3**) into its mono-cation, (**5b**) (93% yield). The tetrathioquinodimethane (**2**) was easily obtained from (**5a**) or (**5b**) in almost quantitative yield with triethylamine in acetonitrile at room temperature for 1·5 h.



The tetrathioquinodimethane (**2**) thus obtained was slightly air sensitive; δ 2·40 (6H, s, Me) and 7·30 (10H, m). The donor properties of (**2**) were demonstrated by the formation of the charge-transfer complex (**4**) upon addition of a solution of DDQ in benzene.

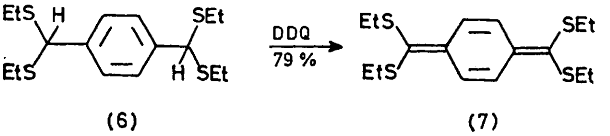
Dehydrogenation of (**2**) with 2 equiv. of DDQ in refluxing benzene for 3 h afforded directly the same 1 : 1 complex (**4**)† as above in 85% yield, m.p. 230—235 °C (decomp.), λ_{max} (MeCN) 762, 508, 416, 345, 258 (sh), 230, and 217 nm. The almost complete disappearance of the i.r. carbonyl band at 1670 cm^{-1} of DDQ and the appearance of the phenoxyl radical band[4] at 1550 cm^{-1} indicated the almost complete one electron transfer from the donor (**2**) to the acceptor DDQ (see **4**).This was also supported by the appearance of e.s.r. signals due to (**4**) in the solid state or in methylene chloride solution.

The direct formation of complex (**4**) can be explained by the initial dehydrogenation of (**3**) to CBDT followed by charge-transfer complex formation with a second DDQ molecule.

The specific electric resistivity of complex (**4**) was $2{\cdot}8 \times 10^5$ Ω cm at room temperature.

Direct dehydrogenation of (**2**) with 2 equiv. of TCNQ instead of DDQ also afforded a *ca.* 1 : 1 complex, purification of which has not been successful, however.

To elucidate the effect of structural variation, the preparation of acyclic tetrathio-derivatives of quinodimethane was investigated. Thus, reaction of the tetraethylthio-*p*-xylene (**6**) (obtained from ethanethiol and terephthalaldehyde) with 1 equiv. of DDQ in refluxing benzene for 4 h gave the desired quinone derivative (**7**) as red oil in 79% yield, b.p. 156—163 °C at 0·025 mmHg.



However the tetraethyl compound (**7**) showed no donor properties towards DDQ.

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† Ratio determined by elemental analysis.

[1] M. Narita and C. U. Pittman, Jr., *Synthesis*, 1976, 489; E. M. Engler, *Chem. Technol.*, 1976, **6**, 274.

[2] Y. Ueno, A. Nakayama, and M. Okawara, *J. Amer. Chem. Soc.*, 1976, **98**, 7440; *Synthesis*, 1975, 277; Y. Ueno, Y. Masuyama, and M. Okawara, *Chem. Letters*, 1975, 603; Y. Ueno and M. Okawara, *ibid.*, 1974, 1135.

[3] One patent describes the structure of cyclohexa-2,5-diene-1,4-diylidenebis-1,3-dithiole, without characterization; M. G. Miles, J. D. Wilson, and M. H. Cohen, U.S.P., 3,779,814 (1973).

[4] E. A. Chandross and R. Kreilick, *J. Amer. Chem. Soc.*, 1963, **85**, 2530.