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# TETRATHIOQUINODIMETHANE CHEMISTRY. A NEW APPROACH TO THE PREPARATION OF CHARGE-TRANSFER COMPLEX BY LITHIUM IODIDE REDUCTION

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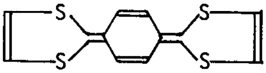
A great interest has been stimulated in the 1:1 complex of tetrathiofulvalene (TTF) with tetracyanoquinodimethane (TCNQ) by the finding of the unusual electric and magnetic properties.[1] In connection with our studies on TTF[2] we have examined the preparation of a tetrathioquinodimethane (TTQ)-type[3] organic sulfur donor compound, which has more conjugated structure than TTF.

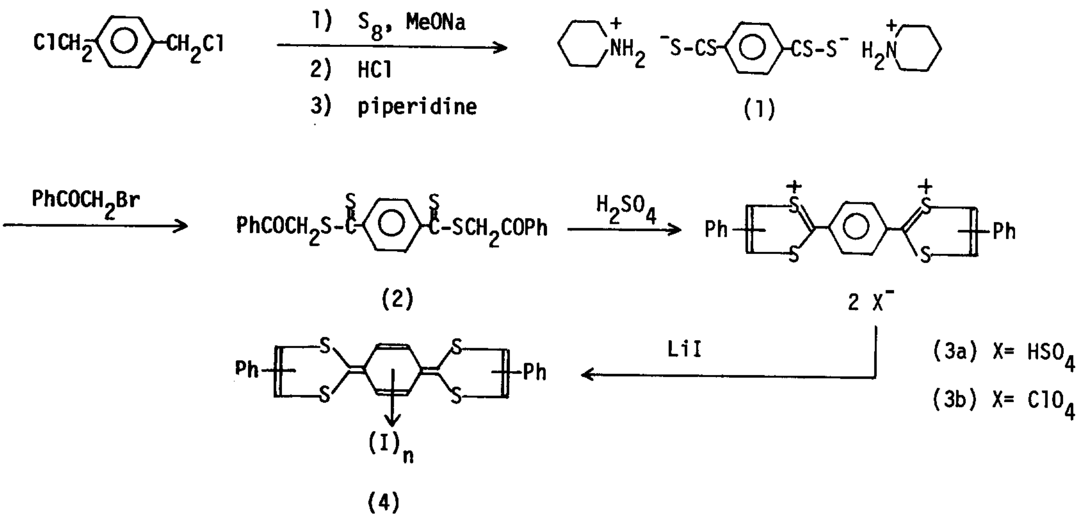
TTF



TTQ

This paper describes the charge-transfer complex formation of the diphenyl derivative of TTQ by lithium iodide reduction of the corresponding sulfur-stabilized dication. The synthetic sequence is summarized in Scheme I.[4]

Hitherto unknown tetrathioterephthalic acid was successfully prepared by the application of the method of Becke.[5] To a solution of sodium methoxide (0.04 mol) in methanol (60 ml), elemental sulfur (0.04 mol) was added and refluxed for 2 hr. p-Xylylene chloride (0.0097 mol) was added to the above mixture during 1 hr, and the resulting mixture was further refluxed for 7 hr. After usual work-up, the deep violet solution of tetrathioterephthalic acid was obtained, which was isolated as dipiperidinium salt (1) in 61% yield by addition of piperidine,[6] m.p. 146-148°C, $\nu_{CSS^-}$ 990 $cm^{-1}$, $\lambda_{max}$ (EtOH) 333, 514 nm .



Scheme I

Diphenyl tetrathioterephthalate (2) was easily prepared in 84% yield by the reaction of salt (1) with phenacyl bromide in methylene chloride, m.p. 148-150°C (MeCN and EtOH), $\nu_{C=O}$ 1690 $cm^{-1}$, $\nu_{C=S}$ 1200 $cm^{-1}$, $\lambda$max (MeCN) 243, 325, 508 nm, NMR ($CDCl_3$) ($\delta$) 8.25 (m, 8H), 7.75 (m, 6H), 5.07 (s, 2H), 4.75 (s, 2H).

The cyclization reaction was simply carried out by dissolving the seter (2) in cold conc. sulfuric acid. The product, dication (3a) was isolated as orrange crystals in quantitative yield by pouring the reaction mixture into ethyl acetate, m.p. 176-178°C, $\lambda$max (MeCN) 245.5, 281, 318, 412 nm, NMR ($CF_3COOH$) ($\delta$) 7.73 (m, 10H), 8.47 (s, 4H), 9.05 (s, 2H).

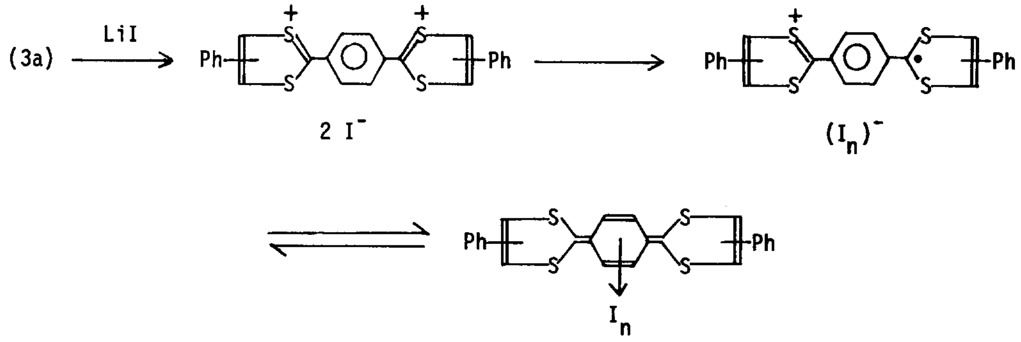
The structure of (3a) was substantiated by spectral data. The absence of C=O band and the presence of the strong and broad band at 1170 $cm^{-1}$ ($HSO_4^-$) in the ir spectrum of (3a) indicate the dehydrative cyclization is complete at both $\beta$-ketodithioester functions attached to the phenyl group. The nmr spectrum has, in addition to a singlet of the central phenyl protons (4H) at $\delta$8.47, a singlet of 1,3-dithiolium ring protons (2H) at $\delta$9.05. Appearance of the above two signals at considerable down-field indicates the highly electron deficient cationic structure of (3a). The salt (3a) was converted to the corresponding perchlorate salt (3b) on treatment with 70% perchloric acid in 83% yield.

The reduction of the dication (3a) with lithium iodide proceeded cleanly to give the greenish black crystals of iodine complex (4) in 80% yield. Thus, the dication (3a) was added to a solution of excess lithium iodide in acetone to give immediately the crystals (4), which was isolated by dilution with water, m.p. 144-147°C. The ratio of the diphenyl derivative of TTQ and iodine moiety was estimated to be 5:14 (n= 2.8) by the elemental analysis.[7]

The complex (4) gave a deep green solution when dissolved in polar solvents such as acetone, acetonitrile, dimethylformamide, or methanol. In contrast to the sulfate salt (3a) [ $\lambda$max (MeCN) 245.5, 281, 318, 412 nm] or perchlorate salt (3b) [ $\lambda$max (MeCN) 247.5, 281, 318, 443 nm], a very big bathochromic shift was observed in the uv spectrum of (4) [ $\lambda$max ($CH_2Cl_2$) 244, 293, 409, 647, 740, 900, 1015 nm].

This shows clearly the highly conjugated structure of (4) instead of the simple dicationic structure like (3a) or (3b). This is also consistent with the appearance of the sharp esr signals in solid state or methylene chloride solution of the complex (4).

The formation of the complex (4) might be best explained by the electron transfer[8] from iodide anion to the dication and further aggregation of iodine moiety.



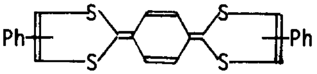
The complex (4) seems to exsist as the equilibrium mixture of ion-radical salt and neutral charge-transfer complex as formulated above. The starting material (3a) was recovered from the complex (4) by treatment with excess conc. sulfuric acid.

The specific resistivity of the complex (4) was estimated to be $8.5\times10^5$ $\Omega$cm at room temperature.

An atempt was made to isolate the diphenyl derivative of TTQ (5) by zinc reduction of (3a) or (3b) in acetonitrile.

Substitution of the solvent with benzene gave the deep red benzene solution ( λmax 475, 508 nm), which seemed to contain the donor (5), due to the facile complex formation with acceptors such as DDQ or TCNQ. The donor (5), however, was extremely air-sensitive and rapidly decomposed in contact with air.

Further studies on the complex formation of the TTQ derivatives are now in progress.



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2) Y. Ueno, A. Nakayama, and M. Okawara, J. Am. Chem. Soc., 98, 7440 (1976); Y. Ueno, Y. Masuyama, and M. Okawara, Chem. Letters, 603 (1975); Y. Ueno and M. Okawara, ibid., 1135 (1974).

3) One patent literature described the structure of TTQ. However, no identification, as well as physical and chemical properties were given. M. G. Miles, J. D. Wilson, and M. H. Cohen, U.S. Patent, 3,779,814 (1973).

4) All new compounds obtained here had satisfactory physical, spectral, and analytical data.

5) F. Becke and H. Hagen, German Patent, 1,274,121 (1968).

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7) "Nonstichiometric ratio" of the TTF-iodine complex has been reported, eg. $(TTF)_{26}I_{63}$; F. Wudl, J. Am. Chem. Soc., 97, 1961 (1975).

8) The charge-transfer complex of the onium iodide was first observed spectrophotometrically by Kosower in the case of N-alkyl pyridinium iodide. E. M. Kosower, J. A. Skorcz, J. Am. Chem. Soc., 82, 2195 (1960).