p-Phenylenebistetrathiafulvalene

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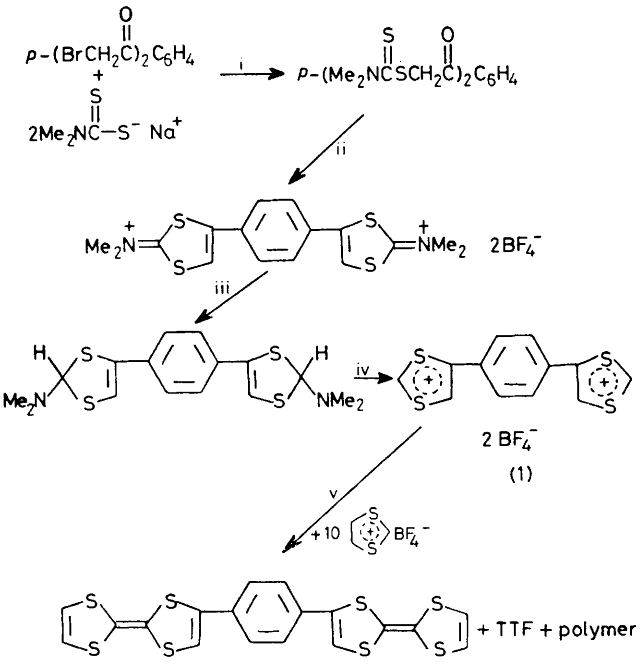
Summary The synthesis and properties of *p*-phenylenebistetrathiafulvalene are described; this molecule contains two donor units which allows the preparation of charge-transfer (CT) complexes with a band structure higher than the quasi-one-dimensional structure characteristic of all presently known electrically conducting organic CT complexes.

One goal of research in organic solid-state chemistry is to discover systems that are more highly electrically conducting than those already known. An approach to this problem involves the synthesis of molecules containing two donor or two acceptor units. This would allow the preparation of conducting charge-transfer (CT) complexes whose band structure could be of higher dimensionality than one-dimensional structures now known to be responsible for high conductivity.

We here describe the synthesis and properties of a compound which might fulfil these criteria: *p*-phenylenebis-tetrathiafulvalene (*p*-PBTTF) (**2**) (see Scheme).



SCHEME. i, EtOH, heat; ii, iv, HBF_4–AcOH; iii, $NaBH_4$–MeOH; v, Et_3N–sulpholan.

Steps i, ii, iv, and v employed standard procedures.[1] Previously, step iii had been carried out on the 2-SMe, rather than the 2-NMe_2 dithiolium cation in order to prevent interference in the isolation of molecules of type (**2**) by the $Me_2NH_2{}^+BF_4{}^-$ generated in step iv. In the present case, (**2**) was found to be so insoluble in common solvents that its separation was easy. Step v was carried out in the usual way[1] except that a large excess of 1,3-dithiolium fluoroborate was employed to prevent polymerization of (**2**). As expected, all steps except the last one produced high yields. The last step afforded (**2**) in 21% yield together with a high yield of tetrathiafulvalene (TTF).

Compound (**2**) is insoluble in most common solvents but sparingly soluble in chlorobenzenes, dioxan, carbon disulphide, cyclohexane, benzonitrile, and propylene carbonate. It can be purified by Soxhlet extraction with CS_2 or cyclohexane for 24—48 h followed by thick layer chromatography. It was isolated as a reddish-orange microcrystalline solid exhibiting the following properties: m.p. 241·9—242·4 °C; i.r.(KBr) ν_{max} 3075w, 1775w, 1570w, 1540w, 1400w, 1255w, 1210w, 1125w, 1085w, 920w, 822m, 800m, 783m, and 747s cm^{-1}; ^1H n.m.r. (CS_2, Me_4Si) δ 6·2, 6·37, and 7·25, 3 singlets in ratio 2 : 1 : 2; u.v.–visible (*p*-dioxan) λ_{max} 926sh (ϵ 19,800), 310 (21,700), 320 (21,600), and 440 (4020) nm; mass spectra, *m/e* 102, 126, 146, 178, 214, 279, 304, and 482. Satisfactory elemental analyses were obtained.

In the solution electrochemistry of (**2**), one would expect four reversible oxidation waves; also, the second ionization should occur at lower potential than for TTF since there are in essence two molecules of TTF per molecule of (**2**).

In fact, (**2**) exhibits only two oxidation waves in benzonitrile at 0·43 and 0·84 V *vs.* S.C.E. (*cf.* TTF $E_1 = 0{\cdot}40$; $E_2 = 0{\cdot}86$ V). From the peak-to-peak separation of *ca.* 30 mV for the first wave, we can infer that it corresponds to a two-electron wave. Confirmation for the two-electron oxidation was obtained by controlled potential coulometry (propylene carbonate), where values of 1·9 and 1·8 electrons were observed in separate experiments for the first wave. Coulometric oxidation of (**2**) to include both waves resulted in a net change of 4·0 electrons.

The e.s.r. spectrum of the *p*-PBTTF radical cation [prepared *via* reaction of H_2O_2 and HBF_4[2] with (**2**) in sulpholan–acetonitrile] consisted of a 1 : 3 : 3 : 1 pattern with *g* 2·0078, a_H *ca.* 1·25 G [*cf.* $TTF^{\ddagger}$ (MeCN) quintet, *g* 2·0084, a_H 1·26 G], attributable to a monosubstituted TTF unit and to coupling with 3 essentially equivalent hydrogens.

Acceptors react with *p*-PBTTF to produce deep coloured, extremely insoluble products. For example, with tetracyanoquinodimethane (TCNQ) (in benzonitrile), (**2**) yields small crystals of a *p*-PBTTF–TCNQ complex of *ca.* 1 : 1 stoicheiometry whose room temperature resistivity is *ca.* ten times that of TTF–TCNQ.

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[2] F. Wudl, *J. Amer. Chem. Soc.*, 1975, **97**, 1962.