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DESIGN AND SYNTHESIS OF POLY(SUBSTITUTED) TETRATHIAFULVALENE PRECURSORS

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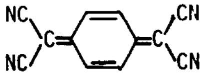
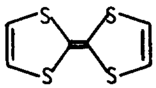
Interest in organic conductors assumed considerable importance in the early sixties and really blossomed with the synthesis of tetracyano-p-quino-dimethane (*TCNQ:1*) and *TCNQ*-tetrathiafulvalene (*TTF:2*) charge transfer salts.[1] In spite of considerable work in the last 15 years, the detailed molecular requirements for high conductivity in organic materials are poorly established and have been the subject of speculation in the literature.[1,2]



TCNQ:1

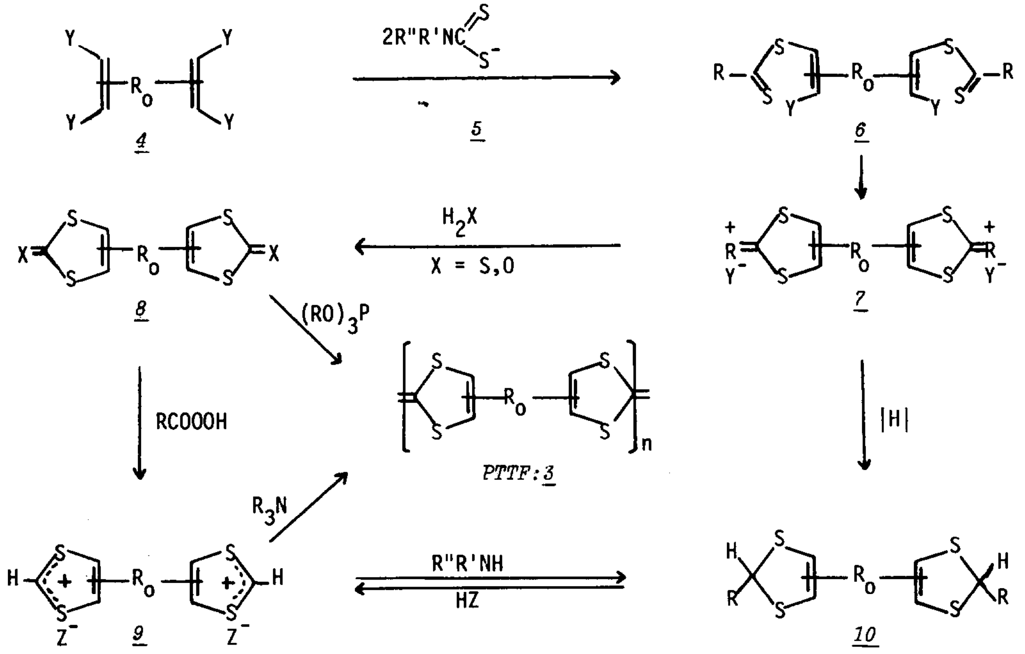


TTF:2

Although the entire field of monomeric and polymeric conductors is still in its early stages, the following interesting arguments, observations and results have already been reported: 1) The high conductivity of (modified) *TTF-TCNQ* compounds;[3] 2) The violene redox system;[4] 3) The increase in polymer conductivity by proper design of monomer;[5] 4) The hyperelectronic polarizability of eka-conjugated polymers;[6] 5) The superconductivity of poly(sulfurnitride);[7] 6) The theoretical possibility of synthesizing superconducting systems (Little's spine proposal).[8]

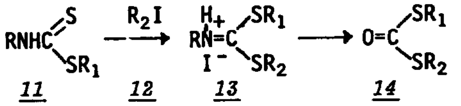
The question which confronts the synthetic polymer chemist is: Can some or all of the above observations and arguments be used in the design and synthesis of potential polymeric conductors? In the case of poly(substituted) tetrathiafulvalenes, *PTTF:3*, at least two answers can be given: 1) Polymerize functionalized cation precursors of *TTF*, without worrying about the structural order of the resulting polymer anticipating that a conductive polymer will result when the *PTTF* reacts with a proper acceptor. This approach has been tried,[9] but the results were not spectacular. 2) Polymerize specially designed functionalized precursors of *TTF* which, in principle, could give conjugated, highly ordered polymers which could be extended to violene-like polymers with the Little spine concept. The design and synthesis of such highly ordered poly(tetrathiafulvalenes) have already been worked out[10] and here we report some arguments and results.

The most versatile and suitable *PTTF* precursors for our purposes would be the bis(1,3-dithiol-2-immonium) salts of the general structure _7_ in Scheme 1 (where Y = reactive halogen, R = R"R'N, HZ = H_2SO_4, $HClO_4$, etc. and R_0 any linkage). This scheme represents the basic reactions which could lead to *PTTF:3* and introduces a new method of synthesizing bis(1,3-dithiole) precursors. The pivotal structure in this new synthetic route to *TTF* precursors is the salt _7_.[10,11]



Scheme 1

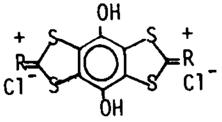
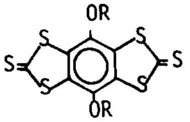
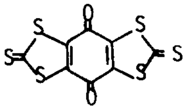
The starting point for the synthesis of salt _7_ was found in Delepine's synthesis of imidodithiocarbonic ester salts (_13_) from dithiocarbamic esters (_11_) and alkyliodide.[12]



$$\underset{11}{RNHC(=S)SR_1} \xrightarrow[12]{R_2I} \underset{13}{RNH^+=C(SR_1)(SR_2)\ I^-} \longrightarrow \underset{14}{O=C(SR_1)(SR_2)}$$

We reasoned that an intermediate _6_, which inherently contains two dithiocarbamic esters and two alkylating centers appropriately juxtoposed for Delepine's reaction, would be formed in the reaction of _4_ and _5_ in route to salt _7_. Indeed chloranil, a specific example of _4_, and dimethylammonium dimethyldithiocarbamate react to give the bis(1,3-dithiol-2-immonium) salt I of Table 1. The syntheses of specific structures _7_ and _8_ are given in Table 1.

Table 1. Poly (1,3,5,7 tetrathia-s-indacene) Precursors.[a]

Structure	No.	R	mp°C	Yield %
	I	$\overset{+}{N}(CH_3)_2$	275 dec. (water)	47[b]
	II	H-	260 dec. (dichlorobenzene)	95[c]
	III	$CH_3C(O)$-	295-296 (dioxane)	95[d]
	IV	CH_3-	268-270 (p-methylanisole)	80[e]
	V	$C_6H_5CH_2$-	202-204 (ethylacetate)	90[f]
	VI		230 dec. (benzene)	95[g]

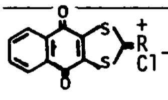
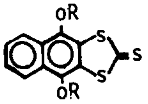
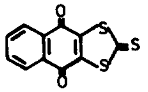
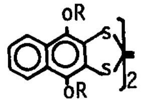
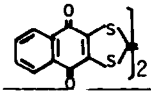
a. Bis(1,3-dithiol-2-ones) are prepared from hydrolysis with hydrochloric acid of an alcoholic suspension of I (reflux 2 days) which give a diketone analogous to dithione II, and similar reactions which give the compounds III-V. b. Prepared by dropwise addition of alcoholic solution of dimethylammonium dimethylcarbamate in a well agitated suspension of chloranil in alcohol-ether (2:1), refluxing of the mixture for 0.5-1h, filtration and recrystallization of the crude product from hot (90°C) 0.5 N hydrochloric acid solution. c. Prepared by passing hydrogen sulfide for 3-4h at 0.5°C in a suspension of I in aprotic solvents. d. Prepared by addition of acetic anhydride in a slightly basic solution of II in sodium hydroxide under nitrogen at 5-10°C. e. Prepared by addition of diazomethane in ether in ethereal suspension of II. f. Prepared by addition of benzylbromide in acetonic suspension of II and potassium carbonate under nitrogen, reflux for 4h, filtration and recrystallization. g. Prepared by oxidation of II with chromic acid, continuous extraction of the dark red solid with benzene.

In order to establish the scope and limitations of this new synthesis, and to gain information concerning the polycoupling reaction of Scheme 1, analogous reactions which would give model 1,3-dithiole precursors were attempted with different starting materials. Starting with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (*DDQ*) and 2,3-dichloro-1,4 napthoquinone (*DNQ*) the compounds listed in Table 2 were synthesized.

If, for example, chloranil is used as starting material, the completion of the reaction Scheme 1 yields symmetric poly(1,3,5,7-tetrathia-s-indacene), (*PTTI*). The polymeric derivatives *PTTI* will be the subject of another report.[14]

We acknowledge the Connecticut Research Foundation for support for this research.

Table 2. (Bis naptho [2,3]) tetrathiafulvalenes and their precursors.[a]

Structure	No.	R	mp°C	Yield %
	VII	$\overset{+}{N}(CH_3)$	226-228 dec. (water)	65[b]
	VIII	H-	220-221	45[c]
	IX	$CH_3C(O)$-	198-200 (dioxane)	95[d]
	X	CH_3-	184-165	95[d]
	XI		165-166 (methylcyclohexane)	95[e]
	XII	$CH_3C(O)$-	333-334	30-90[f]
	XIII	CH_3-	315-316	30-90[f]
	XIV	H-		95[g]
	XV		>360	95[h]

a. 1,3-dithiol-2-ones are prepared from hydrolysis of a solution of VII in 0.5 hydrochloric acid (reflux 24h) which give a 1,3-dithiol-2-one analogous to thioketone XI and similar reactions which give the compounds IX-XI. b. Reference 13. c. Prepared by reduction of XI with sodium dithionite. d. Prepared as the corresponding bis(1,3-dithiole-2-thiones) of Table 1. e. Prepared by passing hydrogen sulfide for 4h at 0-5°C in a suspension of VII in aprotic solvents and stirring at room temperature for 12-18h. f. Prepared by coupling of 1,3-dithiole-2-thiones, IX or X and the anologous 1,3-dithiol-2-ones with trimethylphosphite[11,12]. g. Prepared from hydrolysis of ester XII or ether XIII with pyridine (reflux 12h under N_2) or boron tribromide (stirring under N_2 at room temperature in methylene chloride). h. Prepared by oxidation of alcoholic solution of XIV by air or *DDQ*.

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