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# NEW CONDUCTING SALTS CONTAINING UNSYMMETRICAL π-DONORS

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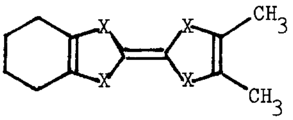
Abstract : This communication describes the synthesis and the electrochemical properties of a new type of donor containing sulfur or selenium atoms : the dimethyltetramethylenetetraselenafulvalene 1 and the dimethyltetramethylenetetrathiafulvalene 2. The electrical conductivity of their charge transfer complexes and of some of their radical cation salts are reported.

The discovery of a superconducting state in a series of TMTSF radical cation salts[1] has stimulated research in the preparation of new π-donors of the fulvalene type. A partial understanding of the origin of the electrical conductivity of such systems and the identification of some factors responsible of this property [2, 3] have prompted us to prepare the organic molecules 1 and 2 :



1 : X = Se (DMCTSF)

2 : X = S (DMCTTF)

The cyclohexyl substitution and dimethyl substituants have always led, for the corresponding symmetrical compounds, to salts of TTF - TCNQ type [4, 5] and $(TTF)_n^+ X^-$, which are good or even excellent conductors. Our decision to prepare such unsymmetrical π-donors was made in order to increase the dimensionality of their complexes thus improving the interchain coupling and consequently their conductivity. Generally in this field, the tetraselenium derivatives offer better results.

To prepare the tetraheterofulvalenes 1 and 2 we needed some intermediates the characteristics of which are displayed in the table I.

From these intermediates several different methods could be used to synthesize 1 and 2. One of them is described by CAVA and GONNELLA [6] as a specific method which leads to the unsymmetrical species without any formation of the symmetrical analogs. This procedure is shown in the following scheme (equation I) :

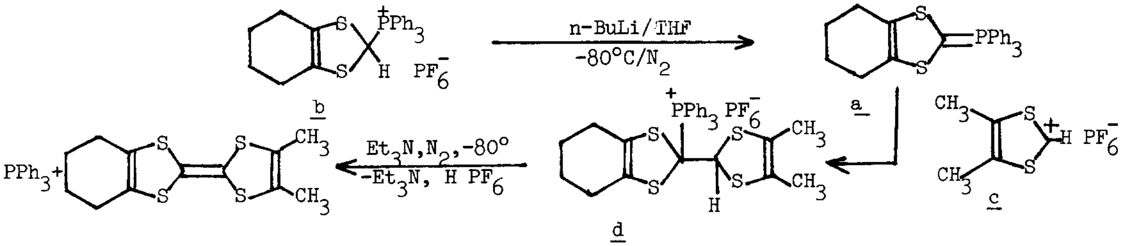
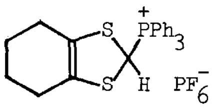
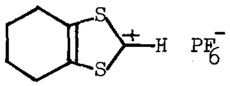
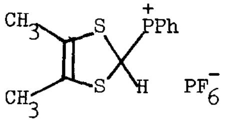
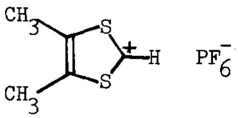
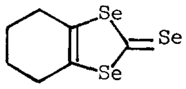
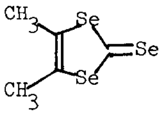


Table I : Physical and spectroscopic properties of intermediates used in the synthesis of tetraheterofulvalenes 1 and 2.

| Salts | m.p. (°C) | IR (KBr) ($cm^{-1}$) | $^1H$ N.M.R.* δ (ppm) | $^{13}C$ N.M.R.* δ (ppm) |
|---|---|---|---|---|
|  a) | 193 | 3060 - 2920<br>1630 - 1440<br>1050 - 770<br>700 | 1.00 - 1.16 (m, 4H)<br>1.46 - 1.83 (m, 4H)<br>6.90 (d, 1H) | 22.40 - 25.83<br>42.01 , 42.85<br>118.14 - 131.08<br>131.33 - 135.53<br>136.58 |
|  | 155 | 3090 - 2960<br>1520 - 1430<br>950 - 840 | 1.80 - 2.16 (m, 4H)<br>3.03 - 3.36 (m, 4H)<br>10.86 (s, 1H) | 21,92 - 26,84<br>118,14 - 174,58 |
|  b) | 180 | 3060 - 2990<br>1590 - 1440<br>1110 - 850<br>730 - 690 | 1.30 (s, 6H)<br>6.80 (d, 1H)<br>8.16 (m, 15H) | 13,22<br>42,19 , 43,01<br>118,11 - 131,03<br>131,26 - 135,30<br>136,62 |
|  | 160 | 3090 - 1510<br>1450 - 1100<br>950 - 850<br>740 | 2.80 (s, 6H)<br>10.83 (s, 1H) | 14,60 - 118,20<br>173,34 |
|  | 145 | 2970 - 1580<br>1470 - 970<br>890 | 1.66 - 2.00 (m, 4H)<br>2.46 - 2.83 (m, 4H) | 22,80 - 28,09<br>147,76 - 207,03 |
|  | 150 | 2970 - 1630<br>1400 - 980<br>880 - 780 | 2.30 (s, 6H) | 15,53 - 144,99<br>206,36 |

* : $CD_3CN$ + TMS used with the phosphonium and dithiolylium salts.
$CDCl_3$ + TMS used with the selenones.

$^{31}P$ N.M.R.($CHCl_3/H_3PO_4$ ext.) δ(ppm) : a) = 14.51 ; b) = 14.81

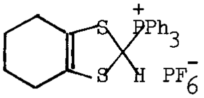
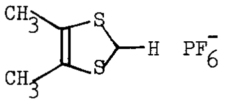
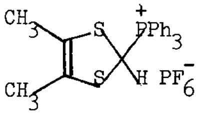
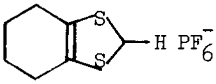
We used it as follows :

- The wittig reagent a was obtained at -80°C by deprotonation of the 1,3-dithiole 2-triphenylphosphonium hexafluorophosphate salt b (564 mg, 1 mmol.) in the presence of n-BuLi (0.37 ml, 1 mmol.) in anhydrous THF (50 ml).

- The condensation of a with 4,5-dimethyl 1,3-dithiolylium hexafluorophosphate c (276 mg, 1 mmol.) leads to a phosphonium salt d as an intermediate. This salt treated with an excess of $Et_3N$, gave the desired tetrathiafulvalene 2 with some small amounts of the corresponding symmetrical TTF's.

The results obtained are reported in the table II.

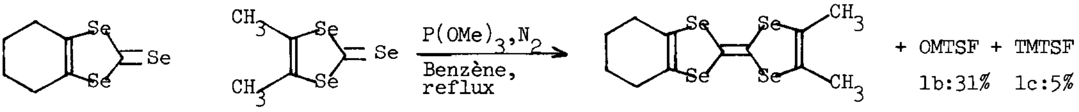
Table II : Ratios of the different TTF's isolated in the reaction (I) :

| Starting materials | | Composition (%) of the mixture of TTF's | | |
|---|---|---|---|---|
| Phosphonium | dithiolylium | unsymmetrical TTF | OMTTF | TMTTF |
|  |  | 81 | 8.5 | 10.5 |
|  |  | 81 | 6.5 | 12.5 |

It can be seen that the reaction is not completely selective. During the course of this reaction there is an autoduplication of the involved salts. This result iduced us to study systematically the selectivity of this procedure used to prepare unsymmetrically substituted TTF $^{7}$. We showed that it was not possible to use such a method to obtain pure unsymmetrical TTF's because of the intrinsic instability of the ylids in such conditions and because of the side reactions given by the salts involved in it. Column chromatography ($Sio_2$, $CS_2$) is necessary to obtain pure compound 2.

Concerning the selenium analog 1, we used the mixed coupling technique $^{8}$.

- Under nitrogen, the 4,5-tetramethylene 1,3-diselenole 2-selenone (329 mg, 1 mmol.) is left to react with the 4,5-dimethyl 1,3-diselenole 2-selenone (303 mg, 1 mmol.) in the presence of trimethylphosphite (248 mg, 2 mmol.) in refluxing dry benzene (150 ml) for 10 hours. The three expected tetraselenafulvalenes are isolated in the following ratios (see scheme below) as shown by gas phase chromatography.



1 : 64 %

Table III : Characteristics of TTF's 1 and 2 :

| Compounds | $E^2_{1/2}$ (V) (a) | m.p. (°C) | $^1$H N.M.R. (ppm) (b) | m/e | | Elemental analysis | |
|---|---|---|---|---|---|---|---|
| | | | | Calc. | Found | Calc. | Found |
| 1 | 0.5 | 212 | 1.3 (s, 4H)<br>1.1-1.3 (m, 4H)<br>1.8-2.0 (m, 4H) | 477,775 | 477,775 | C : 30.40<br>H : 2.17 | 30.21<br>3.07 |
| 2 | 0.32 | 194<br>(174) (6) | 1.9 (s, 6H)<br>1.58-1.78 (m, 4H)<br>2.00-2.26 (m, 4H) | 285,997 | 285,997 | C : 50.30<br>H : 4.92 | 49.90<br>4.88 |

a) : The half wave potentials were measured with a platinum electrode VS a standard calomel electrode used as reference in a solution of $NBu_4$ $ClO_4$ ($10^{-1}$ M) in 1,1,2-trichloroethane.

b) : $CS_2$ + TMS for 2 and $C_6D_6$ + TMS for 1.

From the very pure compounds 1 and 2 we prepared new materials :

a - charge transfer complexes with TCNQ and then DMTCNQ. These materials were synthesized in acetonitrile by mixing the boiling solutions of each π-donor with eath π-acceptor.

b - Radical cation salts of $(\pi\text{-donor})_nX$ type, were prepared in THF using oxidative electrocrystallization at constant current (10 A), in presence of $NBu_4X$ salt ($10^{-1}$ M) and of the π-donor at a concentration of about $10^{-3}$ M. The single crystals obtained display either a needle shape or lozenge platelets having shiny faces.

The electrical conductivity measurements were carried out using the four contact technique . The room temperature results are shown in table IV.

Table IV : Electrical conductivity of some charge transfer complexes and radical cations salts involving 1 and 2 as π-donor.

| TTF \ $X^-$ | $PF_6$ | $AsF_6$ | $ReO_4$ | $CF_3SO_3$ | TCNQ | DMTCNQ |
|---|---|---|---|---|---|---|
| 1 | 26 | 8 | 26 | 1.5 $10^{-2}$ | insulating | insulating |
| 2 | $3.10^{-2}$ | $4.10^{-2}$ | 4 | insulating | $3.10^{-1}$ | insulating |

These results show clearly that the perrhenates of 1 and 2, the hexafluoroarsenate and phosphate of 2 are conductors. The other salts display a semiconducting or an in sulating behavior. All the salts discussed show a regular decrease in conductivity when the temperature is decreased. Itis likely that the more conductive selenium compounds must display a pseudobidimensional character. The structure determination of these salts is currently under investigation and will be published separately.

REFERENCES :

1. D. Jerome, A. Mazaud, M. Ribault et K. Bechgaard, C.R. Acad. Sci. Paris, 1980, t-290, B-27.
2. M.L. Kaplan, F. Wudl, R.C. Haddon et J.J. Hauser, Chemica Scripta, 1980, 15, 196.
3. J.M. Fabre, E. Torreilles, M. Vigroux et L. Giral, J. Chem. Research (M), 1980, 4564.
4. J.P. Ferraris, T.O. Poehler, A.N. Bloch, D.O. Cowan, Tetrahedron Lett.,1973, 2553.
5. A.N. Block, D.O. Cowan, K. Bechgaard, R.E. Pyle, R.H. Banks, Phys. Rev. Lett., 1975, 34, 1561.
6. N.C. Gonnella, M. Cava, J. Org. Chem., 1978, 43, 269.
7. L. Giral, J.M. Fabre et A. Gouasmia, J. Org. Chem., to appear.
8. D.C. Green, J.C.S. Chem. Comm., 1977, 161.

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