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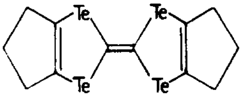
A NEW ELECTRON DONOR: SYNTHESIS OF 2,3,6,7- TETRA(ETHYLTELLURIO)TETRATHIAFULVALENE

Eliezer Aharon-Shalom, James Y. Becker,* Joel Bernstein, Shmuel Bittner* and Sason Shaik

The Organic Metals Group, Department of Chemistry,
Ben-Gurion University of the Negev, Beersheva 84120, Israel

Summary. A new tetratellurio substituted derivative of tetrathiafulvalene has been prepared via a direct one pot three step synthesis.

Since the discovery[1] that the complex between tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) has an electrical conductivity similar to that of metals, a great deal of effort has been directed towards obtaining other conducting complexes with new donors and acceptors. One major synthetic route involves derivatization of TTF either by substitution of the hydrogens[2,3] for alkyl or alkylthio groups or by substitution of the sulfur atoms by selenium[4]. Recently Wudl and Aharon-Shalom reported[5] a successful preparation of the tellurio analog hexamethylenetetratelluriofulvalene (1). This compound was only the second reported organic compound containing four tellurium atoms, the first being a nonfulvenoid derivative[6].



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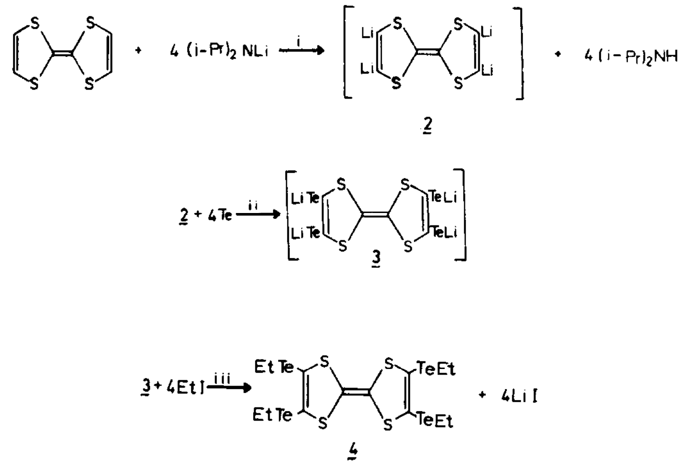
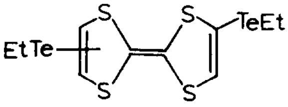
In the present communication we wish to report the synthesis (Scheme 1) of a new organic compound containing four tellurium atoms attached to the TTF skeleton.

The conditions under which the title compound has been prepared in one pot are the following: 4.4 mmole of the lithium reagent in 30 ml THF is made by adding n-butyllithium (dropwise) to a stirred and cooled (-78°C) solution of (i-propyl)$_2$NH under argon. Step (i): After 20 min 1 mmole of TTF (Aldrich) is added to the cold (-78°C) solution of the lithium diisopropylamide. A yellow suspension of the tetralithio derivative 2 is formed within 1h. Step (ii): 4 mmoles of amorphous tellurium powder is added to the cold (-78°C) solution of 2 and after 1.5h it is allowed to warm up slowly to room temperature. The mixture containing



the tellurium suspension becomes clear after 5h at R.T. indicating the completion of the reaction. Step (iii): The solution of 3 is again cooled down to -78°C and an excess of ethyl iodide is added. The solution is allowed to warm up slowly to R.T. and the stirring is continued for another 1h. Most of the THF is distilled off and CH_2Cl_2 is added. The organic solution is washed several times with water till the latter has a neutral pH. The organic phase is dried over $MgSO_4$, filtered and distilled to dryness. The residue is crystallized from $CHCl_3$ (or 3:1 petrol ether-$CHCl_3$) to give yellow-orange needles of 4 (35% yield based on TTF) m.p. 88-90°C; elemental analysis calcd. for $C_{14}H_{20}S_4Te_4$: C=20.33 H=2.44 ; Found C =20.56 H=2.41: (m/z M^+ (40eV,200°C): 828, based on ^{128}Te. When only two-fold excess of the lithium reagent (step i) and (step ii) are used a ditellurio derivative, 5 (yellow, 20%, m.p. 85°C; m/z M^+: 516 based on ^{128}Te) is obtained:



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Some physical properties of both 4 and 5 are summarized in Table 1. The pattern of the UV-VIS spectra of both 4 and 5 is somewhat similar to all other known TTF analogues, except for the appearance of a new strong absorption band below 250 nm (243 nm for 4 and 232 nm for 5). The first two redox potentials for each of 4 and 5 are comparable to those of TTF (0.48V and 0.86V, respectively). This similarity may indicate that in these compounds ionization occurs primarily from the bonded network, with little participation of the tellurium lone pairs, unlike what has been suggested for 1.[5]

When MeI is added (in step (iii)) instead of EtI, the tetramethyl analog is formed (yellow, NMR: δ=2.22(s) ppm). However, when CH_2Cl_2 or $BrCH_2CH_2Br$ is added dark solids precipitate whose nature has not yet been established. Currently attempts are being made to prepare salts and complexes of 4 with different acceptors, to determine their crystal structure and to measure their electrical properties.

We have prepared a complex of 4 with TCNQ (precipitated as dark violet needles from CH_3CN) which has a mixed stack structure.[8] Its conductivity at room temperature is $\sim 10^{-2}\Omega^{-1}cm^{-1}$. This value is remarkably high relative to other known[9] mixed stack complexes of TCNQ which have conductivity in the order of 10^{-6}-$10^{-11}\Omega^{-1}cm^{-1}$. Clearly the inclusion of tellurium atoms in 4 plays an important role in increasing the conductivity.

Table 1

compound	UV-VIS, nm (ε)[a]	^{1}H n.m.r., δ(ppm)[b]	$E^1_{\frac{1}{2}}$(V)[c]	$E^2_{\frac{1}{2}}$(V)[c]	I.R. (KBr), cm^{-1})
4	243(17700), 282 (18050) 325(16800), 410 (4000), 470(1700)	1.75(t), 2.91(q)	0.56	0.90	590(m), 715(s), 765(m), 890(m), 950(m), 1045(m), 1190(s), 1375(m), 2900(m)
5	232(19000), 290(14800), 322(16750), 385(3100), 455(770)	1.75(t); 2.88(q) 6.53(s); 6.55(s)	0.53	0.93	585(m), 710(m), 760(s) 790(m), 865(s), 965(m), 1095(s), 1195(s), 1370(w) 1440(m), 2920(s), 3060(m)

[a] In CH_2Cl_2. [b] In $CDCl_3$ and TMS as internal standard. [c] Reversible waves, in CH_3CN-CH_2Cl_2 (1:1), 0.1M tetrabutylammonium fluoroborate, vs Ag wire at 100mV/s sweep rate.

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References

1. J.Ferraris, D.O. Cowan, V. Walutka and J.H. Perlstein, J. Am. Chem. Soc. 1973, 95, 948; L.B. Coleman, M.J. Cohen, D.J. Sandman, F.G. Yamagishi, A.F. Garito and A.J. Heeger, Solid State Commun. 1973, 12, 1125.
2. R.R. Schumaker, V.Y. Lee and E.M. Engler, J. Org. Chem. 1984, 49, 564; R.R. Schumaker and E.M. Engler, J. Am. Chem. Soc. 1977, 99, 5521; 1980, 102, 6651; Idem and V.V. Patel J. Chem. Soc. Chem. Commun. 1979, 516; E.M. Engler, V.Y. Lee, R.R. Schumaker, S.S.P. Parki R.L. Greene and J.C. Scott, Mol. Cryst. Liq. Cryst. 1984, 107, 19.
3. W.P. King, A.N. Bloch and D.O. Cowan, J. Chem. Soc, Chem. Commun. 1977, 660.
4. E.M. Engler and V.V. Patel, J. Am. Chem. Soc. 1974, 96, 7376; S. Etemad, T. Penney, E.M. Engler, B.A. Scott and P.E. Seiden, Phys. Rev. Lett. 1975, 34, 741; A.N. Bloch, D.O. Cowan, K. Bechgaard, R.E. Pyle, R.H. Banks and T.O. Poehler, Phys. Rev. Lett. 1975, 34, 1561.
5. F. Wudl and E. Aharon-Shalom, J. Am. Chem. Soc. 1982, 104, 1154.
6. D.J. Sandman, J.C. Stark, G.P. Hamilt, W.A. Burke and B.M. Foxman, Inter. Conf. on Low Dimensional Conductors, Boulder, Colorado, Aug. 9-14, 1981; R.P. Shibaeva, V.F. Kaminsk Cryst. Struct. Commun. 1981, 10, 663.
7. D.G. Green, J. Org. Chem. 1979, 44, 1476.
8. E. Aharon-Shalom, J.Y. Becker, J. Bernstein, S. Bittner and S. Shaik, submitted for publication.
9. J.H. Perlstein, Angew. Chem. Int. Ed. Engl. 1977, 16, 519; D.J. Sandman, G.P. Caesar, P. Nielsen, A.J. Epstein and T.J. Holmes, J. Amer. Chem. Soc., 1978, 100, 202; D.J. Sandman, G.D. Zoski, W.A. Burke and G.P. Hamill, J. Chem. Soc. Chem. Commun., 1981, 829; R.C. Wheland, J. Amer. Chem. Soc., 1976, 98, 3926; J.B. Torrance, Phys. Rev. Lett, 1981, 46, 253; J.J. Mayerle and J.B. Torrance, Bull. Chem. Soc. Jpn., 1981, 54, 3170.

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