Synthesis of Tris(ethylenedithio)benzene, Tris(methylenedithio)benzene, and Tris(ethyleneoxythio)benzene as Candidates for the Preparation of Organic Ferromagnets

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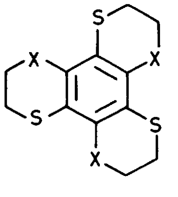
Tris(ethylenedithio)benzene (TEDTB), tris(methylenedithio)benzene (TMDTB), and tris(ethyleneoxythio)benzene (TEOTB) have been prepared and TEDTB electrocrystallized to give a conducting tetrafluoroborate radical ion salt (TEDTB)$_2$BF$_4$.

The substitution of tetrathiafulvalene with two ethylenedithio groups to give the highest superconduction transition temperature to date for an organic metal[1] and the ferromagnetic properties expected on coupling a dication and a radical cation of aromatic π-electron systems of C_3 symmetry[2] led us to predict that tris(ethylenedithio)benzene (TEDTB) (**1**) would be a good candidate for the preparation of radical ion salts showing interesting electrical and magnetic properties. We describe here the synthesis of (**1**)† and the related tris(methylenedithio)benzene (TMDTB) (**2**) and tris(ethyleneoxythio)benzene (TEOTB) (**3**). We have also prepared bis(ethylenedithio)benzene (DEDTB) (**4**) and bis(ethyleneoxythio)benzene (DEOTB) (**5**) because their readily available precursors make them attractive model compounds for testing the sequence of reactions selected for the synthesis of (**1**)—(**3**).

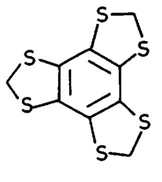
Table 1. Redox potentials at a 3 mm^2 platinum disc electrode.

Compound[a]	(E_p −0.03)/V[b,c]
(**1**)	1.10
(**2**)	Irreversible
(**3**)	0.99
(**4**)	1.17
(**5**)	1.15

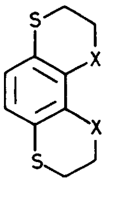
[a] 1 mM in MeCN with Et$_4$NBF$_4$ (0.2 M) at room temp. [b] V *vs.* s.c.e. [c] Scan speed 0.2 V s^{-1}.



(**1**) X = S
(**3**) X = O



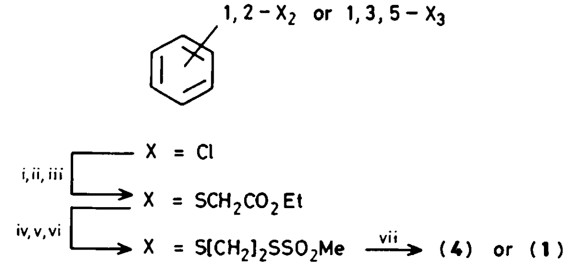
(**2**)



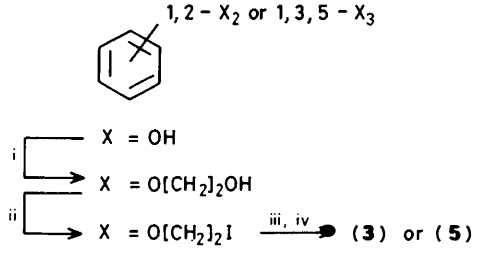
(**4**) X = S
(**5**) X = O

Compounds (**1**) and (**4**) have been obtained from 1,2-dichloro- and 1,3,5-trichloro-benzenes, according to Scheme 1, but in low yields (12 and 8% respectively) owing to the number of steps involved. The commercial availability of 1,2-dihydroxy- and 1,3,5-trihydroxy-benzenes and the efficient hydroxyethylenation using ethylene carbonate[6] provided a route to (**3**) and (**5**) in acceptable yields (32 and 26% respectively) (Scheme 2). The reduced activation of a β oxygen relative to a β sulphur made the reaction with potassium methanesulphonate more sluggish and a higher temperature and an aprotic solvent [dimethylformamide (DMF)] were needed; under these conditions an appreciable amount of (**3**) was formed directly in step iii.

In an attempt to shorten the synthesis of (**1**) and (**4**) we added 1,2-dibromoethane to 1,2-dithiolato- and 1,3,5-trithiolatobenzenes in hexamethylphosphoramide (HMPA) and obtained respectively 1,2-(ethylenedithio)benzene and all the 1,3,5-trisubstituted benzenes containing (2-bromoethylthio)- and/or (vinylthio)-substituents. The formation of 1,2-(ethylenedithio)benzene from 1,2-dithiolatobenzene led us to try the reaction of hexathiolatobenzene with dibromoethane and



Scheme 1. *Reagents and conditions:* i, Pr^{i}SNa, HMPA, 25 °C, 2 h (ref. 3); ii, Na, 100 °C, 2 h, (ref. 4); iii, BrCH$_2$CO$_2$Et, 50 °C, 2 h; iv, LiAlH$_4$, tetrahydrofuran (THF), reflux 12 h; v, SOCl$_2$, benzene, reflux 2 h; vi, MeSO$_2$SK, EtOH, reflux 18 h (ref. 5); vii, AlCl$_3$, MeNO$_2$, (ref. 5).



Scheme 2. *Reagents and conditions:* i, ethylene carbonate, Et$_4$NBr, DMF, 150 °C, 14 h (ref. 6); ii, Ph$_3$PI$_2$, HMPA, (ref. 7); iii, MeSO$_2$SK, DMF, EtOH, reflux 18 h; iv, AlCl$_3$, MeNO$_2$.

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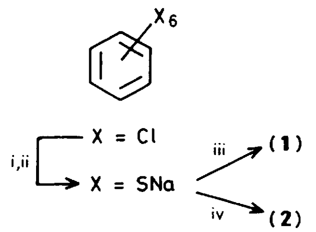
† All new compounds gave satisfactory elemental analyses and spectral data. (**1**): m.p. 310 °C; ^{1}H n.m.r. (CDCl$_3$), δ (Me$_4$Si) 3.25; *m/z* (electron impact, 70 eV) 348 (M^+) (100%), 320 (32), 292 (21), 264 (14). (**2**): m.p. 295 °C; ^{1}H n.m.r. (CDCl$_3$), δ (Me$_4$Si) 4.44 (s); *m/z* 306 (M^+). (**3**): m.p. 305 °C; ^{1}H n.m.r. (CDCl$_3$), δ (Me$_4$Si) 3.13—3.53 (6H, m), 4.63—4.96 (6H, m); *m/z* 300 (M^+) (100%), 272, 244, 216, 188. (**4**): oil; ^{1}H n.m.r. (CCl$_4$), δ (Me$_4$Si) 3.23 (8H, s), 6.82 (2H, s); *m/z* 258 (M^+) (100%), 243 (20), 230 (23), 215 (14), 202 (13). (**5**): m.p. 138 °C; ^{1}H n.m.r. (CCl$_4$), δ (Me$_4$Si) 2.93—3.23 (4H, m), 4.23—4.57 (4H, m), 6.43 (2H, s); *m/z* 226 (M^+) (100%), 198 (14), 170 (35), 142 (18), 114 (67).



Scheme 3. *Reagents and conditions:* i, $\mathrm{Pr^iSNa}$, HMPA, 25 °C, 2 h; ii, Na, 100 °C, 2 h; iii, CH_2BrCH_2Br; iv, CH_2Br_2.

dibromomethane as an expedient route to (**1**) and (**2**) (Scheme 3). Convenient access was effectively provided to (**1**) (32%) and (**2**) (38%) by this route.

With the exception of (**2**) whose radical cation deprotonates too readily,[8] all the compounds (**1**)—(**5**) show, in MeCN, reversible oxidation to give the monocation [E_p ~1.1 V *vs.* standard calomel electrode (S.C.E.)] and an irreversible oxidation to give the dication (E_p ~1.5 V *vs.* s.c.e.) by means of cyclic voltammetry; the associated redox potentials are listed in Table 1.

Single crystals of a BF_4 radical cation salt of (**1**) were grown on a platinum electrode at −10 °C from a CH_2Cl_2–Bu_4NBF_4 solution using the low constant current technique (I = 4 μA). Black platelets of (TEDTB)BF_4 were collected whose physical properties $\sigma_{RT} = 10^{-2}\ \Omega^{-1}\ cm^{-1}$ and X-ray crystal structure are described elsewhere.[9] These results open the way to a new series of conducting radical ion salts from which the generation of triplet dicationic species is planned by direct solid state oxidation of the salts[10] or by dehydrogenation of (**1**) and (**3**) to give compounds of lower two-electron oxidation potential.

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