

New Alkoxyated Dibenzo[1,4]dichalcogenines as Donors for Low-dimensional Materials: Electrochemistry and Cation-radical Salts

Lars Engman,* Jonas Hellberg, and Christina Ishag†

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Svante Söderholm

Department of Physics III, Royal Institute of Technology, S-100 44 Stockholm, Sweden

The synthesis of new alkoxyated dibenzo[1,4]dichalcogenines‡ (3a–c), (3e–f), (3h), (4a–h), and (5a) is presented. The first cyclovoltammetric half-wave potentials of these compounds range from 0.62 to 1.06 V vs. standard calomel electrode (s.c.e.). Cation radical salts of several different stoichiometries have been prepared from the new donors.

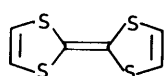
Organic materials with high electric conductivity or unusual magnetic properties have attracted increasing interest during the last decade.¹ Of the many systems investigated, those based on tetrathiafulvalene [TTF, (1)], were most extensively studied, mainly due to the high conductivity and superconductivity of their charge-transfer and cation-radical salts. However, as the study of electroactive organic materials contains several interesting, and sometimes spectacular, features and potential applications² (such as electrodes in energy cells and electrolytes in capacitors, temperature-sensitive switches and magnetic-field probes), the search for materials of high conductivity should not be the only goal. It was also felt that more systematic

studies should be directed towards systems other than the TTF-type. Dibenzo[1,4]dichalcogenines (2) are known to generate stable cation radicals,³ and charge-transfer salts,⁴ and a cation-radical salt⁵ has been isolated.

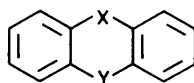
The few examples of alkoxylation of the parent system indicate a lower oxidation potential and a more stable cation radical.⁶ Charge-transfer salts of these alkoxyated systems have also been isolated.⁷ Since many of the salts developed to date are of the mixed-stack type and are therefore insulating, there has been little activity in investigating other compounds of this type. However, we felt that both alkoxylation and chalcogen substitution could be easily varied in these compounds, and with the analogues in hand it should then be possible to study the structural and electronic properties of their cation-radical salts as determined by changes in electric and magnetic properties. We have therefore synthesized a series of donors (3)–(5). Their cyclovoltammetric behaviour is presented along with some preliminary results on some of their cation radical salts.

Synthesis.—Before choosing a strategy for the construction of the new compounds (3a–c), (3e, f), (3h), (4a–h), and (5a),⁸ the synthetic pathways to the known unsubstituted compounds (2a–f) were evaluated to see if they could be extended to alkoxyated derivatives. It was found that rather drastic conditions were required for the preparation of compounds (2): thianthrene (2d) was obtained from benzene and sulphur in the presence of aluminium chloride;⁹ phenoxathiine (2a) was similarly prepared from sulphur and diphenyl ether;¹⁰ phenoxatellurine (2c) was produced in ca. 50% yield when diphenyl ether was treated with tellurium tetrachloride at 240 °C and the resulting 10,10-dichlorophenoxatellurine was reduced with potassium hydrogen sulphite,¹¹ phenothiatellurine (2e) was similarly obtained from diphenyl sulphide albeit in much lower yield (6%).¹² Phenoxaselenine (2b) was formed when phenoxatellurine was boiled neat with elemental selenium;¹³ selenanthrene (2f) was prepared by heating the disulphide of thianthrene with elemental selenium.¹⁴

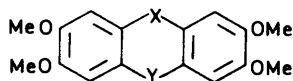
Clearly, these harsh reaction conditions would not be suitable for the preparation of the electron-rich compounds required. However, the high-yielding (71%) synthesis of 2,3,7,8-tetra-methoxythianthrene (3d),^{8a} from veratrole and sulphur dichloride in acetonitrile at ambient temperature, indicates that



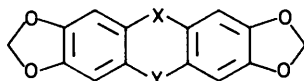
(1)



- (2) a: X = O, Y = S
 b: X = O, Y = Se
 c: X = O, Y = Te
 d: X = S, Y = S
 e: X = S, Y = Te
 f: X = Se, Y = Se



- (3) a: X = O, Y = S
 b: X = O, Y = Se
 c: X = O, Y = Te
 d: X = S, Y = S
 e: X = S, Y = Se
 f: X = S, Y = Te
 g: X = Se, Y = Se
 h: X = Se, Y = Te
- (4) a: X = O, Y = S
 b: X = O, Y = Se
 c: X = O, Y = Te
 d: X = S, Y = S
 e: X = S, Y = Se
 f: X = S, Y = Te
 g: X = Se, Y = Se
 h: X = Se, Y = Te



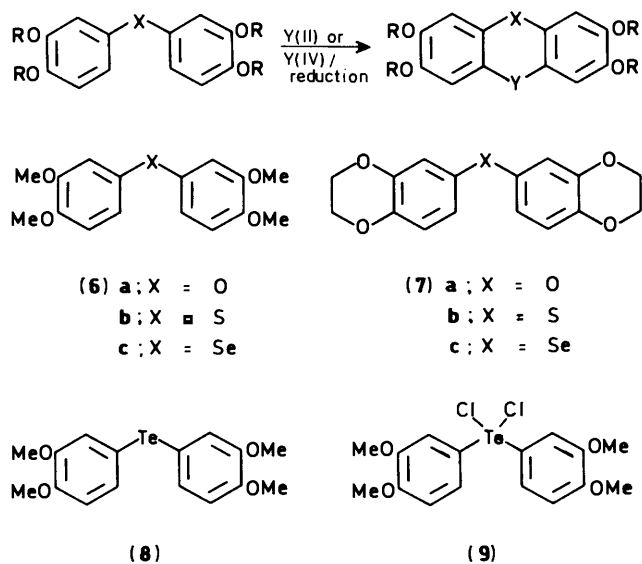
- (5) a: X = O, Y = S
 b: X = S, Y = S
 c: X = Se, Y = Se

† On leave from the University of Khartoum, Faculty of Science, Department of Chemistry, PO Box 321, Khartoum, Sudan.

‡ Dichalcogenine refers to a six-membered ring in which two of the carbon atoms have been replaced by elements of group 6.

§ Ref. 7b reports the cyclovoltammetric behaviour of compound (3e) but no synthetic procedure or physical properties were given.

alkoxylated dibenzo[1,4]dichalcogenines might be efficiently assembled using considerably milder conditions. For the construction of compounds (3) and (4) we decided to use a strategy involving electrophilic ring closure of preformed alkoxylated diaryl chalcogenides as indicated in Scheme 1. By



Scheme 1.

varying the electrophile Y (e.g. SCl_2 , SeCl_4 , TeCl_4) it should be possible to synthesize different heterocyclic systems from the same diarylchalcogenide.

The required alkoxylated diaryl ethers (6a) and (7a) were synthesized in 44 and 60% yield, respectively, by treatment of the appropriate sodium phenoxide with the suitable bromoaromatic compound in *N,N*-dimethylformamide at 160 °C in the presence of copper(I) iodide (Ullman diaryl ether synthesis).¹⁵ Treatment of compounds (6a) and (7a) with sulphur dichloride in dry chloroform provided the desired phenoxathiines (3a) and (4a) in 59 and 80% yield, respectively.

Cyclization of compounds (6a) and (7a) with selenium tetrachloride at ambient temperature in chloroform, followed by reduction with aqueous sodium disulphite, afforded the phenoxaselenines (3b) and (4b) in 44 and 62% yield, respectively.

The cyclization reactions with tellurium tetrachloride proceeded very sluggishly at ambient temperature. However, in refluxing chloroform, and in the presence of a catalytic amount of tin(IV) chloride, the phenoxatellurines (3c) and (4c) were obtained in 28 and 27% yield, respectively, after reduction.

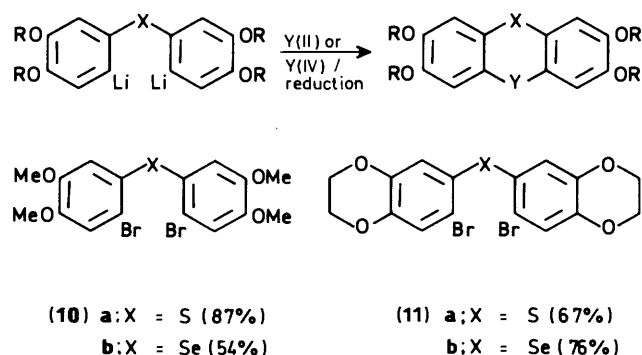
The alkoxylated diaryl sulphides (6b) and (7b) were prepared in 83 and 49% yield, respectively, by using the previously described copper-assisted nucleophilic substitution of an aryl bromide. Chlorosulphonation of veratrole and benzodioxane respectively, followed by zinc reduction, provided the alkoxylated thiophenols. In an alternative preparation of the sulphide (7b), 6-lithio-2,3-dihydro-1,4-benzodioxine in THF was treated with bis(benzenesulphonyl) sulphide to provide compound (7b) in 77% yield. Cyclization of the sulphide (7b) with sulphur dichloride in the presence of a catalytic amount of tin(IV) chloride afforded the thianthrene (4d) in low yield (20%). An attempt to prepare compound (4d) directly from benzodioxane and sulphur dichloride by analogy with the preparation of tetramethoxythianthrene (3d)^{8a} also resulted in a poor yield (14%) of the desired compound.

Treatment of sulphide (6b) with selenium tetrachloride in chloroform yielded the phenothiaselenine (3e) in 42% yield after reduction. Similarly, compound (7b) afforded phenothiaselenine

(4e) in 23% yield. We attempted to prepare compound (4e) from the selenide (7c) and sulphur dichloride, however, the formation of a phenothiaselenine was observed only in the presence of tin(IV) chloride. Unfortunately, according to the ^1H n.m.r. and mass spectra and the elemental analysis, the desired compound was contaminated with the thianthrene (4d) (1:1 mixture, 25% total yield) and we were unable to separate the two.

Tellurium tetrachloride failed to give any heterocyclic compounds with the sulphides (6b) and (7b), even in the presence of tin(IV) tetrachloride. Neither could telluride (8) be cyclized with sulphur dichloride. In the latter reaction chlorination of tellurium occurred to produce bis(3,4-dimethoxyphenyl)tellurium dichloride (9).

At this point we realized that another strategy had to be developed for the construction of the remaining dibenzo[1,4]-dichalcogenines (3) and (4). Previous results from our laboratories¹⁶ indicated that it might be possible to prepare dibenzo[1,4]dichalcogenines by the reaction of a 2,2'-dilithiated diarylchalcogenide with a suitable chalcogen electrophile as outlined in Scheme 2. The required 2,2'-dilithiated diaryl-



(12)

Scheme 2.

chalcogenides were prepared from butyl-lithium and the corresponding 2,2'-dibromodiarylchalcogenide which was readily available by regiospecific dibromination of the respective diarylchalcogenides. Thus, compounds (10a, b) and (11a, b) were formed in the yields indicated when diarylchalcogenides (6b, c) and (7b, c), respectively, were treated with two equivalents of bromine in refluxing acetic acid for 1 h.

The lithiations of bromoaromatic compounds (10) and (11) were carried out at -78 °C in tetrahydrofuran. When the addition of 1,1-dichloro-2,5-dihydrotellurophene (12) [a versatile^{16,17} Te(II)-equivalent formed by the loss of butadiene] was complete, the temperature was allowed to rise slowly to ambient. Work-up afforded the phenothiatellurines (3f) and (4f) in 40 and 11% yield, respectively. The phenoselenatellurines (3h) and (4h) were obtained similarly in 18 and 7% yield, respectively.

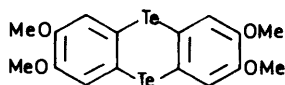
An attempt was made to prepare telluranthrene (13) using the strategy outlined in Scheme 2. However when the telluride (14) was dilithiated and treated with compound (12) as described above, no heterocyclic tellurium compounds were isolated. Instead, the formation of butyl 3,4-dimethoxyphenyl telluride and bis(3,4-dimethoxyphenyl) ditelluride was observed. These

Table 1. Yields, m.p.s, analytical, and ^1H n.m.r. data for 2,3,7,8-tetramethoxydibenzo[1,4]dichalcogenines (3)

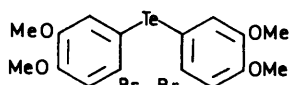
Compound	X	Y	Yield (%)	M.p. (°C)	Analysis (%)				$\delta_{\text{H}}(\text{CDCl}_3)$			
					Calc.		Found		Aromatic		Others	
					C	H	C	H				
(3a)	O	S	59	168	59.99	5.03	60.0	5.0	6.60 (2 H, s), 6.64 (2 H, s)	3.84 (6 H, s), 3.86 (6 H, s)		
(3b)	O	Se	44	156	52.33	4.39	52.55	4.35	6.75 (2 H, s), 6.77 (2 H, s)	3.85 (6 H, s), 3.87 (6 H, s)		
(3c)	O	Te	28	140—141	46.21	3.88	46.45	3.9	6.87 (2 H, s), 6.95 (2 H, s)	3.85 (6 H, s), 3.89 (6 H, s)		
(3e)	S	Se	42	167	50.13	4.21	50.15	4.2	7.11 (2 H, s), 7.31 (2 H, s)	3.87 (12 H, s)		
(3f)	S	Te	40	174	44.49	3.73	44.7	3.7	7.27 (2 H, s), 7.31 (2 H, s)	3.86 (6 H, s), 3.88 (6 H, s)		
(3h)	Se	Te	18	156	40.13	3.37	40.5	3.35	7.36 (2 H, s), 7.37 (2 H, s)	3.86 (6 H, s), 3.88 (6 H, s)		

Table 2. Yields, m.p.s, analytical, and ^1H n.m.r. data for 2,3;7,8-bis(ethylenedioxy)dibenzo[1,4]dichalcogenines (4)

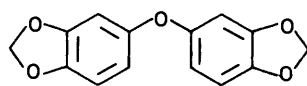
Compound	X	Y	Yield (%)	M.p. (°C)	Analysis (%)				$\delta_{\text{H}}(\text{CDCl}_3)$			
					Calc.		Found		Aromatic		Others	
					C	H	C	H				
(4a)	O	S	80	165—168	60.75	3.82	60.6	3.75	6.58 (2 H, s), 6.62 (2 H, s)	4.21 (8 H, s)		
(4b)	O	Se	62	171—172	52.91	3.33	52.9	3.3	6.69 (2 H, s), 6.80 (2 H, s)	4.21 (8 H, s)		
(4c)	O	Te	27	204—205	46.66	2.94	46.5	2.9	6.81 (2 H, s), 6.98 (2 H, s)	4.21 (8 H, s)		
(4d)	S	S	20	196—197	57.82	3.64	57.7	3.6	7.00 (4 H, s)	4.22 (8 H, s)		
(4e)	S	Se	23	195—196	50.67	3.19	50.85	3.2	7.09 (2 H, s), 7.13 (2 H, s)	4.21 (8 H, s)		
(4f)	S	Te	11	195—196	44.91	2.83	45.05	2.85	7.26 (2 H, s), 7.32 (2 H, s)	4.22 (8 H, s)		
(4g)	Se	Se	2	200—202	45.09	2.84	45.45	2.85	7.21 (4 H, s)	4.21 (8 H, s)		
(4h)	Se	Te	7	162—163	40.47	2.55	40.9	2.6	7.35 (2 H, s), 7.37 (2 H, s)	4.21 (8 H, s)		



(13)



(14)



(15)

materials possibly result from the decomposition (*via* benzyne formation) of the initially formed 2,2'-dilithiated diaryl telluride.

The selenanthrene (4g) was prepared using a modification of the literature procedure for the synthesis of 2,3,7,8-tetramethoxyselenanthrene (3g).^{8b,18} When selenium dioxide was heated at 140 °C for 6 h with two equivalents of benzodioxane and a small amount of water in a flask equipped with a reflux condenser, the selenide (7c) was formed in 16% yield. If another equivalent of selenium dioxide was added at this point, without isolation of the selenide, and heating continued for 30 h, the highly crystalline selenanthrene (4g) could be isolated in low yield (2%) by chromatography and recrystallization from ethanol.

For yields, melting points, analytical, and ^1H n.m.r. data of the new dibenzo[1,4]dichalcogenines (3) and (4), see Table 1 (tetramethoxy series), and Table 2 (bisethylenedioxy series). 2,3;7,8-Bis(methylenedioxy)phenoxathiine (5a) was prepared in 80% yield from the diaryl ether (15) and sulphur dichloride.

Electrochemistry and Cation-radical Salts.—The search for interesting new cation-radical salts is sometimes an elaborate trial and error process, since it is impossible to predict the final crystal structure of the salt.¹⁹ One of the tools for evaluating potential electron donors (and acceptors) is cyclic voltammetry,

(*c.v.*) by which one can estimate the readiness of oxidation and the stability of the resulting species.

Since the cyclic voltammetry experiments are performed under virtually the same conditions as the electrocrystallization, one can assume (with some certainty) that if the cation-radical is not stable enough to survive the time scale of the potential cycle (*i.e.* less than 30 s), it will not survive the week-long electrolysis, although there are exceptions to this assumption (*vide infra*). A stable cation radical is desirable in any case, since a greater degree of variation in the conditions for electrocrystallization is possible. In our case the donors (3)—(5) gave quasi-reversible first half-wave potentials in most cases. The values are given in Table 3 for both acetonitrile and dichloromethane, the most commonly used solvents for electrocrystallization. The one-electron character of these oxidations has previously been proved for compounds (3d)^{3d} and (3g).^{6b} Several features are noteworthy: (a) most donors gave a measurable cathodic peak current (those who did not were measured only by the anodic peak current and the values are given in brackets). With increasing chalcogen substitution, less reversible sweeps were usually obtained. This reflects a higher reactivity of the corresponding cation-radical and might be explained assuming a higher degree of localization of electron deficiency to the chalcogen atom; (b) for a given chalcogen substitution, the first oxidation potential always increased in the same order when ring substituents were introduced (*e.g.* methoxy < methylenedioxy < ethylenedioxy). This probably reflects, in contrast to the other substituents, the ability of the methoxy groups to adopt a coplanar arrangement with the aromatic rings, thereby providing better overlap between the 2*p*-orbitals of oxygen and the π -system of the rings;^{7b} (c) it is a known fact that increasing chalcogen substitution normally leads to a lowering of the oxidation potential²⁰ of a donor. However, in our case, the lowest oxidation potentials were found for the donors with oxygen substitution, *e.g.* in the tetramethoxy series O,Te < O,S \approx O,Se < (S,S \approx S,Te \approx Se,Se \approx Se,Te \approx S,Se). This might be explained assuming a more planar structure for the

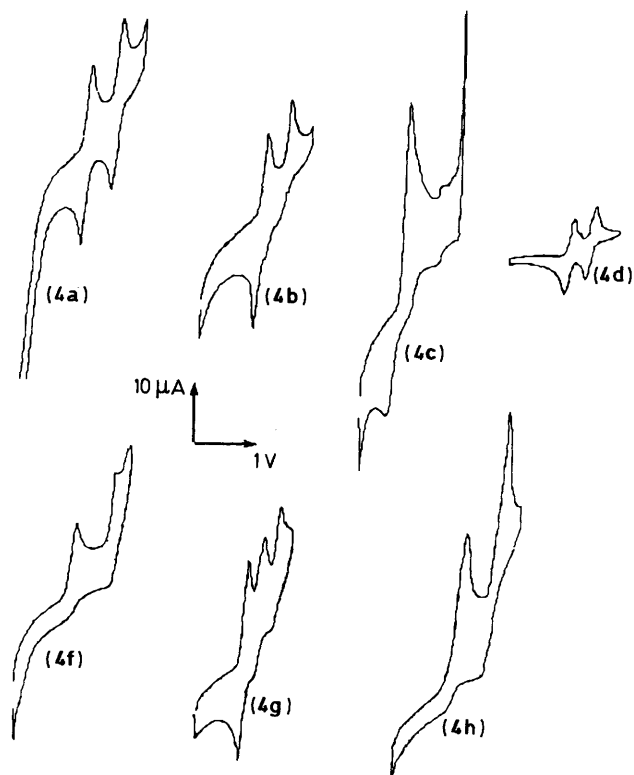


Figure. Some representative cyclic voltammograms. Scan rate 100 mV s^{-1} in acetonitrile containing *ca.* 1% trifluoroacetic anhydride

oxygen heterocycles. Meyers²¹ *et al.* have reported a planar structure for benzo-1,4-dioxine and a decreasing dihedral angle of the central ring with increasing chalcogen substitution.

A more planar conformation of a donor molecule gives a higher degree of delocalization over the aromatic π -systems, thereby facilitating cation radical formation. Note, however, that we are dealing with the ease of formation of a cation radical (*i.e.* a kinetic effect). Hinrichs^{7b} showed that the cation radical of the non-planar tetramethoxythianthrene (3d) is in fact planar in the tri-iodide salt. Complete charge transfer to the acceptor seems to be the condition which must be fulfilled for obtaining solids with a planar donor of this type. Since incomplete charge-transfer (mixed-valence salts) is a requirement for metallic conductivity in the charge-transfer salts,²² these materials could be expected to be poor conductors. By the electrochemical method, though, the anode is effectively working as an acceptor and the cation-radical is formed prior to crystallization.* Some representative voltammograms are shown in the Figure.

For our electrocrystallization work, we decided to start with the new donors (4) and (5a) together with a tetrahedral (ClO_4^-) and an octahedral anion (AsF_6^-). Cation-radical salts were grown under constant current conditions in a divided cell. Most donors gave polycrystalline salts without solvent incorporation. The results are summarized in Table 4.† Donor (5a) failed to give any crystals despite several changes of conditions and solvent.

The low number of cation radical salts synthesized does not

* The electrocrystallization technique does not preclude the unwanted 1:1 stoichiometry. An interesting extension would be to examine the unknown alkoxyated dibenzo-1,4-dioxines. A project for the synthesis of these compounds has recently been started in our laboratories.

† Stoichiometry determined from elemental analysis.

Table 3. Half-wave oxidation potentials for donors (3)–(5). Values are given in volts *vs.* s.c.e. Numbers in brackets refer to values measured only by the anodic peak current (due to irreversibility). For details see the Experimental section

Compound	CH_2Cl_2		MeCN^a	
	$E_{\frac{1}{2}}^1$	$E_{\frac{1}{2}}^2$	$E_{\frac{1}{2}}^1$	$E_{\frac{1}{2}}^2$
(3a)	0.87	1.44	0.77	1.24
(3b)	0.89	1.42	0.79	1.21
(3c)	0.65	(1.45)	(0.70)	(1.65)
(3d)	0.98	1.37	0.86 ^b	1.21 ^b
(3e)	1.02	1.37	0.90 ^c	1.21 ^c
(3f)	0.79	(1.21)	(0.86)	1.50 (1.74)
(3g)	1.06	(1.43)	0.87 ^d	1.19 ^d
(3h)	(0.98)	(1.10, 1.65)	(0.90)	(1.46)
(4a)	1.01	1.52	0.92	1.39
(4b)	1.02	1.42	0.92	(1.30)
(4c)	(0.92)		0.62	1.30
(4d)	1.10	1.51	1.01	1.33
(4e)	1.15	(1.52)	1.04	1.32, 1.63
(4f)	(1.05)	(1.80)	(0.94)	(1.58)
(4g)	1.18	(1.55)	1.06	(1.34, 1.55)
(4h)	(1.08)	(1.55)	(0.95)	(1.42)
(5a)	0.98	1.46	0.85	1.29
(5b)			1.01 ^e	1.29 ^e
(5c)			1.01 ^e	1.42 ^e

^a Containing *ca.* 1% trifluoroacetic anhydride. ^b Ref. (6b) 0.53 and 0.88 V. ^c Ref. (7b) 0.98 and 1.24 V. ^d Ref (6b) 0.90 and 1.24 V. ^e From ref. (7b).

Table 4. Stoichiometry and quality of cation radical salts prepared

Donor	Anion	Solvent	Stoichiometry	Type
(4a)	AsF_6^-	CH_2Cl_2	2:1	PoCr
	ClO_4^-	CH_2Cl_2	3:2:0.1	PoCr
(4c)	AsF_6^-	CH_2Cl_2	4:3	PoCr
(4d)	AsF_6^-	CH_2Cl_2	1:1	SiCr
	ClO_4^-	CH_2Cl_2	3:2	SiCr
(4e)	AsF_6^-	CH_2Cl_2	1:1	PoCr
	ClO_4^-	CH_2Cl_2	1:1	PoCr
(4g)	AsF_6^-	CH_2Cl_2	1:1	PoCr
	ClO_4^-	CH_2Cl_2	1:1	PoCr
	ClO_4^-	MeCN	3:2	PoCr

permit any definite conclusions to be drawn but the results obtained so far demonstrate the difficulty of predicting something as basic as stoichiometry. 'Molecular engineering' of these systems will therefore be very difficult. The appearance of stoichiometries other than 1:1 indicates that salts other than diamagnetic insulating ones might be isolated.

Most donors tend to give polycrystalline salts, apparently due to low solubility of the cation radical in the solvents used. It is also interesting to note that although compound (4c) does not give a reversible half-wave potential in the cyclic voltammery experiment, it does give a characterizable salt when electrolysed. The c.v.-irreversibility is, in this case, probably due to the fast escape (by crystallization) of the donor from solution.

The electronic properties of the salt of compound (4d) with AsF_6^- has been investigated further. The salt is an insulator $\sigma_{RT} \approx 10^{-8} (\Omega \text{ cm})^{-1}$ (4-probe measurement), as expected from the 1:1 stoichiometry. The conductivity is activated with $E_a = 0.5 \text{ eV}$, confirmed by absorption measurements. E.s.r. spectroscopy reveals very few spins: *ca.* $4 \cdot 10^{18} \text{ spin mol}^{-1}$, thus indicating a high degree of spin pairing (dimerization). Detailed studies of the physical measurements on this interesting class of cation-radical salts, and their interpretation, is now under way and will be published elsewhere.

Experimental

All melting points are uncorrected. N.m.r. spectra (δ /p.p.m.) were obtained with a Bruker WP 200 instrument operating at 200 MHz and were recorded for CDCl_3 solutions containing tetramethylsilane as the internal standard. Mass spectra were recorded with an LKB 9000 mass spectrometer. Chloroform was washed several times with water to remove ethanol and was dried over CaCl_2 . Dimethylformamide was dried over MgSO_4 , distilled, and kept over molecular sieves (4 Å). Tetrahydrofuran was distilled from potassium-benzophenone. 3,4-Dimethoxyphenol and 3,4-(methylenedioxy)phenol (sesamol) were commercially available (Aldrich). Selenium tetrachloride,²³ 1,1-dichloro-2,5-dihydro-1,4-benzodioxole,¹⁷ 3,4-dimethoxybromobenzene,²⁴ 5-bromo-1,3-benzodioxole,²⁵ 6-bromo-2,3-dihydro-1,4-benzodioxine,²⁶ and bis(3,4-dimethoxyphenyl) selenide¹⁸ were prepared according to literature methods.

Tetrabutylammonium salts were obtained by mixing aqueous solutions of tetrabutylammonium hydrogen sulphate together with the appropriate sodium or potassium salt of the anion. The crystallized and filtered salts were purified by several recrystallizations from methanol with hot filtration. Final purification was achieved by dissolving the salt in hot dry acetone, adding dry hexane until the solution became opalescent, and then crystallization in a freezer. Cyclic voltammetry was performed under nitrogen in a thermostatted, undivided IBM cell with a platinum-button working electrode and a platinum-wire counter electrode with an s.c.e. reference electrode. The cell was controlled with a PAR 173 galvanostat equipped with a 175 programmer and a 179 coulometer. Scan rate = 100 mV s^{-1} . Substrate concentration was 2 mmol l^{-1} in a 0.15M electrolyte solution in dry dichloromethane or acetonitrile with ca. 1% trifluoroacetic anhydride. Electrocrystallization was performed in dry, argon-purged 0.1M dichloromethane or acetonitrile in tetrabutylammonium tetrafluoroborate in a divided cell at a constant current of 4–6 μA over 9–12 days.

Bis(3,4-dimethoxyphenyl) Ether (6a).—Sodium hydride (80% dispersion in mineral oil; 1.2 g, 40 mmol) was added to a stirred solution of 3,4-dimethoxyphenol (6.0 g, 39 mmol) in dry dimethylformamide (200 ml) under nitrogen (gas evolution). After 30 min, 3,4-dimethoxybromobenzene (8.4 g, 39 mmol) and copper(I) iodide (3.9 g, 20 mmol) were added and the temperature raised to 160 °C. The solution was evaporated after 20 h and the dark residue was dissolved in dichloromethane, washed with water, dried, and submitted to gradient chromatography²⁷ to yield compound (6a) (5.0 g, 44%), m.p. 95 °C (lit.²⁸ 94.5–95 °C); δ_{H} 3.83 (6 H, s), 3.87 (6 H, s), 6.50 (2 H, dd, J 2.7 and 8.7 Hz), 6.63 (2 H, d, J 2.7 Hz), and 6.80 (1 H, d, J 8.7 Hz).

Bis(2,3-dihydro-1,4-benzodioxin-6-yl) Ether (7a).—This was similarly prepared in 60% yield from 6-bromo-2,3-dihydro-1,4-benzodioxine and 2,3-dihydro-1,4-benzodioxin-6-ol. The latter compound was obtained in 71% yield from commercially available (Aldrich) 2,3-dihydro-1,4-benzodioxine-6-carbaldehyde in analogy with a literature procedure²⁹ (Found: C, 67.3; H, 4.95. Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_5$: C, 67.13; H, 4.90%); m.p. 64–65 °C, δ_{H} 4.22 (8 H, s), 6.46–6.53 (4 H, several peaks), and 6.78 (2 H, dd, J 0.7 and 8.3 Hz).

Bis(1,3-benzodioxol-5-yl) Ether (15).—This was prepared in 16% yield from 5-bromo-1,3-benzodioxole and 3,4-(methylenedioxy)phenol using the above procedure [one equiv. of copper(I) iodide was used] (Found: C, 65.2; H, 3.9. Calc. for $\text{C}_{14}\text{H}_{10}\text{O}_5$: C, 65.11; H, 3.87%); m.p. 48–49 °C; δ_{H} 5.94 (4 H, s), 6.42 (2 H, dd, J 2.4 and 8.3 Hz), 6.53 (2 H, d, J 2.4 Hz), and 6.71 (2 H, d, J 8.3 Hz).

Bis(3,4-dimethoxyphenyl) Sulphide (6b).—This was prepared in 83% yield from 3,4-dimethoxybromobenzene and 3,4-dimethoxythiophenol³⁰ using the procedure for compound (6a) [one equiv. of copper(I) iodide was used], m.p. 95–96 °C (lit.³¹ 96–97 °C).

Bis(2,3-dihydro-1,4-benzodioxin-6-yl) Sulphide (7b).—To a stirred solution of 6-bromo-2,3-dihydro-1,4-benzodioxine (32.26 g, 0.15 mol) in dry THF (250 ml), was added butyllithium (1.6M in hexane; 100 ml) at –78 °C over a few minutes. After 40 min at –78 °C bis(benzenesulphinyl) sulphide³² (25.15 g, 80 mmol) was added in portions. After 2 h of additional stirring the solution was allowed to warm to ambient temperature, and water (50 ml) was added. The two phases were separated, the organic phase was concentrated under reduced pressure and combined with the dichloromethane used to wash the aqueous phase. The resulting dichloromethane solution was washed twice with water, dried, and evaporated to give crude material (24.8 g). Gradient chromatography (hexane–toluene–dichloromethane) afforded pure (7b) (17.42 g, 77%) as a pale yellow viscous oil which could be crystallized from ethanol, m.p. 41–42 °C (Found: C, 63.7; H, 4.7. Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_4\text{S}$: C, 63.56; H, 4.67%). δ_{H} 4.22 (8 H, s) and 6.75–6.86 (6 H, several peaks).

Bis(3,4-ethylenedioxyphenyl) Selenide (7c).—2,3-Dihydro-1,4-benzodioxine (7.2 g, 53 mmol), selenium dioxide (2.9 g, 26 mmol) and water (1 ml, 56 mmol) were heated under reflux at 140 °C for 6 h. Unchanged 2,3-dihydro-1,4-benzodioxine was then distilled off under reduced pressure and the residue in CH_2Cl_2 was treated with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_5$. Gradient chromatography of the CH_2Cl_2 -soluble material afforded the almost pure selenide (7c) (1.45 g, 16%) as an oil, δ_{H} 4.21 (8 H, s), 6.76 (2 H, d, J 8.3 Hz), 6.95 (2 H, dd, J 8.3 and 2.0 Hz), and 6.99 (2 H, d, J 2.0 Hz). The material was used for bromination (*vide infra*) without further purification.

2,3;7,8-Bis(ethylenedioxy)phenoxathiine (4a).—Sulphur dichloride (0.36 g, 3.5 mmol) in dry chloroform was added dropwise to a stirred solution of bis(2,3-dihydro-1,4-benzodioxin-6-yl) ether (7a) (1.0 g, 3.5 mmol) in dry chloroform (70 ml) at 0 °C. During the addition, the colour of the reaction mixture gradually changed to dark green. After 1 h at 0 °C and 30 min at ambient temperature the reaction mixture was washed with water, dried, and evaporated. Gradient chromatography afforded compound (4a) (0.89 g).

2,3;7,8-Tetramethoxyphenoxathiine (3a) and 2,3;7,8-bis-(methylenedioxy)phenoxathiine (5a) were similarly prepared from the diaryl ethers (6a) and (15), respectively.

2,3;7,8-Bis(ethylenedioxy)phenoxaselenine (4b).—Selenium tetrachloride (0.76 g, 3.4 mmol) in dry chloroform (10 ml) was added to a stirred solution of bis(2,3-dihydro-1,4-benzodioxin-6-yl) ether (7a) (1.0 g, 3.5 mmol) in dry chloroform (75 ml). After 1.5 h the orange reaction mixture was shaken with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_5$, washed with water, dried, and evaporated. Gradient chromatography of the residue afforded compound (4b) (0.77 g).

2,3;7,8-Tetramethoxyphenoxaselenine (3b) was similarly prepared from the diaryl ether (6a).

2,3;7,8-Tetramethoxyphenothiaselenine (3e) and 2,3;7,8-bis(ethylenedioxy)phenothiaselenine (4e) were prepared from the diaryl sulphides (6b) and (7b), respectively, using the above procedure [reaction time 24 h].

2,3;7,8-Bis(ethylenedioxy)phenoxatellurine (4c).—To a stirred solution of bis(2,3-dihydro-1,4-benzodioxin-6-yl) ether (7a) (1.0 g, 3.5 mmol) in dry chloroform (75 ml) was added

tellurium tetrachloride (0.94 g, 3.5 mmol) and a solution of tin(IV) chloride (0.12 g, 0.46 mmol) in chloroform (10 ml). The reaction mixture was then stirred overnight at reflux temperature. The product was reduced as described above [compound (4b)] with $\text{Na}_2\text{S}_2\text{O}_5$ and compound (4c) (0.39 g) was isolated by gradient chromatography.

2,3,7,8-Tetramethoxyphenoxatellurine (3c) was similarly prepared from the diaryl ether (6a).

2,3,7,8-Bis(ethylenedioxy)thianthrene (4d).—To a stirred solution of bis(2,3-dihydro-1,4-benzodioxin-6-yl) sulphide (7b) (1.6 g, 5.3 mmol) in chloroform (80 ml) was added a mixture of sulphur dichloride (0.53 g, 5.3 mmol) and tin(IV) chloride (0.15 g, 0.58 mmol) in dry chloroform (15 ml). The reaction mixture was heated at reflux for 10 h when an additional amount of sulphur dichloride (0.16 g) was added. After another 2 h of heating, the cooled reaction mixture was shaken with water and passed through a short column of silica gel (CH_2Cl_2). Evaporation and crystallization from ethanol afforded compound (4d) (0.35 g). In an alternative preparation of compound (4d), a mixture of sulphur dichloride (7.71 g, 75 mmol) and tin(IV) chloride (13.3 g, 51 mmol) in chloroform (10 ml) was added to a stirred solution of 2,3-dihydro-1,4-benzodioxine (10.2 g, 75 mmol) in chloroform (50 ml). After having been stirred overnight, the resulting deep blue solution was diluted with tetrahydrofuran (120 ml) and sodium borohydride was added until the solution was decolorized. The crystalline material was filtered and combined with the evaporated filtrate (11.4 g). The dichloromethane-soluble portion was subjected to gradient chromatography to give almost pure (4d) (1.69 g, 13.6%).

Bis(2-bromo-4,5-dimethoxyphenyl) Sulphide (10a).—Bromine (1.06 g, 6.6 mmol) in acetic acid (5 ml) was added to a solution of the bis(4,5-dimethoxyphenyl) sulphide (6b) (1.0 g, 3.3 mmol) in acetic acid (25 ml). After 1 h, the reaction mixture was poured into water (100 ml) and the precipitated material was recrystallized from ethanol to yield compound (10a) (1.32 g, m.p. 145–146 °C (lit.,³³ 147–148 °C).

Bis(2-bromo-4,5-dimethoxyphenyl) Selenide (10b), Bis(2-bromo-4,5-ethylenedioxyphenyl) Sulphide (11a), and Bis(2-bromo-4,5-ethylenedioxyphenyl) Selenide (11b).—These were similarly prepared from the diarylchalcogenides (6c), (7b), and (7c) respectively. In all cases the chalcogenide was refluxed for 1 h with bromine.

(10b). M.p. 117 °C (Found: C, 37.6; H, 3.15. Calc. for $\text{C}_{16}\text{H}_{16}\text{Br}_2\text{O}_4\text{Se}$: C, 37.60; H, 3.16%); δ_{H} 3.72 (6 H, s), 3.88 (6 H, s), 6.81 (2 H, s), and 7.11 (2 H, s).

(11a). M.p. 140–142 °C (Found: C, 41.55; H, 2.65. Calc. for $\text{C}_{16}\text{H}_{12}\text{Br}_2\text{O}_4\text{S}$: C, 41.76; H, 2.63%); δ_{H} 4.24 (8 H, s), 6.70 (2 H, s), and 7.15 (2 H, s).

(11b). M.p. 129–131 °C (Found: C, 38.2; H, 2.4. Calc. for $\text{C}_{16}\text{H}_{12}\text{Br}_2\text{O}_4\text{Se}$: C, 37.90; H, 2.39%); δ_{H} 4.22 (8 H, s), 6.79 (2 H, s), and 7.13 (2 H, s).

2,3,7,8-Tetramethoxyphenothiatellurine (3f).—Bis(2-bromo-4,5-dimethoxyphenyl) sulphide (10a) (0.40 g, 0.86 mmol) in tetrahydrofuran (20 ml) under nitrogen was dilithiated with butyl-lithium (1.6M; 1.1 ml) at –78 °C. After 1 h, 1,1-dichloro-2,5-dihydrothiophene (12) (0.22 g, 0.87 mmol) in tetrahydrofuran (5 ml) was added and the temperature slowly (1 h) raised to ambient. Evaporation of the solvent, followed by extraction with dichloromethane, gradient chromatography and recrystallization from ethanol of the residue afforded compound (3f) (0.20 g).

2,3,7,8-Tetramethoxyphenoselenatellurine (3h), 2,3,7,8-Bis(ethylenedioxy)phenothiatellurine (4f) and 2,3,7,8-Bis(ethyl-

enedioxy)phenoselenatellurine (4h) were similarly prepared from the diaryl chalcogenides (10b), (11a), and (11b), respectively.

2,3,7,8-Bis(ethylenedioxy)selenanthrene (4g).—Selenium dioxide (2.9 g, 26 mmol) was added to the reaction mixture obtained (before work-up) in the preparation of selenide (7c) and heating was continued for a further 30 h. Work-up as described for the preparation of (7c) gave an oil which crystallized from ethanol to yield compound (4g) (0.42 g).

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References

- 1 See for example: Proceedings from ICSM 86; *Synth. Methods.*, 1987, **19**.
- 2 For an excellent review of potential applications of organic solids see; D. O. Cowan and F. M. Wiygul, *Chem. Eng. News*, 1986, 28.
- 3 (a) C. Barry, G. Cauquis, and M. Maurey-Mey, *Bull. Soc. Chim. Fr.*, 1966, 2510; (b) G. Cauquis and M. Maurey-Mey, *ibid.*, 1973, 291; (c) W. Schroth, R. Borsdorf, R. Herzschuh, and J. Seidler, *Z. Chem.*, 1970, **10**, 147; (d) O. Hammerich and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537.
- 4 (a) B. Hetnarski and A. Grabowska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1969, **17**, 333; (b) C. A. Heller, R. A. Zingaro, and E. A. Meyers, *Can. J. Chem.*, 1974, **52**, 3814; (c) D. P. Rainville, R. A. Zingaro, and J. P. Ferraris, *ibid.*, 1980, **58**, 1133; (d) W. Hinrichs, P. Berges, and G. Klar, *Z. Naturforsch., Teil B*, 1986, **41**, 1133.
- 5 G. Cauquis and M. Maurey-Mey, *Bull. Soc. Chim. Fr.*, 1973, 2870.
- 6 (a) K. W. Stender, G. Klar, and B. Knittel, *Z. Naturforsch., Teil B*, 1985, **40**, 774; (b) A. W. Addison, T. H. Li, and L. Weiler, *Can. J. Chem.*, 1977, **55**, 766; (c) R. S. Glass, W. J. Britt, W. N. Miller, and G. S. Wilson, *J. Am. Chem. Soc.*, 1973, **95**, 2375.
- 7 (a) W. Hinrichs and G. Klar, *J. Chem. Res. (S)*, 1982, 336; (b) W. Hinrichs, Dissertation, Hamburg, 1983.
- 8 (a) Compound (3d) was synthesized by a published method; T. Weiss and G. Klar, *Liebigs Ann. Chem.*, 1978, 785; (b) Compound (3g) was synthesized according to T. Weiss, W. Nitsche, F. Böhnke, and G. Klar, *ibid.*, 1973, 1418.
- 9 G. Dougherty and P. D. Hammond, *J. Am. Chem. Soc.*, 1973, **57**, 117.
- 10 C. M. Suter and C. E. Maxwell, *Org. Synth.*, Coll. Vol. II, 1943, 485.
- 11 H. D. K. Drew, *J. Chem. Soc.*, 1926, 223.
- 12 A. Gioaba and O. Maior, *Rev. Roum. Chim.*, 1970, **15**, 1967. For another synthesis of compound (2e) see: N. Petraghani, *Tetrahedron*, 1960, **11**, 15.
- 13 H. D. K. Drew, *J. Chem. Soc.*, 1928, 511.
- 14 N. M. Cullinane, A. G. Rees, and C. A. J. Plummer, *J. Chem. Soc.*, 1939, 151.
- 15 J. Lindley, *Tetrahedron*, 1984, **40**, 1433.
- 16 L. Engman, *J. Heterocycl. Chem.*, 1984, **21**, 413.
- 17 J. Bergman and L. Engman, *J. Am. Chem. Soc.*, 1981, **103**, 2715.
- 18 G. V. Boyd, M. Doughty, and J. Kenyon, *J. Chem. Soc.*, 1949, 2196.
- 19 For an elegant review of the sensitivity of electronic properties to crystal structure of a class of TCNQ-salts with some *N*-heterocyclic donors see J. Kommandeur, *Nouv. J. Chim.*, 1985, **9**, 341.
- 20 J. Hellberg and L. Engman, *Synth. Methods.*, 1987, **19**, 727.
- 21 E. A. Meyers, R. A. Zingaro, D. Rainville, K. J. Irgolic, N. L. M. Dereu, R. Chakraborty, and G. C. Pappalardo, in 'Proceedings of the Fourth Int. Conf. of the Organic Chemistry of Selenium and Tellurium,' eds. F. J. Berry and W. R. McWhinnie, University of Aston in Birmingham, 1983, p. 391–405.
- 22 J. Torrance, *Acc. Chem. Res.*, 1979, **12**, 79.
- 23 H. Rheinbold in Houben-Weyl, 'Methoden der Organischen Chemie,' Band IX, ed. E. Müller, Georg Thieme Verlag, Stuttgart, 1955, p. 1006.
- 24 M. Bruce, *J. Chem. Soc.*, 1959, 2366.
- 25 H. Normant and C. Feugas, *C.R. Seances Acad. Sci.*, 1964, **258**, 2846.
- 26 P. M. Heertjes, A. A. Knape, H. Talsma, and P. Andriess, *J. Chem. Soc.*, 1954, 18.

- 27 P. Baeckström, F. Björkling, H.-E. Högberg, and T. Norin, *Acta Chem. Scand., Ser B*, 1984, **38**, 779.
- 28 E. Matarasso-Tchiroukhine, *C.R. Seances Acad. Sci.*, 1960, **250**, 1867.
- 29 I. M. Godfrey, M. V. Sargent, and J. A. Elix, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1353.
- 30 K. Fries, H. Koch, and H. Stukenbrock, *Ann.*, 1929, **468**, 162.
- 31 E. Matarasso-Tchiroukhine, *Bull. Soc. Chim. Fr.*, 1962, **29**, 851.
- 32 F. De Jong and M. J. Janssen, *J. Org. Chem.*, 1971, **36**, 1645.
- 33 K. von Deuten, W. Hinrichs, T. Weiss, and G. Klar, *J. Chem. Res.*, 1985, (S), 52; (M), 0501.

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