

## Phenanthro[1,10-*cd*:8,9-*c'**d'*]bis[1,2]-dithiole and -diselenole as Novel Electron Donors

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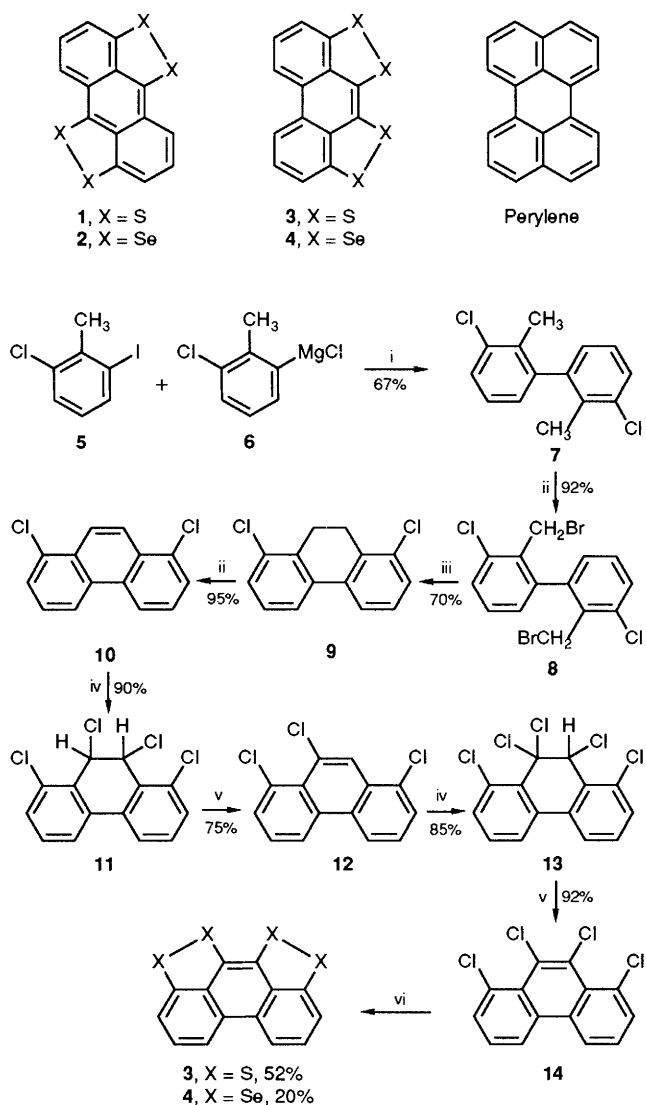
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The preparation of the title compounds is reported along with their formation of electrically highly conductive charge-transfer complexes with the common electron acceptors TCNQ, TCNQF<sub>4</sub>, and DDQ.

Bis(*peri*-dichalcogen) anthracenes, anthra[9,1-*cd*:10,5-*c'**d'*]-bis[1,2]-dithiole **1** and -diselenole **2**, are superior electron donors,<sup>1</sup> which show structural resemblance to perylene, forming radical-cation salts which can be regarded as low-dimensional organic metals.<sup>2</sup> In this connection, bis(*peri*-dichalcogen) phenanthrenes might also be potential heterocycles, which upon two-electron oxidation are isoelectronic

with perylene. However, the close arrangement of the two heterocyclic rings as compared with the *peri*-dichalcogen anthracenes is expected to lead to different solid-state properties. Reported herein is the syntheses and properties of the novel electron donors phenanthro[1,10-*cd*:8,9-*c'**d'*]bis[1,2]-dithiole **3** and -diselenole **4**.

The syntheses of compounds **3** and **4** were carried out

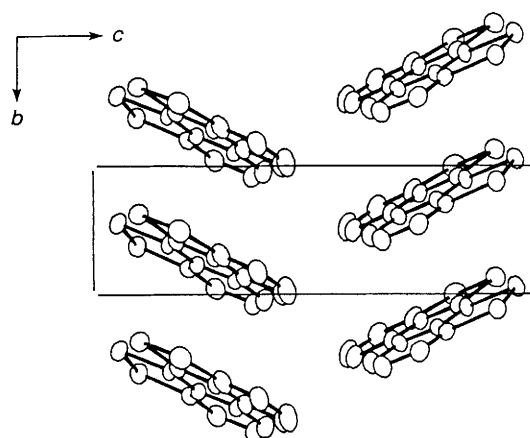


**Scheme 1** Reagents and conditions: i,  $\text{NiCl}_2(\text{PPh}_3)_2$ , tetrahydrofuran (THF), reflux, 2 h; ii, *N*-bromosuccinimide,  $\text{CCl}_4$ , reflux, 2 h; iii, PhLi, THF, room temp., 2 h; iv,  $\text{Cl}_2$ ,  $\text{CCl}_4$ , reflux, 12 h; v, KOH, EtOH, reflux overnight; vi,  $\text{Na}_2\text{X}_2$ , dimethylformamide,  $140^\circ\text{C}$ , 48 h

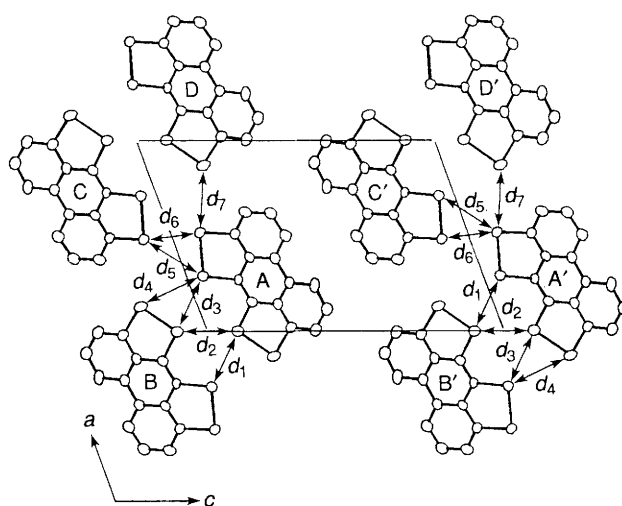
according to Scheme 1. All the reaction steps except the final one proceeded in high yields. However, the last step was troublesome; a conventional substitution reaction<sup>1</sup> of 1,8,9,10-tetrachlorophenanthrene **14** with sodium disulfide in *N,N*-dimethylformamide (DMF) at  $140^\circ\text{C}$  gave **3** in only 5% yield as blackish brown needles [from carbon disulfide; m.p.  $256^\circ\text{C}$  (decomp.)]. Addition of copper(II) chloride however gave an improved yield (52%) of **3**. A similar treatment of **14** with sodium diselenide gave **4** in 20% yield as black needles [from carbon disulfide; m.p.  $273^\circ\text{C}$  (decomp.)]. In this case, however, copper(II) chloride was ineffective in improving the yield.

An X-ray crystallographic analysis<sup>†</sup> showed that molecule **4** is nearly planar with maximum deviation from the least-

<sup>†</sup> Crystal data for **4**:  $\text{C}_{14}\text{H}_6\text{Se}_4$ ,  $M = 490.04$ , monoclinic, space group  $P2_1$ ,  $a = 10.475(2)$ ,  $b = 4.1029(5)$ ,  $c = 15.253(2)$  Å,  $\beta = 109.78(1)^\circ$ ,  $V = 616.9(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.639$  g cm<sup>-3</sup>, graphite-monochromated Cu-K $\alpha$  (1.5418 Å) radiation, crystal dimensions  $0.56 \times 0.04 \times 0.03$  mm,  $\mu(\text{Cu-K}\alpha) = 131.9$  cm<sup>-1</sup>, Rigaku AFC-6C diffractometer, 1148 unique reflections,  $R = 0.040$ ,  $R_w = 0.039$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Fig. 1** Crystal structure of **4** viewed along the *a* axis



**Fig. 2** Crystal structure of **4** viewed along the *b* axis. The symmetry operations are the following: A( $x, y, z$ ), A'( $x, y, 1 + z$ ), B( $-x, 0.5 + y, -z$ ), B'( $-x, -0.5 + y, 1 - z$ ), C( $1 - x, 0.5 + y, -z$ ), C'( $1 - x, -0.5 + y, 1 - z$ ), D( $1 + x, y, z$ ), D'( $1 + x, y, 1 + z$ ). Some distances:  $d_1 = 3.63$ ,  $d_2 = 3.67$ ,  $d_3 = 3.95$ ,  $d_4 = 3.99$ ,  $d_5 = 3.78$ ,  $d_6 = 3.53$ ,  $d_7 = 3.51$  Å.

squares plane of  $0.101$  Å for one of the selenium atoms. The crystal structure consists of stacking columns along the *b* axis, in which the molecules are separated by van der Waals contacts (Fig. 1). The neighbouring stacks are tilted in opposite directions to form a typical herring-bone pattern. In addition, there are strong heteroatomic interactions of facing heterocyclic rings among the columns (Fig. 2). The side-by-side interactions successively continue in a zig-zag through two-dimensional space to achieve a heteroatom sheet in the *ab* plane.

Cyclic voltammetry of **3** and **4** exhibits two reversible one-electron redox waves in each case. The half-wave oxidation potentials of both compounds are almost the same; **3**: 0.65 and 1.02 V; **4**: 0.64 and 1.02 V vs. Ag/AgCl, but considerably higher than those of the structural isomer **2** (0.47 and 0.78 V), reflecting a difference between the HOMO energy levels of both dichalcogen arenes. In addition, the close proximity of the two heterocyclic rings in **3** and **4** as compared with **2** raises the second oxidation potential, so increasing the separation between the first and second redox waves.

Although compound **3** formed no charge-transfer complex with 7,7,8,8-tetracyanoquinodimethane (TCNQ), as indicated by the absence of a charge-transfer band in solution, solid complexes were isolated from chlorobenzene solution with the stronger electron acceptors, 2,3,5,6-tetrafluoro-

**Table 1** Charge-transfer complexes of **3** and **4**

Complex	D:A	Appearance	$T_{\text{decomp.}}/$ $^{\circ}\text{C}$	$10^{-3} h\nu^a/$ $\text{cm}^{-1}$	$\sigma^b/\text{S}$ $\text{cm}^{-1}$
<b>3</b> ·TCNQF <sub>4</sub>	2:1	Black powder	296	2.2, 6.4, 9.3	2.0
<b>3</b> ·DDQ	1:1	Brown powder	228	5.0, 10.5	0.1
<b>4</b> ·TCNQ	1:1	Black powder	276	2.5, 9.5	55.5
<b>4</b> ·TCNQF <sub>4</sub>	2:1	Black fine needles	>300	2.4, 6.2, 8.7	8.0
<b>4</b> ·DDQ	1:1	Brown powder	249	4.5, 9.5	0.07

<sup>a</sup> Measured on KBr disk. <sup>b</sup> Measured on compressed powder samples with a four-probe method at room temp.

7,7,8,8-tetracyanoquinodimethane (TCNQF<sub>4</sub>) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (Table 1). On the other hand, **4** formed complexes with all the acceptors including TCNQ. The complex **4**·TCNQ showed a high electric conductivity of 55.5 S cm<sup>-1</sup> for a compressed powder sample at room temperature. In addition, the TCNQF<sub>4</sub> and DDQ complexes of **3** and **4** are rare examples of conductive materials containing these acceptors.<sup>3,4</sup> The TCNQ as well as TCNQF<sub>4</sub> complexes showed a broad electronic absorption in the infrared region, indicating the presence of segregated columnar structures with incomplete charge transfer, which can be related to their high conductivities.<sup>5</sup> These results

support the potential of *peri*-dichalcogen phenanthrenes **3** and **4** as superior electron donors. Experiments to obtain their radical-cation salts are underway.

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## References

- 1 H. Endres, H. J. Keller, J. Queckborner, J. Veigel and D. Schweitzer, *Mol. Cryst. Liq. Cryst.*, 1982, **86**, 111; H. Endres, H. J. Keller, J. Queckborner, D. Schweitzer and J. Veigel, *Acta Crystallogr. Sect. B*, 1982, **38**, 2855.
- 2 H. J. Keller, D. Nothe, H. Pritzkow, D. Wehe, M. Werner, P. Koch and D. Schweitzer, *Mol. Cryst. Liq. Cryst.*, 1982, **62**, 181.
- 3 G. Saito, H. Kumagai, J. Tanaka, T. Enoki and H. Inokuchi, *Mol. Cryst. Liq. Cryst.*, 1985, **120**, 337.
- 4 J. J. Mayerle and J. B. Torrance, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3170; K. Nakasuji, H. Kubota, T. Kotani, I. Murata, G. Saito, T. Enoki, K. Imaeda, H. Inokuchi, M. Honda, C. Katayama and J. Tanaka, *J. Am. Chem. Soc.*, 1986, **108**, 3460; H.-J. Räder, U. Scherer, P. Wolf and K. Müllen, *Synth. Metals*, 1985, **32**, 15.
- 5 J. B. Torrance, B. A. Scott and F. B. Kaufman, *Solid State Commun.*, 1975, **17**, 1369.