CHEMISTRY LETTERS, pp. 779-782, 1994.

Synthesis and Properties of 1,2:5,6-Bis(ethylenedithio)pyracylene

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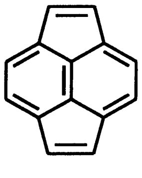
A novel π-donor, 1,2:5,6-bis(ethylenedithio)pyracylene (**2**), was prepared by dithioacetalization of 1,5-pyracenedione with 1,2-ethanedithiol followed by ring expansion on treatment with tellurium tetrachloride. **2** showed two reversible low oxidation potentials by cyclic voltammetry. Single crystal X-ray analysis of **2** revealed unique three dimensional donor networks.

Buckminsterfullerene (C_{60}) has generated an explosion of research activity in various fields of science.[1,2] C_{60} is made up of a number of pyracylene units in the cluster, and pyracylene (**1**) is a prototype antiaromatic molecule with a planar 12-π periphery.[3] Therefore, the reactivity and properties of **1** and its derivatives are of considerable interest. However, the chemistry of **1** has not been explored due to the difficulty of the preparation of **1**.[3] In this paper we wish to report a novel synthesis of 1,2:5,6-bis(ethylenedithio)pyracylene (**2**), which will promise a good donor for making various charge transfer salts. Namely, **2** can be regarded as an isoelectronic structure of bis(ethylenedithio)tetrathiafulvalene (**4**), whose radical cation salts are superconductors[4] with T_c values as high as 11.6 K.[5]



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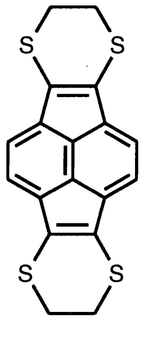

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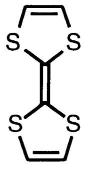

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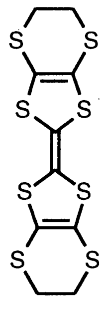

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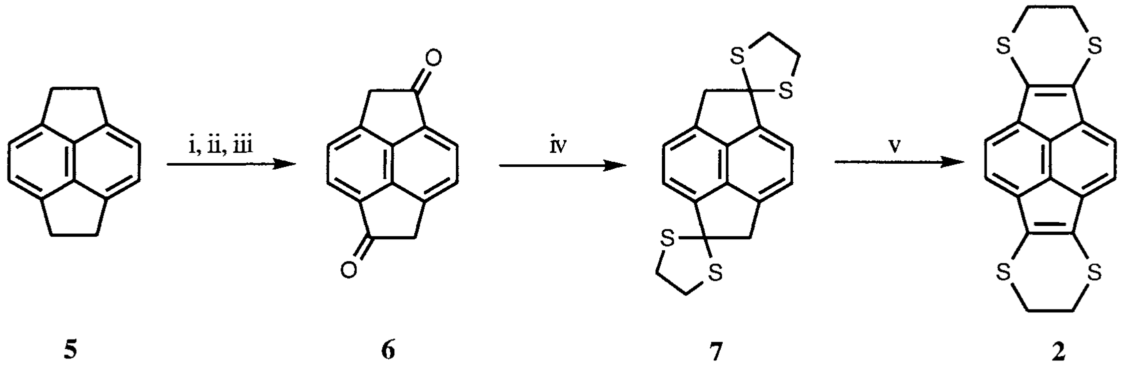
The synthesis of **2** was summarized in Scheme 1. The key step is the conversion of 1,5-pyracenedione[6] into **2** via dithioacetalization with ethanedithiol and the subsequent ring expansion on treatment with tellurium tetrachloride ($TeCl_4$).[7] Although the ring expansion of the dithiolane ring can be done by other reagents such as N-chlorosuccinimide(NCS) or halogens,[8] only the present method is applicable for preparation of **2**. Pyracylene is too reactive to tolerate NCS and related reagents.



Scheme 1. Reagents and conditions: i, Pb_3O_4, AcOH, 60 °C, 12 h, 62%; ii, NaOH, H_2O-EtOH, reflux, 2 h, 84%; iii, CrO_3, AcOH, room temperature, 4 h, 60%; iv, $(CH_2SH)_2$, $AlCl_3$, CH_2Cl_2, room temperature, 6 h, 52%; v, $TeCl_4$, C_6H_6, room temperature, 4 h, 56%.

The ^1H NMR signals of **2** in $CDCl_3$ appear at δ=3.27 and 6.39 ppm, which indicate some paramagnetic ring current, and the ^{13}C NMR signals appear at δ=26.79, 119.97, 125.99, 129.56, 140.36 ppm. The signals were moved to lower fields (^1H NMR 3.92, 8.93 ppm, ^{13}C NMR 26.92, 121.31, 131.40, 138.49, 171.44) when the NMR spectra were measured in D_2SO_4. Thus, **2** was readily oxidized to aromatic 10-π electron system by the action of D_2SO_4. Cyclic voltammetry of **2** exhibits two reversible oxidation waves at potentials comparable to that of tetrathiafulvalene (**3**), and **2** is an even better donor than **4**, illustrating the multistage redox systems of pyracylene (Table 1). The difference between the first and second oxidation potentials of **2** is considerably less than that of **4**, which indicates the decrease of coulombic repulsion.

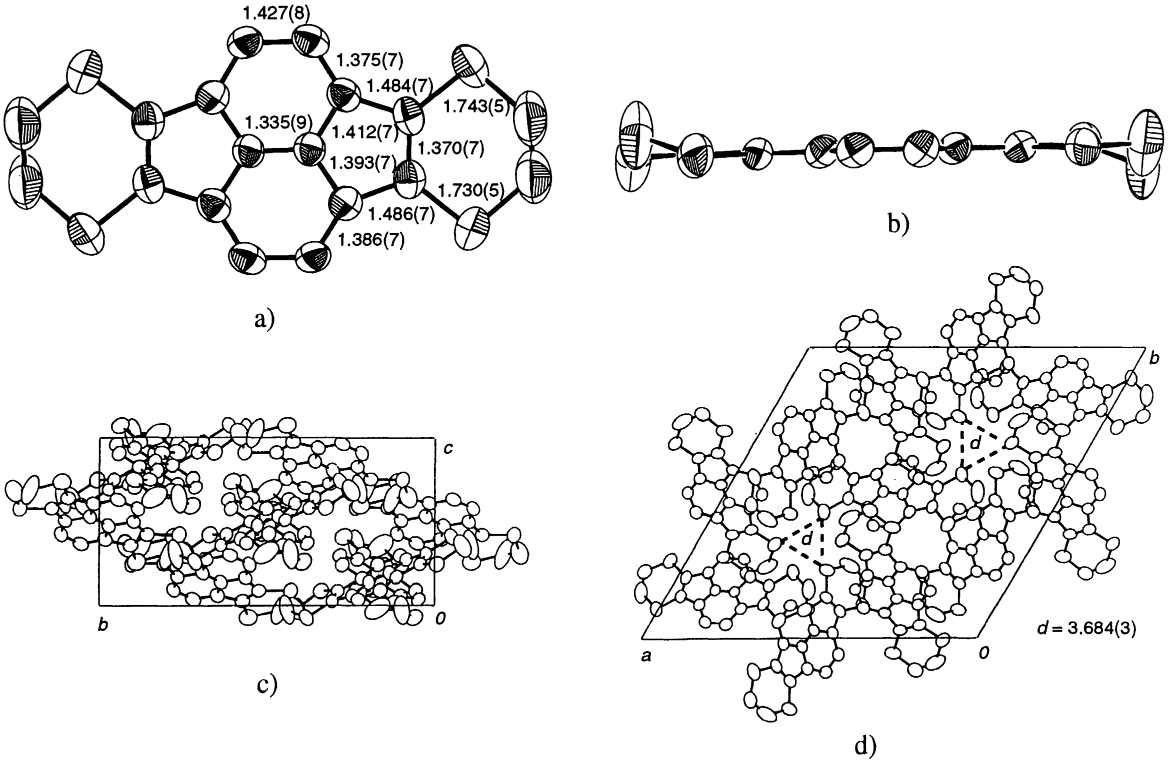
Table 1. Oxidation potentials $E_{1/2}$ (V vs. SCE)

Compound	First $E_{1/2}$	Second $E_{1/2}$	ΔE
2[a]	0.43	0.75	0.32
3[b]	0.35	0.75	0.40
4[b]	0.54	0.96	0.42

a) In PhCN/*n*-Bu_4NClO_4 at room temperature: scan rate, 50 mV s^{-1}: electrode, Pt.
b) Ref. 9. Measured in MeCN.

The X-ray crystal structure of compound **2** has been determined, and bond lengths are given in Fig. 1. Molecule **2** is essentially planar similar to the parent pyracylene[3] and the maximum atomic deviation from the molecular plane is 0.569 Å for one of the carbon atoms of ethylenedithio moieties. The carbon atoms of ethylenedithio moiety are disordered. The S...S contacts (3.684(3) Å) between the molecules are slightly shorter than sum of van der Waals distances (3.7 Å), and the molecular packing of **2** reveals unique three dimensional donor networks. This crystal structure is quite different from that of **4**.[10] Crystal data for **2**: $C_{18}H_{12}S_4$, M = 356.53, rhombohedral (hexagonal axes), space group $R\bar{3}$(h) (#148), a = 21.615(1), c =

9.1388(6) Å, $V = 3545.1(4)$ Å^3, $Z = 9$, $D_c = 1.503$ g cm^{-3}, 824 observed reflections ($I > 3\sigma(I)$), $R = 0.053$, $R_w = 0.056$.



a)

b)

c)

d)

Fig. 1. Crystal structure of 1,2:5,6-bis(ethylenedithio)pyracylene (**2**). (The hydrogen atoms were omitted. The view direction is a) perpendicular and b) parallel to the molecular plane. The molecular packing viewed along c) the *a* axis and d) the *c* axis.)

This new multistage redox donor **2** easily forms the charge transfer salts with various inorganic or organic acceptors. The details about the charge transfer salts will be discussed elsewhere.[11)]

The authors express their sincere thanks for discussion with Professor H. Suzuki of Kyoto University. This work was partially supported by a Grant-in-Aid for Scientific Research No. 05740434 from the Ministry of Education, Science and Culture.

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12) Physical properties of new compounds are as follows:

2: 56%, mp 199-201 °C (from hexane-CH_2Cl_2); ^1H NMR ($CDCl_3$) δ=3.27 (8H, s), 6.39 (4H, s); ^{13}C NMR ($CDCl_3$) δ=26.79, 119.97, 125.99, 129.56, 140.36; UV λ_{max} (MeCN) 499 (ε 1630), 471 (1610), 393 (29400), 373 (28200), 354 (19500), 278 (19300), 231 (46400), 210 nm (38500); UV λ_{max} (H_2SO_4) 834 (ε 18600), 501 (12600), 453 (47700), 430 (34400), 366 (14200), 309 (15800), 237 (21100), 208 nm (23000); IR (KBr) 2916, 1666, 1456, 1408, 1378, 1286, 1162, 1008, 836 cm^{-1}; MS (20 eV) m/z (rel intensity) 356 (M^+; 19), 328 (14), 281 (26), 207 (100); HRMS (70 eV) Found: 355.9824. Calcd for $C_{18}H_{12}S_4$: 355.9821. Found: C, 60.55; H. 3.23%. Calcd for $C_{18}H_{12}S_4$: C, 60.64; H, 3.39%.

5 was prepared according to the reported procedure.[6a)] Compounds **6** and **7** contained small amounts of 1,6-regio isomers. These mixtures were directly used for the next step without separation. The same product was formed in the last step of the synthetic sequence.

6: 60%, mp >250 °C (from hexane-CH_2Cl_2); ^1H NMR ($CDCl_3$) δ=3.94 (4H, s), 7.55 (2H, s), 8.07 (2H, s); IR (KBr) 1780, 1715, 1393, 1340, 1270, 845 cm^{-1}; MS (20 eV) m/z (rel intensity) 208 (M^+, 100) 180 (47), 152 (80). Found C, 80.65; H, 3.99%. Calcd for $C_{14}H_8O_2$: C, 80.76; H, 3.87%.

7: 52%; mp >250 °C (from hexane-CH_2Cl_2); ^1H NMR ($CDCl_3$) δ=3.56-3.74 (8H, m), 4.22 (4H, s), 7.33 (2H, d, J=7.0 Hz), 7.55 (2H, d, J=7.0 Hz); IR (KBr) 2924, 1414, 1274, 1218, 996, 966, 840, 760 cm^{-1}; MS (20 eV) m/z (rel intensity) 360 (M^+, 26), 332 (100), 304 (88), 272 (98), 240 (86). Found: C, 59.71; 4.54%. Calcd for $C_{18}H_{16}S_4$: C, 59.96; H, 4.47%.

(Received January 27, 1994)