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Synthesis and Properties of 1,6-Diselenapyrene (DSPY) and Its Methyl Chalcogeno Derivatives

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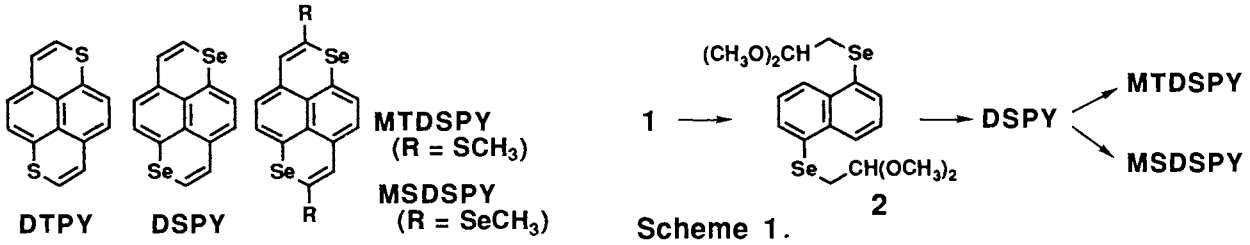
1,6-Diselenapyrene, a first selenium analog of peri-condensed Weitz-type donors based on pyrene, and its methyl chalcogeno derivatives showed the relatively good donor ability. The relationship between the charge transfer energy and the stacking mode are discussed briefly.

Peri-condensed Weitz-type donors, dithiaperylene, dithiapyrene and their derivatives, have been designed and synthesized to explore new organic molecular conductors.[1,2] These donors possess characteristics in their conjugated electronic structure other than tetrathiafulvalene type. Among them, 2,7-bis(methylthio)-1,6-dithiapyrene (MTDTPY) produced metallic conducting charge transfer (CT) complexes with chloranil and bromanil as rare examples of organic molecular metals of non-TTF and non-TCNQ types.[2b,c] Recently, Bechgaard and his co-workers have extended their work to the synthesis of the oxygen analog, 1,6-dioxapyrene.[3] We now report the synthesis and some physical properties of a selenium analog, 1,6-diselenapyrene (DSPY), and its methyl chalcogeno derivatives.



Scheme 1.

As shown in Scheme 1, the final step of the synthesis of DSPY is a similar procedure to that adopted for the DTPY synthesis, because of the benefit of the short synthetic route.[2a] Thus, 1,5-dibromonaphthalene **1** was treated successively with four equivalents of *tert*-butyllithium, two equivalents of selenium powder, and two equivalents of bromoacetaldehyde dimethyl acetal in THF to give 1,5-bis[(2,2-dimethoxyethyl)seleno]naphthalene **2** (59% yield from **1**). Treatment of the acetal (**2**) with a mixture of polyphosphoric acid and phosphoric acid in benzene gave DSPY as orange needles (6-10% yield).[4,5] The final ring closure giving the desired six-membered diselenapyrene skeleton has been supported clearly by the ^{1}H NMR data.

Introduction of methylthio groups was performed by treating DSPY with a large excess of lithium diisopropylamide (LDA) and dimethyldisulfide in THF to give 2,7-bis(methylthio)-1,6-diselenapyrene (MTDSPY) as yellowish orange plates (71% yield). The treatment of DSPY with a large excess of LDA, selenium powder, and iodomethane gave the methylseleno derivative, 2,7-bis(methylseleno)-1,6-diselenapyrene

(MSDSPY) as yellowish brown plates (63% yield). The ^{1}H NMR chemical shifts for DSPY (δ 6.12 - 6.67) appeared at lower field in comparison with those of DTPY (δ 5.54 - 6.22), which indicates the slight decrease of the paramagnetic ring current effect in DSPY. The data of cyclic voltammetry showed that the donors based on DSPY skeleton possess the relatively good donor ability like DTPY.[6] As a preliminary investigation, the preparation of charge transfer (CT) complexes of these new donors with various organic and inorganic acceptors were performed . The stacking mode of the CT complexes can be estimated by the CT transition energies in the solid state measured on a compressed pellet dispersed in KBr.[2c] The CT transition energies obtained are as follows: DSPY-chloranil; 0.82, DSPY-DDQ; 1.24, DSPY-TCNQ; 0.37, MTDSPY-TCNQ; 0.72, MSDSPY-TCNQ; 0.75 eV. DSPY-TCNQ showed the low energy transition, which indicates that this is not the usual mixed stacking type complex and has possibility to have the highly electrical conductivity.[2c] Electrochemical crystallizations were also under investigation by using various inorganic electrolytes. So far the salt of DSPY with I_3 showed the low energy of CT transition at 0.37 eV.

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References

1) K. Bechgaard, *Mol. Cryst. Liq. Cryst.*, **125**, 81 (1986).

2) a) 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.*, **108**, 3460 (1986); b) K. Nakasuji, M. Sasaki, T. Kotani, I. Murata, T. Enoki, K. Imaeda, H. Inokuchi, A. Kawamoto, and J. Tanaka, *ibid.*, **109**, 6970 (1987); c) K. Nakasuji, *Pure Appl. Chem.*, **62**, 477 (1990); d) K. Nakasuji, A. Oda, J. Toyoda, and I. Murata, K. Imaeda, and H. Inokuchi, *J. Chem. Soc., Chem. Commun.*, **1989**, 1553; e) K. Nakasuji, A. Oda, J. Toyoda, and I. Murata, *ibid.*, **1990**, 366.

3) J. B. Christensen, I. Johannsen, and K. Bechgaard, *J. Org. Chem.*, **56**, 7055 (1991).

4) All new compounds described here gave satisfactory elemental analysis and spectroscopic data. Selected physical data: **2**; mp 67-68 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.10 (4H, d, J = 5.4 Hz), 3.32 (12H, s), 4.57 (2H, t, J = 5.4 Hz), 7.44 (2H, dd, J = 7.3 and 8.6 Hz), 7.88 (2H, d, J = 7.3 Hz), 8.42 (2H, d, J = 8.6 Hz); MS *m/z* (relative intensity) 464 (M^+, 11%). DSPY; mp 213-215 °C; ^{1}H NMR (270 MHz, $CDCl_3$ with 0.1% Et_3N) δ 6.12 (2H, d, J = 10.1 Hz), 6.24 (2H, d, J = 10.1 Hz), 6.32 (2H, d, J = 7.6 Hz), 6.67 (2H, d, J = 7.6 Hz); MS *m/z* (relative intensity) 336 (M^+, 49%); UV λ_{max} (THF) 476, 452, 412 nm. MTDSPY; mp 173-175 °C; ^{1}H NMR (270 MHz, $CDCl_3$ with 0.1% Et_3N) δ 2.39 (6H, s), 6.42 (2H, s), 6.46 (2H, d, J = 7.9 Hz), 6.79 (2H, d, J = 7.9 Hz); MS *m/z* (relative intensity) 428 (M^+, 100%). MSDSPY; mp 189-191 °C; ^{1}H NMR (270 MHz, $CDCl_3$ with 0.1% Et_3N) δ 2.29 (6H, s), 6.41 (2H, d, J = 7.8 Hz), 6.63 (2H, s) 6.74 (2H, d, J = 7.8 Hz); MS *m/z* (relative intensity) 522 (M^+, 100%).

5) It was difficult to obtain a large amount of DSPY, since only small scale reactions gave reliable results though the yield was low.

6) The oxidation potentials (E_1^{ox} and E_2^{ox}) for DSPY, MTDSPY, MSDSPY, and DTPY, respectively, are as follow (V vs. SCE in benzonitrile, 0.1 M Bu_4NClO_4, Pt working electrode, 200 mV s^{-1}): E_1^{ox}, 0.37, 0.41, 0.44, 0.37; E_2^{ox}, 0.84, 0.73, 0.73, 0.80.

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