full-matrix least squares. The hydrogen atoms were found on a ΔF map and refined isotropically. The ethyl alcohol molecule is disordered about the origin. The final conventional R factor for the 2962 reflections considered observed with $I > 3\sigma(I)$ was 0.071.

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Supplementary Material Available: Bond lengths and bond angles for **10**, **19**, and **20**, as well as fractional coordinates and anisotropic thermal parameters for each compound (9 pages). Ordering information is given on any current masthead page.

Novel Peri-Condensed Weitz-Type Donors: Synthesis, Physical Properties, and Crystal Structures of 3,10-Dithiaperylene (DTPR), 1,6-Dithiapyrene (DTPY), and Some of Their CT Complexes

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Abstract: 3,10-Dithiaperylene (DTPR, **1a**), 1,6-dithiapyrene (DTPY, **2a**), and their diphenyl derivatives, Ph$_2$DTPR (**1b**) and Ph$_2$DTPY (**2b**), were prepared as examples of molecular design for condensed type donors with two sulfur atoms. The electrochemistry indicates that these heterocycles are actually two-stage redox systems with low oxidation potentials, indicating large enhancement of the donor ability. They may be aptly termed peri-condensed Weitz-type donors. We obtained relatively high conductive (compressed powder samples) CT complexes utilizing these donors and TCNQ-type acceptors. In addition, especially noteworthy is the high conductivity of Ph$_2$DTPR–DDQ$_{0.75}$ (σ = 0.5 S cm^{-1}) despite the fact that the complex consists of neither TTF-type donor nor TCNQ-type acceptor. In addition, these heterocycles gave stable iodine complexes, in accord with the relatively low values of their oxidation potentials. The conductivities of these iodine complexes of compressed powder samples are the same order of magnitude with that of the iodine complex of perylene. The crystal structures of Ph$_2$DTPR, Ph$_2$DTPR–ClO$_4$, DTPY, and (Ph$_2$DTPY)$_2$–I$_3$ show columnar stacks of donor molecules. Significant differences in bond lengths between the neutral and cationic forms are observed.

I. Introduction

Most of the charge-transfer (CT) complexes with high electrical conductivity are formed from the component donor molecules based on 1,3- or 1,2-dichalcogenole skeleton such as tetrathiafulvalene (TTF) or tetrathiotetracene (TTT), respectively.[2] One way to the development of this chemistry and physics is to explore a new class of donors which do not contain such dichalcogenole rings so as to extend the range of molecular conductors.[3,4] Recently, Wudl and co-workers synthesized a new condensed organosulfur π-donor, 3,4:3′,4′-bibenzo[*b*]thiophene (BBT) designed as *an isoelectronic heterocycle with perylene in the neutrtal state.*[4]

Our molecular design strategy for new organic electron donors is the replacement of two of the sp^2 carbon atoms in a polycyclic arene by two polarizable chalogens. This might produce a heterocycle with an increased donor ability, since *the two electron oxidation state, the dication, of the resulting molecule is isoelectronic with the original arene.* We now report examples of such a molecular design for new condensed π-donors and some studies of their CT complexes.

II. Results and Discussion

A. Synthesis and Physical Properties. We have synthesized 3,10-dithiaperylene (DTPR, **1a**) and its 2,11-diphenyl derivative (Ph$_2$DTPR, **1b**) as our initial targets among many possible isomers, selecting perylene as the basic skeleton. Reductive coupling of ketones **3**[5] with TiCl$_4$–Zn[6] in THF gave **4a** (60%) and **4b** (74%), which were converted to **5a** (40%) and **5b** (70%) by photochemical dehydrocyclization with 400-W high pressure Hg lamp. Dehydrogenation of the cyclized products **5** with *N*-chlorosuccinimide[7] in CH$_2$Cl$_2$ at −30 °C afforded the desired products, DTPR (**1a**, 40%) as yellow leaflets and Ph$_2$DTPR (**1b**, 36%) as red needles. Very recently, Bechgaard and his co-workers[8] have reported the crystal structure and solid state properties of the CT complex of 1,6-dithiapyrene (DTPY, **2**) with TCNQ which shows metallic conducting behavior down to 4 K. Since DTPY also falls under the same category of our molecular design, we have studied some of the properties of DTPY and its 3,8-diphenyl derivative (Ph$_2$DTPY, **2b**) independently. According to the Tilak procedure, DTPY (**2a**)[9] and Ph$_2$DTPY (**2b**) were prepared in improved yields (22 and 20% from the disulfides **6**, respectively), which make the

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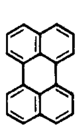

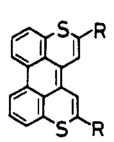

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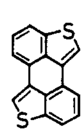
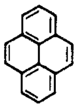
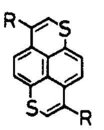
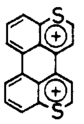


BBT

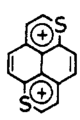




2 a; R = H, b; R = Ph

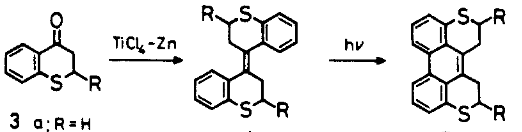


1^{2+}



2^{2+}

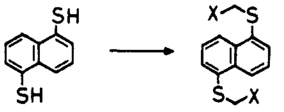
donors more easily accessible for the study of solid-state properties.



3 a; R = H
b; R = Ph

4

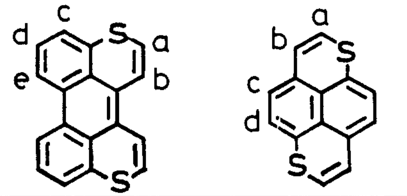
5



6 a; X = CH(OEt)₂
b; X = COPh

The proton NMR spectra of **1** and **2** reveal upfield shifts by more than 1 ppm compared with those of perylene and pyrene, respectively, suggesting the decreased aromatic character in the ground states[10] (Table I). As would be expected, their electrochemistry shows that these heterocycles are actually two-stage redox systems with low oxidation potentials (Table II), indicating large enhancement of the donor ability. These heterocycles may be aptly termed "peri-condensed" Weitz type donors,[11] since these heterocycles produce two new aromatic sextets in one of the canonical formula for the oxidation state as shown in $\mathbf{1}^{2+}$ or $\mathbf{2}^{2+}$. The values of the first half-wave oxidation potential (E^{ox}_1) of **1a** and **2a** are comparable to those of TMTSF (0.42)[12] and TTF (0.34),[13] respectively. Interestingly, these four heterocycles were oxidized to stable dications merely by dissolution in concentrated H_2SO_4 (Table I). This behavior is, to our knowledge, the first reported example for polycyclic condensed systems[14] and is closely related to a feature of two-stage redox systems with relatively low oxidation potentials. These facts eloquently speak to the adequacy of our simple idea to design new donors of condensed π-electron systems.

Table I. ^1H NMR Chemical Shifts of **1a**, **1b**, **2a**, and **2b** (in CS_2–CD_2Cl_2) and Their Dications (in D_2SO_4)



	1a	1b	2a	2b	$1a^{2+}$	$1b^{2+}$	$2a^{2+}$	$2b^{2+}$
a	6.25		5.48	5.37	10.37		10.63	10.37
b	6.71	7.14	5.68		9.59	9.69	9.92	
c	7.04	7.2	6.12	5.97	8.81	8.68	9.40	9.26
d	7.17	7.2	5.95	6.10	8.54	8.44	9.64	9.47
e	7.89	8.0			9.21	9.08		

Table II. Oxidation Potentials[a] of **1a**, **1b**, **2a**, and **2b**

	1a[b]	1b[c]	2a[d]	2b[d]
E_1^{ox}	0.42	0.58	0.36	0.36
E_2^{ox}	0.76	0.96	0.75	0.73

[a] V vs. SCE. [b] In DMF/Et_4NClO_4 at −60 °C. [c] In CH_2Cl_2/n-Bu_4NClO_4 at room temperature. [d] In CH_3CN/Et_4NClO_4 at room temperature.

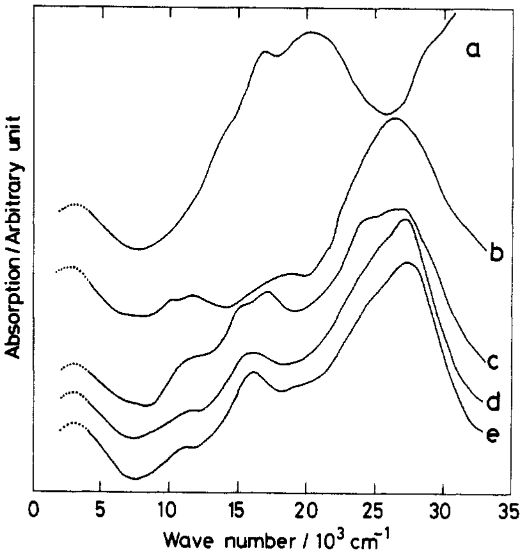


Figure 1. Absorption spectra of (a) Ph_2DTPR–$DDQ_{0.75}$, (b) TTF–TCNQ, (c) DTPY–TCNQ, (d) DTPY–THBTCNQ, and (e) DTPY–DHBTCNQ as powders dispersed in KBr.

We prepared CT complexes utilizing these donors with various acceptors. From the present experiments, two points we believe are worth making. First, relatively high conductivities (compressed powder samples) could be realized by the complexes composed of non-fulvalene-type donors and TCNQ-type acceptors such as DTPY–TCNQ (σ = 4 Scm^{-1}),[15] DTPY–THBTCNQ[16] (σ = 0.4), DTPY-DHBTCNQ[16] (σ = 0.3). Especially noteworthy is the high conductivity of Ph_2DTPR–$DDQ_{0.75}$ (σ = 0.5) despite the fact that the complex consists of neither TTF-type donor nor TCNQ-type acceptor.[18] Such findings are substantiated by the following considerations. The differences between oxidation potential of the donor and reduction potential of the acceptor, $\Delta E^{o,r}$, are +0.02 for Ph_2DTPR–$DDQ_{0.75}$ and +0.18, +0.25, and +0.22 for DTPY–TCNQ, DTPY–THBTCNQ, and DTPY–DHBTCNQ, respectively, which meet the requirement proposed for incomplete CT.[2b,19] Actually, the degree of CT for the three DTPY complexes were estimated to be ca. 0.6 by using the nitrile stretching

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(10) These molecules might be regarded as a kind of ambiguous aromatic species: Haddon, R. C.; Kaplan, M. L.; Marshall, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 1235.

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(16) Abbreviations used: THBTCNQ, tetrahydrobarreleno–TCNQ; DHBTCNQ, dihydrobarreleno–TCNQ. The properties of these two acceptors have been published.[17]

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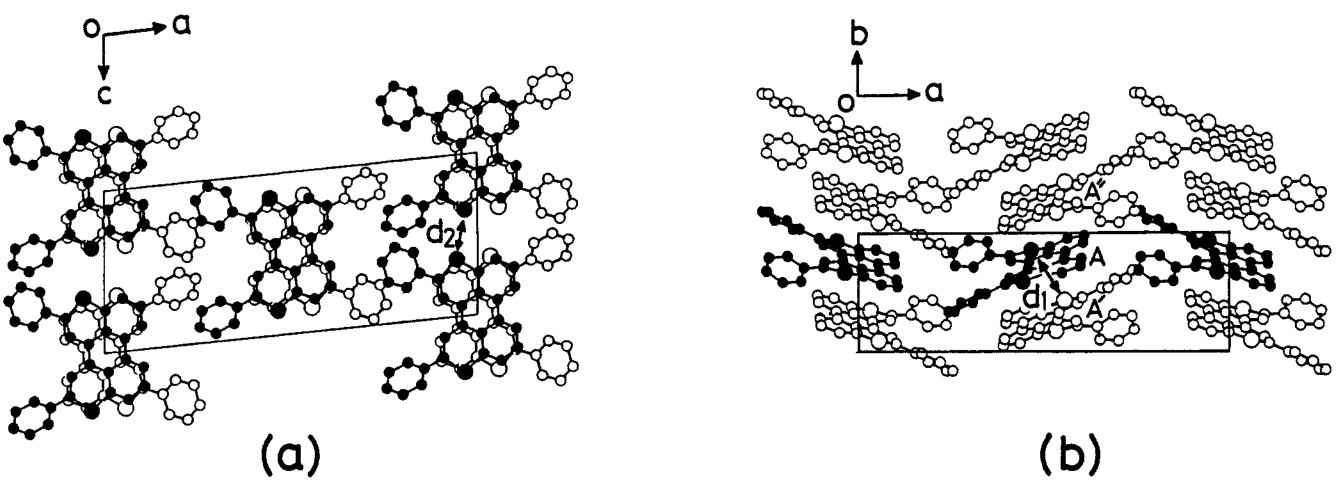

Figure 2. Crystal structures of Ph_2DTPR viewed along (a) the *b* axis and (b) the *c* axis.

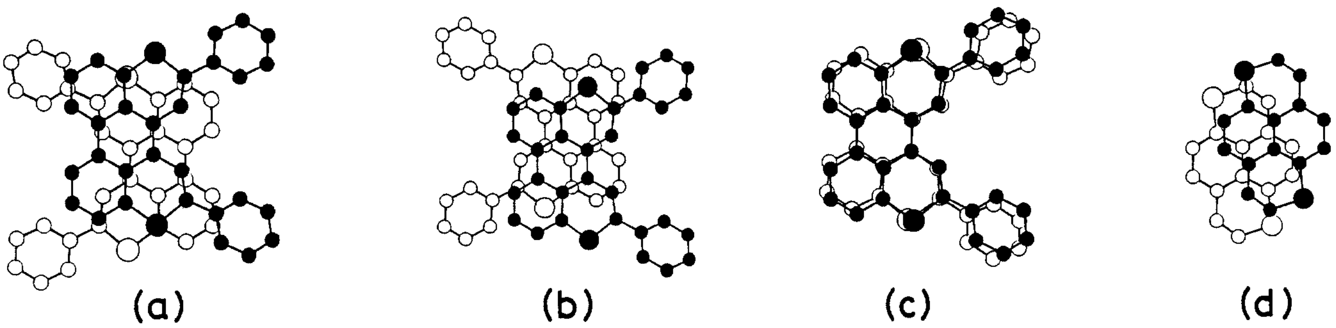
(a) (b) (c) (d)

Figure 3. The modes of the molecular overlap. The view direction is perpendicular to the molecular plane: (a) the neutral Ph_2DTPR; (b) and (c) the cation radicals of PH_2DTPR; (d) the neutral DTPY.

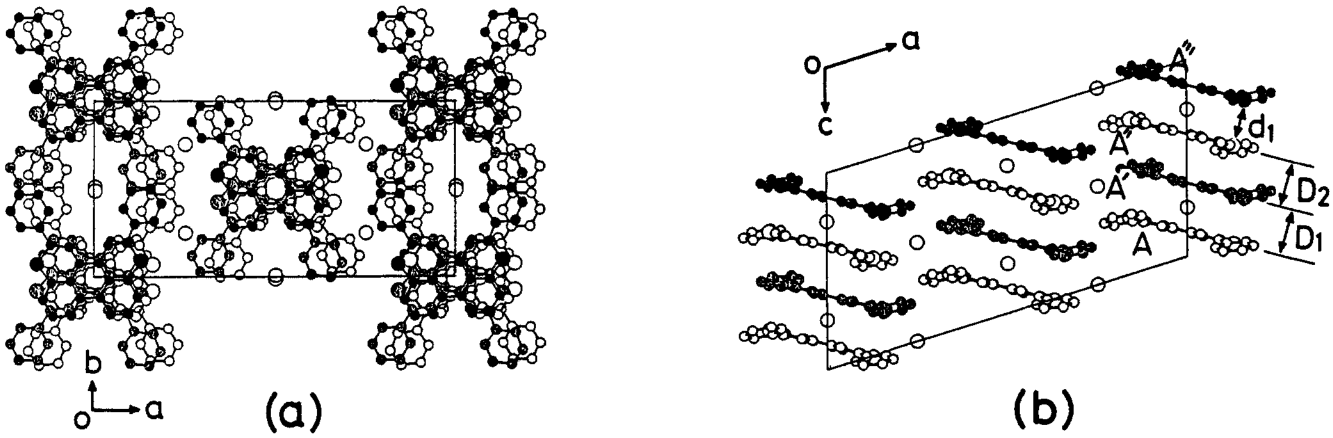

Figure 4. Crystal structures of $Ph_2DTPR-ClO_4$ viewed along (a) the *c* axis and (b) the *b* axis. The symmetry operations are the following: A(*x*, *y*, *z*), A'(2 − *x*, *y*, 1.5 − *z*), A''(*x*, −*y*, −0.5 + *z*), A'''(2 − *x*, −*y*, 1 − *z*).

frequencies (see Experimental Section and ref 8) according to the IR method of Chappell et al.[20] Furthermore, electronic spectrum (Figure 1) for each complex clearly shows a low-energy absorption band near 3000 cm^{-1}, which might be assigned to an intrastack CT transition in a segregated stack.[21] Second, these heterocycles gave stable iodine complexes in accord with the relatively low values of their oxidation potentials. The conductivities of compressed powder samples of $DTPR-I_{2.2}$, $Ph_2DTPR-I_{1.8}$, and $DTPY-I_3$ are 3×10^{-2}, 1×10^{-2}, and 6×10^{-2} S cm^{-1}, respectively, which are the same order of magnitudes with those of compressed powder samples of the iodine complexes of perylene and BBT.[4,22]

B. Crystal Structures. Thorup and his co-workers have reported the crystal structure of DTPY–TCNQ which consists of regular, segregated stacks of the donor and acceptor.[8] We now present here the crystal structures of Ph_2DTPR, $Ph_2DTPR-ClO_4$, DTPY, and $(Ph_2DTPY)_2-I_3$. The crystal data are shown in Table III. All these crystals are found to contain columnar stacks of the donor molecules. In addition, significant differences in bond lengths between the neutral and cationic forms are observed.

(1) Crystal Structures of Ph_2DTPR and $Ph_2DTPR-ClO_4$. The neutral Ph_2DTPR's stack along the *b* axis (Figure 2). The molecule is noncentrosymmetric. The two phenyl groups arrange in the opposite directions alternately in order to reduce their

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Table III. Crystal Data

compd	Ph_2DTPR	$Ph_2DTPR–ClO_4$	DTPY	$(Ph_2DTPY)_2–I_3$
formla	$C_{30}H_{18}S_2$	$C_{30}H_{18}S_2·ClO_4$	$C_{14}H_8S_2$	$C_{52}H_{32}S_4I_3$
form wt	442.6	542.0	240.3	582.9
cryst syst	monoclnc	monoclnc	monoclnc	triclnc
space group	*P*21/*n*	*C*2/*n*	*P*21/*n*	$P\bar{1}$
a, Å	24.652	27.155	12.875	11.568
b, Å	7.796	12.705	4.026	13.202
c, Å	10.742	14.295	9.952	7.236
α, deg				88.78
β, deg	95.74	107.15	93.67	86.91
γ, deg				76.66
Z	4	8	2	2

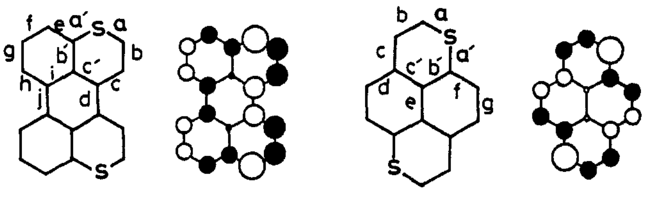

Figure 5. Numbering scheme for bond lengths and highest occupied molecular orbitals of DTPR and DTPY.

intermolecular steric repulsion. The DTPR skeleton is nearly planar, although sulfur atoms deviate 0.27 and −0.13 Å from the least-squares plane of the DTPR. The interplanar distances are 3.57 Å between the DTPR molecules A and A′ and 3.50 Å between A and A″. The shortest intrastack (d_1) and interstack (d_2) S···S contacts are 3.94 and 3.91 Å, respectively. The molecules overlap with a mode of the diagonal shifts in the stack (Figure 3).

The unit cell views of $Ph_2DTPR–ClO_4$ along the *c* and *b* axes are shown in Figure 4. The Ph_2DTPR molecules, which are noncentrosymmetric, stack along the *c* axis. The ClO_4 anions shown as the open circles are disordered. Although the maximum deviation in the DTPR plane is 0.11 Å for the carbon atom, C-7,[23] the sulfur atoms of the cation radicals deviate only 0.01 Å from the least-squares plane. Therefore, the planarity of the DTPR skeleton is higher in the cation radical than in the neutral form. The interplanar distances are 3.43 Å for D_1 and 3.96 Å for D_2. This large difference (0.53 Å) indicates the strong dimerization of the cation radicals. The molecular overlap modes exhibit the lateral shift between diads and the nearly eclipse in a diad, respectively (Figure 3b and c). Apparently, there are no short interstack S···S contacts, while the intrastack contact (d_1) is 3.49 Å (Figure 4). Two phenyl rings in the Ph_2DTPR's are twisted about the C–C bond to the DTPR skeleton by 23° and 27° for the neutral molecule and 24° and 29° for the cation radical. The dihedral angles are similar to those, 26.1° and 26.5°, found in the two forms of the iodine complexes of tetraphenylbithiopyranylidene, Ph_4BTP.[24]

The selected bond lengths are summarized in Table IV. The degree of CT in TTF–TCNQ type complexes can be estimated by a variety of experimental methods which include the correlation between bond length and ionicity of the component molecules. This is associated with the structural feature that the relatively large changes in bond lengths can be expected[25] in the fulvalenoid or quinoid skeletons such as TTF[26] or TCNQ[27] type molecules. The bond length vs. ionicity method is also applied to the CT complexes containing the BTP skeletons as donor.[24,28] The DTPR skeleton contains the BTP moiety as a fulvalenoid type conjugation. The highest occupied molecular orbital of the DTPR skeleton is shown in Figure 5. It is expected that removal of electrons from this orbital will cause lengthening of the bonds b and d and shortening of the bonds a, a′, and c of the bithiapyranylidene moiety in the resulting oxidized state. Interestingly, as shown in Table IV, this is the case. The largest change was observed for the bond d (0.054 Å) of the BTP moiety incorporated in a peri-condensed type skeleton.

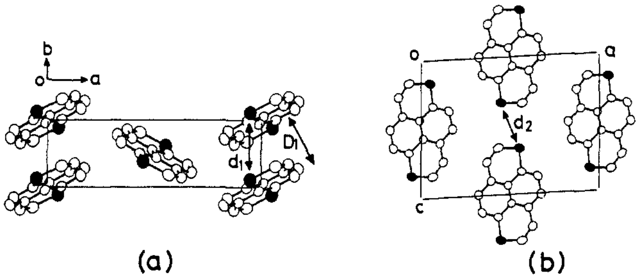

Figure 6. Crystal structures of the neutral DTPY: (a) view along the *c* axis and (b) view along the *b* axis.

(2) Crystal Structures of DTPY and $(Ph_2DTPY)_2–I_3$. DTPY is centrosymmetric, the centroid being at (0, 0, 0.5) and (0.5, 0.5, 0). Figure 6 shows the unit cell views of the neutral DTPY along the *c* and *b* axes. The DTPY's stack along the *b* axis. The molecule is nearly planar with maximum deviation of 0.018 Å for the sulfur atoms. The average interplanar distance (D_1) is 3.71 Å, and the intrastack S···S distance (d_1) is 4.03 Å. There is a shorter interstack S···S distance (d_2), 3.63 Å (Figure 6b). The molecular overlap in the stack exhibits a mode of diagonal shift (Figure 3d).

The stereoviews of the crystal packing of $(Ph_2DTPY)_2–I_3$ are shown in Figure 7. There exist two crystallographically independent Ph_2DTPY molecules, A and B, both of which have a center of symmetry. The DTPY moieties are nearly planar with maximum deviations of 0.08 Å for the sulfur atoms in the molecule A and 0.06 Å for the carbon atoms, C-17 and C-22, in the molecule B.[23] However, the donor molecules as a whole exhibit molecular nonplanarity to a large extent, since the two phenyl groups are twisted relative to the DTPY skeleton in order to reduce the nonbonding repulsion. The dihedral angles between the DTPY and the phenyl groups are 53° in the molecule A and 62° in the molecule B. Despite this large molecular nonplanarity, the planar DTPY skeletons form columnar stacks along the *c* axis with interplanar distance of 3.5 Å. The shortest intrastack S···S distances, d_1 and d_2, are 3.68 and 3.73 Å. Apparently, there are no short interstack S···S contacts, while the relatively short interatomic S···I contacts, d_3 = 3.92 Å, are observed (the expected van der Waals separation is 4.0 Å).

The selected bond lengths of the DTPY skeletons for DTPY, $(Ph_2DTPY)_2–I_3$, and DTPY–TCNQ[8] are summarized in Table V. On going from the neutral to the oxidized state, it is expected that the bond lengths a, a′, and c shorten and the bond length b lengthens, simply considering the node in HOMO of DTPY shown in Figure 5. Interestingly, the changes in these bond lengths for the neutral DTPY and the molecules, A and B, in the I_3 complex are consistent with the fact that the molecules A and B exist in cationic forms. The formal charge of A and B is 0.5 each. In the case of DTPY–TCNQ in which the degree of CT is estimated to be 0.6 from the IR procedure, only the bond b changes reversely.

So far the application of the bond length vs. ionicity method is restricted to the CT complexes containing quinoid or fulvalenoid skeleton. However, the results in this study suggest that the ionicity of the CT complexes containing the peri-condensed Weitz

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(23) See Figure 8 in Experimental Section for the atomic numbering schemes.

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Table IV. Selected Bond Lengths of the DTPR Skeletons[a]

bond	Ph_2DTPR	$Ph_2DTPR-ClO_4$	Δ	bond	Ph_2DTPR	$Ph_2DTPR-ClO_4$	Δ
a	1.743	1.717	−0.026	e	1.385	1.393	+0.008
a′	1.756	1.724	−0.032	f	1.386	1.367	−0.019
b	1.346	1.381	+0.035	g	1.365	1.368	+0.003
b′	1.418	1.427	+0.009	h	1.410	1.397	−0.013
c	1.450	1.419	−0.031	i	1.419	1.413	−0.006
c′	1.447	1.445	−0.002	j	1.453	1.469	+0.016
d	1.395	1.449	+0.054				

[a] Bond lengths were averaged over assumed C_{2v} symmetry.

Table V. Bond Lengths of the DTPY Skeletons[a]

bond	DTPY	$(Ph_2DTPY)_2-I_3$				DTPY-TCNQ[b]	Δ
		A	Δ	B	Δ		
a	1.726	1.713	−0.013	1.726	0.000	1.714	−0.012
a′	1.765	1.731	−0.034	1.749	−0.016	1.737	−0.028
b	1.322	1.354	+0.032	1.350	+0.028	1.307	−0.015
b′	1.436	1.422	−0.014	1.427	−0.009	1.425	−0.011
c	1.474	1.451	−0.023	1.461	−0.013	1.470	−0.004
c′	1.426	1.430	+0.004	1.447	+0.021	1.432	+0.006
d	1.383	1.398	+0.015	1.389	+0.006	1.393	+0.010
e	1.426	1.442	+0.016	1.433	+0.007	1.424	−0.002
f	1.364	1.386	+0.022	1.382	+0.018	1.393	+0.029
g	1.394	1.370	−0.016	1.387	−0.007	1.379	−0.015

[a] Bond lengths were averaged over assumed C_{2h} symmetry. [b] Reference 8.

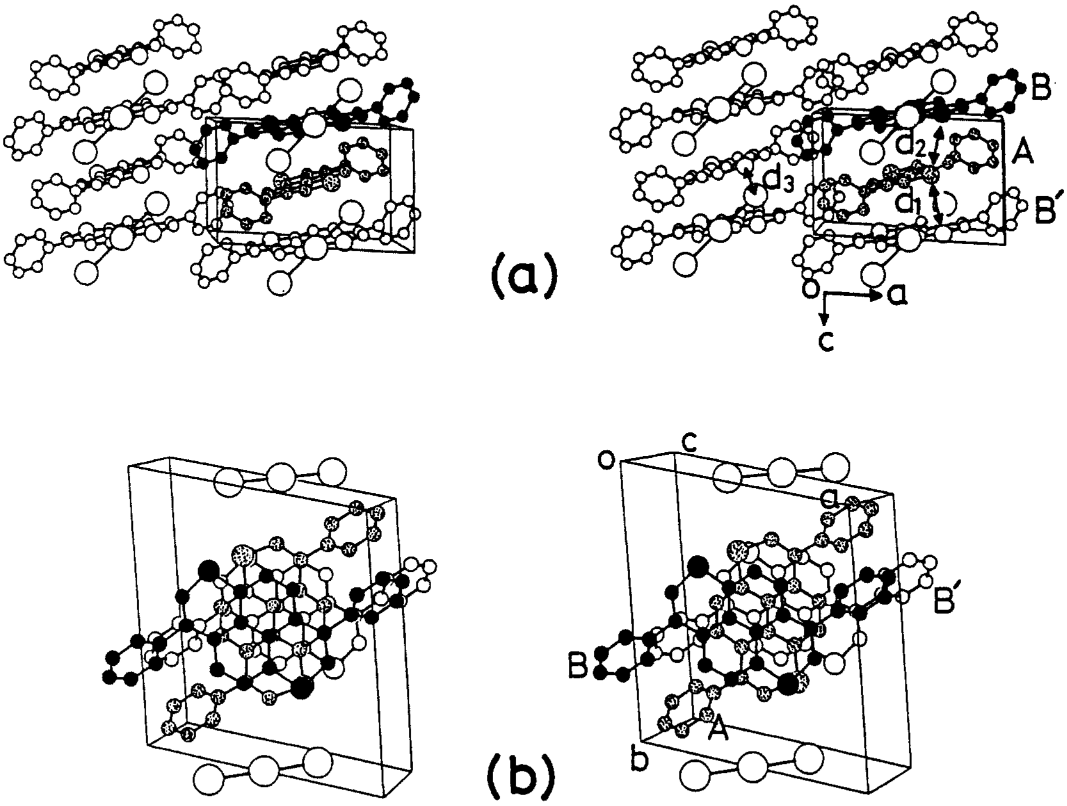

Figure 7. Stereoviews of the crystal packing for $(Ph_2DTPY)_2-I_3$. The view directions are (a) along the *b* axis and (b) normal to the DTPY skeleton of the molecule A.

type heterocycles may be estimated from such a procedure, even if the molecules are peri-condensed types.

The new basic skeletons as donors, which are the relatively strong donors with the properties of two-stage redox system, do form columnar stacks in the crystal structures of both neutral and cation radical states. Currently, a subgoal of our research is the chemical modifications for introduction of the interstack interaction.

III. Experimental Section

General Data. All the melting points are uncorrected. Infrared and electronic spectra were recorded on JASCO DS-402G and Hitachi 340 spectrometers, respectively. Each IR spectrum was calibrated with indene as standard. Proton NMR spectra were measured by using Varian XL-100-15 and JEOL LNM-PMX-60 spectrometers. All chemical shifts are reported in parts per million (δ) relative to internal tetramethylsilane. The cyclic voltammetries were carried out at room temperature under nitrogen by using Yanagimoto P-1100. The electrical conductivities for the compacted pellet were measured with two probe or four probe method.

Preparation of the Donors. Dibenzo[*b*,*b*′]-5,5′,6,6′-tetrahydrobis(4*H*-thiopyran-4-ylidene) (4a). To a mixture of **3a**[7] (3.0 g, 18 mmol) and $TiCl_4$ (3.0 mL, 28 mmol) in THF (60 mL) was added a suspension of zinc powder (3.6 g, 55 mmol) in THF (10 mL) at −70 °C. The reaction mixture was allowed to warm to room temperature and heated to reflux for 30 min. After having been cooled, the mixture was poured into ice–water, hydrolyzed with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$) and concentrated, and the resulting crude residue was recrystallized from ethanol to give **4a** (1.6 g, 60%): colorless needles, mp 160–161 °C; ^1H NMR (CCl_4) δ 2.95 (8 H, s), 7.10 (8 H, s-like); MS, *m/e* (rel intensity) 296 (M^+, 26). Anal. Calcd for $C_{18}H_{16}S_2$: C, 72.93; H, 5.44; S, 21.63. Found: C, 72.85; H, 5.48, S, 21.76.

Dibenzo[*b*,*b*′]-6,6′-diphenyl-5,5′,6,6′-tetrahydrobis(4*H*-thiopyran-4-ylidene) (4b). The title compound was prepared by a similar procedure to that described above (74%): colorless needles (recrystallized from hexane/cyclohexane), mp 222–223 °C dec; ^1H NMR (CS_2/CD_2Cl_2) δ 2.74 (2 H, dd, *J* = 12.6, 11.5 Hz), 3.63 (2 H, dd, *J* = 12.6, 4.1 Hz), 4.38 (2 H, dd, *J* = 11.5, 4.1 Hz), 6.9–7.3 (8 H, m), 7.23 (10 H, br s); MS, *m/e* (rel intensity) 448 (M^+, 91). Anal. Calcd for $C_{30}H_{24}S_2$: C, 80.32; H, 5.39; S, 14.29. Found: C, 80.05; H, 5.39; S, 14.24.

1,2,11,12-Tetrahydro-3,10-dithiaperylene (5a). Nitrogen was bubbled through a solution of **4a** (1.21 g, 4.08 mmol) and iodine (0.97 g) in benzene (2.8 L). Then the solution was irradiated using 400-W high pressure mercury lamp through Pyrex filter for 23 h. The mixture was washed with saturated aqueous $NaHSO_3$ and H_2O. The solvent was removed under reduced pressure, and the resulting crude residue was recrystallized from cyclohexane to give **5a** (0.473 g, 40%): pale yellow leaflets, mp 233–234 °C (sealed capillary); ^1H NMR (CS_2/CD_2Cl_2) δ 3.0–3.2 (4 H, m), 3.3–3.5 (4 H, m), 7.34 (2 H, A of ABX, H-5, 7), 7.38 (2 H, B of ABX, H-4, 9), 8.32 (2 H, X of ABX, H-6, 7), J_{AB} = 7.3 Hz, J_{AX} = 9.1 Hz, J_{BX} = 0.7 Hz; MS, *m/e* (rel intensity) 294 (M^+, 59). Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79; S, 21.78. Found: C, 73.06; H, 4.80; S, 21.50.

2,11-Diphenyl-1,2,11,12-tetrahydro-3,10-dithiaperylene (5b). The title compound was prepared by a similar procedure to that described above (71%): pale yellow needles (recrystallized from cyclohexane), mp 236–237 °C dec; ^1H NMR (CS_2/CD_2Cl_2) δ 3.4–3.8 (4 H, m), 4.3–4.5 (2 H, m), 7.2–7.5 (14 H, m), 8.44 (2 H, X part of ABX); MS, *m/e* (rel intensity) 446 (M^+, 100).

3,10-Dithiaperylene (1a). To a solution of **5a** (551 mg, 1.87 mmol) in CH_2Cl_2 (30 mL) was added *N*-chlorosuccinimide (503 mg, 3.77 mmol) at −30 °C. After stirring at −20 to −10 °C for 1.5 h, the mixture was poured into ice–water, hydrolyzed with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The solvent was removed under reduced pressure, and the resulting crude residue was purified by column chromatography on alumina (eluted with 3:1 hexane/CH_2Cl_2) to give **1a** (217 mg, 40%): yellow leaflets (recrystallized from cyclohexane), mp 228–230 °C (dec, sealed capillary); UV λ_{max} (CH_2Cl_2) 273 (log ϵ 4.02), 297 (4.00), 341 (3.94), 399 (sh) 417 nm (4.32); ^1H NMR (100 MHz, CS_2/CD_2Cl_2) δ 6.25 (2 H, d, *J* = 10.4 Hz, H-2, 11), 6.71 (2 H, d, *J* = 10.4 Hz, H-1, 12), 7.04 (2 H, A of ABX, H-4, 9), 7.17 (2 H, B of ABX, H-5, 8), 7.89 (2 H, X of ABX, H-6, 7), J_{AB} = 7.3, J_{AX} = 8.5, J_{BX} = 1.0 Hz; MS, *m/e* (rel intensity) 290 (M^+, 100). Anal. Calcd for $C_{18}H_{10}S_2$: C, 74.45; H, 3.47. Found: C, 74.19; H, 3.53.

2,11-Diphenyl-3,10-dithiaperylene (1b). To a solution of **5b** (100 mg, 0.224 mmol) in CH_2Cl_2 was added *N*-chlorosuccinimide (63 mg, 0.47 mmol) at −7 to 0 °C, and the mixture was stirred for 1 h. The crude product obtained by a similar procedure for **1a** was purified by column chromatography on silica gel (eluted with 3:1 hexane/benzene) to give **1b** (36 mg, 36%): red needles (recrystallized from cyclohexane), mp 238–239 °C dec; UV λ_{max} (CH_2Cl_2) 274 (log ϵ 4.57), 299 (sh), 373 (3.94), 462 nm (4.43); ^1H NMR (100 MHz, CS_2/CD_2Cl_2) δ 7.14 (2 H, s, H-1, 12), 7.2–7.3 (4 H, AB of ABX), 7.3–7.5 (6 H, m), 7.5–7.7 (4 H, m), 7.99 (2 H, X of ABX, H-6, 7); MS, *m/e* (rel intensity) 442 (M^+, 100). Anal. Calcd for $C_{30}H_{18}S_2$: C, 81.41; H, 4.10; S, 14.49. Found: C, 81.13; H, 4.10; S, 14.64.

1,5-Bis((diethoxyethyl)thio)naphthalene (6a). To a solution of Na (7.23 g, 0.314 gA) and NaI (3.98 g, 0.0266 mol) in ethanol (175 mL) was added over 10 min naphthalene-1,5-dithiol[6] (19.9 g, 0.104 mol) at room temperature. To this solution was added $BrCH_2CH(OEt)_2$ (48.1 g, 0.244 mol) over 5 min, and the reaction mixture was refluxed for 1 h. After cooling, the mixture was treated with H_2O and extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$) and concentrated, and the resulting crude residue was recrystallized from ethanol to give pale yellow microcrystals of **6a** (31.4 g, 71%): mp 61.0–61.5 °C; ^1H NMR ($CDCl_3$) δ 1.17 (12 H, t, *J* = 7.0 Hz), 3.12 (4 H, d, *J* = 5.5 Hz), 3.30–3.82 (8 H, m), 4.64 (2 H, t, *J* = 5.5 Hz), 7.23–7.77 (4 H, m), 8.20–8.48 (2 H); MS, *m/e* (rel intensity) 424 (M^+, 16). Anal. Calcd for $C_{22}H_{32}O_4S_2$: C, 62.23; H, 7.60; S, 15.10. Found: C, 62.18; H 7.58; S, 15.01.

1,5-Bis((benzoylmethyl)thio)naphthalene (6b). To a mixture of naphthalene-1,5-dithiol (5.95 g, 30.9 mmol), K_2CO_3 (20 g), and acetone (150 mL) was added phenacyl bromide (12.5 g, 62.7 mmol) at 0 °C. The mixture was refluxed for 1 h, and the solvent was concentrated under reduced pressure. The resulting crude solid was collected by filtration, washed with H_2O and acetone, and dried under reduced pressure to give **6b** (10.7 g, 81%): faint yellow plates (recrystallized from CH_2Cl_2), mp 174–175 °C; ^1H NMR ($CDCl_3$) δ 4.28 (4 H, s), 7.27–7.97 (14 H, m), 8.30–8.50 (2 H); MS, *m/e* (rel intensity) 428 (M^+, 49); IR 1680 cm^{-1} (KBr). Anal. Calcd for $C_{26}H_{20}O_2S_2(CH_2Cl_2)_{0.2}$: C, 70.63; H, 4.61; S, 14.39; Cl, 3.18. Found: C, 70.35; H, 4.53; S, 14.43; Cl, 2.79.

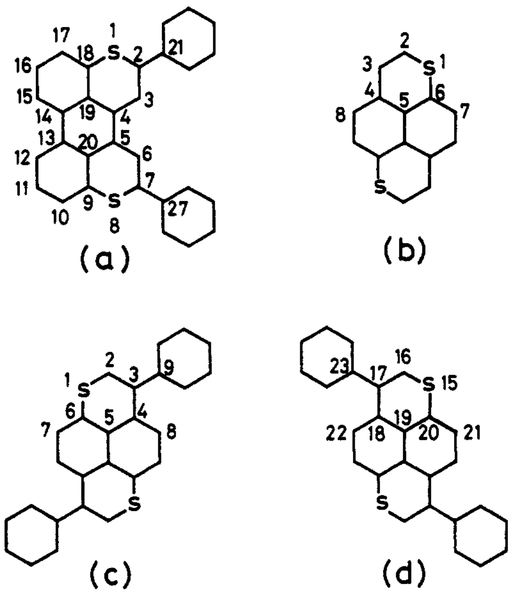

Figure 8. The atomic numbering schemes for (a) Ph_2DTPR, (b) DTPY, (c) the molecule A of $(Ph_2DTPY)_2$–I_3, and (d) the molecule B of $(Ph_2DTPY)_2$–I_3.

1,6-Dithiapyrene (2a). A mixture of P_2O_5 (40 g) and H_3PO_4 (40 mL) was heated in an oil bath to 120 °C. After taking off the oil bath, powdered **6a** (10.0 g, 11.8 mmol) was added over 5 min. The mixture was heated to 125–143 °C for 15 min, poured into a mixture of ice–water and CH_2Cl_2, and neutralized with aqueous NaOH. After filtrating the black precipitates, the filtrate was exhaustively extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting residue was purified by column chromatography on alumina (eluted with benzene) to afford orange needles, which was recrystallized from benzene to give **2a** (1.26 g, 22%): mp 228–229 °C (dec, sealed capillary) (lit.[6] 224–225 °C dec); UV λ_{max} (toluene) 413 (log ϵ 4.09), 454 nm (3.84); ^1H NMR (100 MHz, CS_2/CD_2Cl_2) δ 5.48 (2 H, d, *J* = 10.0 Hz, H-2, 7), 5.68 (2 H, d, *J* = 10.0 Hz, H-3, 8), 5.96 (2 H, d, *J* = 7.7 Hz), 6.12 (2 H, d, *J* = 7.7 Hz); MS, *m/e* (rel intensity) 240 (M^+, 100). Anal. Calcd for $C_{14}H_8S_2$: C, 69.96; H, 3.35; S, 26.68. Found: C, 69.94; H, 3.40; S, 26.38.

3,8-Diphenyl-1,6-dithiapyrene (2b). The title compound was prepared by a similar procedure to that described above (20%): orange plates (recrystallized from cyclohexane), mp 224–225 °C dec; UV λ_{max} (toluene), 417 (log ϵ 4.09), 456 nm (3.92); ^1H NMR (100 MHz, CS_2/CD_2Cl_2) δ 5.37 (2 H, s, H-2, 7), 5.97 (2 H, d, *J* = 7.9 Hz), 6.10 (2 H, d, *J* = 7.9 Hz), 6.9–7.4 (10 H, m); MS, *m/e* 392 (M^+, 100). Anal. Calcd for $C_{26}H_{16}S_2$: C, 79.56; H, 4.11; S, 16.33. Found: C, 79.44; H, 4.12; S, 16.45.

Preparation of CT Complexes. Ph_2DTPR-$DDQ_{0.75}$. To a hot solution of Ph_2DTPR (34 mg, 0.076 mmol) in 1,1,2-trichloroethane (10 mL) was added slowly a hot solution of DDQ (18 mg, 0.078 mmol) in acetonitrile (3 mL). After 2 h, the resulting black precipitates were collected by filtration, washed with CH_2Cl_2, and dried under reduced pressure to give dark violet solids (37 mg, 80%): mp 222–223 °C dec. Anal. Calcd for $C_{30}H_{18}S_2(C_8Cl_2N_2O_2)_{0.75}$: C, 70.55; H, 2.96; N, 3.43. Found: C, 70.58; H, 2.99; N, 3.24.

DTPY-TCNQ. Mixing equal amounts of CH_2Cl_2 solutions of DTPY and TCNQ afforded black microcrystals (52%): mp 196 °C dec. Anal. Calcd for $C_{26}H_{12}S_2N_4$: C, 70.25; H, 2.72; N, 12.60. Found: C, 69.86; H, 2.78; N, 12.59. The degree of CT of 0.59 was deduced from the IR frequency (ω_{CN} = 2201 cm^{-1}).[20]

DTPY-THBTCNQ. To a solution of DTPY (27 mg, 0.11 mmol) in CH_2Cl_2 (15 mL) was added a solution of THBTCNQ (31 mg, 0.11 mmol) in CH_2Cl_2 (5 mL). To this solution was added hexane (5 mL) to give black microcrystals (31%): mp 193 °C dec. Anal. Calcd for $C_{32}H_{20}N_4S_2$: C, 73.26; H, 3.84; N, 10.68. Found: C, 72.37; H, 3.80; N, 10.37. The degree of CT of 0.62 was deduced from the IR frequency (ω_{CN} = 2185 cm^{-1}).[17]

DTPY-DHBTCNQ. This complex was prepared by a similar procedure to that described above (29%): black microcrystals, mp 196 °C dec. Anal. Calcd for $C_{32}H_{18}N_4S_2$: C, 73.54; H, 3.47; N, 10.72. Found: C, 73.28; H, 3.50; N, 10.61. The degree of CT of 0.62 was deduced from the IR frequency (ω_{CN} = 2187 cm^{-1}).[17]

Iodine Complexes of DTPR and Ph$_2$DTPR. These iodine complexes were prepared from a CH$_2$Cl$_2$ solution of the donors and n-Bu$_4$NI$_3$ by electrochemical methods with a current of about 3 μA: DTPR–I$_{2.22}$, black needles, mp 138 °C dec. Anal. Calcd for C$_{18}$H$_{10}$S$_2$I$_{2.22}$: C, 37.79; H, 1.76. Found: C, 37.78; H, 1.79. Ph$_2$DTPR–I$_{1.8}$, dark green needles, mp 162 °C dec. Anal. Calcd for C$_{30}$H$_{18}$S$_2$I$_{1.8}$: C, 53.70; H, 2.70. Found: C, 53.68; H, 2.71.

DTPY–I$_3$. To a solution of DTPY (22 mg, 0.092 mmol) in 1,1,2-trichloroethane (50 mL) was added a solution of I$_2$ (50 mg, 0.20 mmol) in 1,1,2-trichloroethane. The resulting precipitates were collected by filtration and washed with CH$_2$Cl$_2$ to give black microcrystals: mp 104 °C dec. Anal. Calcd for C$_{14}$H$_8$S$_2$I$_3$: C, 27.08; H, 1.30. Found: C, 27.06; H, 1.35.

Crystal Structure Analyses. The single crystals of Ph$_2$DTPR–ClO$_4$ were obtained from dichloromethane solutions of Ph$_2$DTPR and n-Bu$_4$NClO$_4$ with a current of about 3 μA. The single crystals of (Ph$_2$DTPY)$_2$–I$_3$ were prepared by mixing a chlorobenzene solution of Ph$_2$DTPY and iodine. Intensities were collected by using a Rigaku automated 4-circle diffractometer with the Cu Kα radiation monochromatized by graphite. Numbers of the independent reflections are 3317, 3814, 835, and 3489 for Ph$_2$DTPR, Ph$_2$DTPR–ClO$_4$, DTPY, and (Ph$_2$DTPY)$_2$–I$_3$, respectively. The structures were solved by the Monte-Carlo direct method[29] by use of Multan-78 program system[30] and refined by the full-matrix least-squares method. the final R values were 0.042, 0.073, 0.044, and 0.059 for Ph$_2$DTPR, Ph$_2$DTPR–ClO$_4$, DTPY, and (Ph$_2$DTPY)$_2$–I$_3$, respectively. The atomic numbering schemes are shown in Figure 8.

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Supplementary Material Available: Tables of atomic and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Rearrangement of Benzylically Lithiated Methylaryl Alkyl Sulfones[1]

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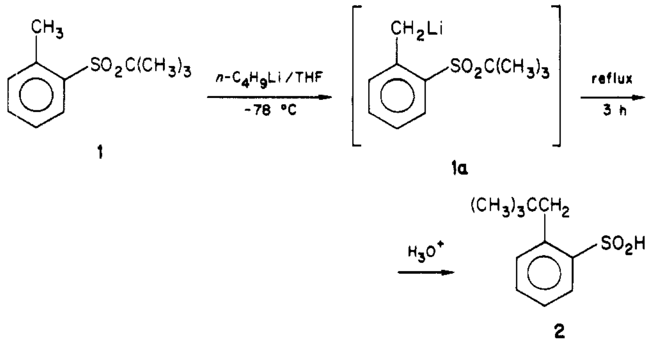
Abstract: Lithiation of appropriate methylaryl alkyl sulfones is followed by migration of the alkyl group from sulfur to the benzylic carbon. Product studies, relative reactivities, and crossover experiments are consistent with a radical–radical anion chain process for this rearrangement.

Directed lithiation[2,3] of aromatic compounds is a phenomenon of broad scope and considerable synthetic utility. Diaryl sulfones,[4] sulfonates,[5,6] and sulfonamides[5,7] are easily metalated, either at an open *ortho* position or at an *ortho* methyl grouping. Each of these three classes of organic sulfur compounds (when metalated at a benzylic site) can undergo rearrangement or coupling condensation, depending upon the starting material.

A previous communication[8] from this laboratory described the rearrangement of o-tolyl *tert*-butyl sulfone (**1**) after metalation by n-butyllithium in THF followed by several hours at reflux. The product o-neopentylbenzenesulfinic acid (**2**), was formed in 75–80% yield, constituting a Truce–Smiles rearrangement[9] with an *alkyl* group as the migrating unit.



Under the influence of amide bases, p-methyl groups can also undergo metalation,[10] as with p-tolyl *tert*-butyl sulfone (**3**). The

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