

Crystal Structures of 2,7-Bis(methylthio)-1,6-dithiapyrene (MTDTPY) and
2,3:7,8-Bis(ethanedithio)-1,6-dithiapyrene (ETDTPY).
Sheet-Like Networks of Dimeric Pairs

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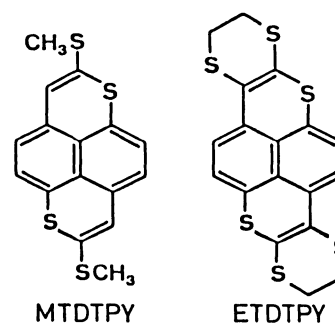
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The crystal structures of methylthio and ethanedithio substituted peri-condensed Weitz type donors, bis(methylthio)dithiapyrene and bis(ethanedithio)dithiapyrene, showed sheet-like networks of dimeric pairs of the donor molecules.

Recent progress to explore organic molecular metals based on tetrathiafulvalene (TTF) type donors¹⁾ offers two important strategies for molecular design of new donors : (1) construction of new multi-stage redox type donors and (2) chemical modifications to introduce interstack interactions. For the molecular design (1), we recently reported new multi-stage redox systems, peri-condensed Weitz type donors.²⁾ For the molecular design (2), just recently we reported the synthesis and properties of two donors, 2,7-bis(methylthio)-1,6-dithiapyrene (MTDTPY) and 2,3:7,8-bis(ethanedithio)-1,6-dithiapyrene (ETDTPY), which involve methylthio and ethanedithio substituents, respectively. An important finding is that MTDTPY produced two metallic CT complexes with tetracyanoquinodimethane and chloranil whose crystal structures contained sheet-like networks of the donor molecules.³⁾ In the present work, the crystal structures of the neutral MTDTPY and ETDTPY were investigated to elucidate the unique nature of these donors in the solid state.

Single crystals of both molecules were obtained by recrystallization from benzene. Crystal data : MTDTPY, C₁₆H₁₂S₄, monoclinic, space group P2₁/c, a = 11.640 (2), b = 13.500 (1), c = 9.451 (1) Å, β = 97.23 (1)°, V = 1473.3 Å³, d_{obsd} = 1.50 g/cm³, d_{calcd} = 1.500 g/cm³, Z = 4. ETDTPY, C₁₈H₁₂S₆, monoclinic space group P2₁/c, a = 15.560 (2), b = 8.720 (1), c = 13.829 (5) Å, β = 116.16 (3)°, V = 1684.1 Å³, d_{obsd} = 1.67 g/cm³, d_{calcd} = 1.660 g/cm³, Z = 4. The final R values of MTDTPY and ETDTPY are 0.062 for 1854 non-zero reflections and 0.081 for 2638 non-zero reflections, respectively.⁴⁾ The bond lengths and numbering schemes are shown in Fig. 1.



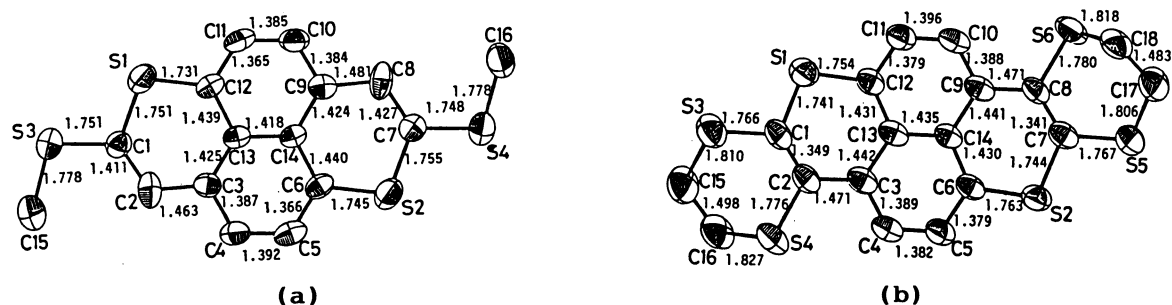


Fig. 1. The bond lengths and numbering schemes of (a) MTDTPY and (b) ETDTPY. Estimated standard deviations are 0.004-0.007 and 0.005-0.010 Å for MTDTPY and ETDTPY, respectively.

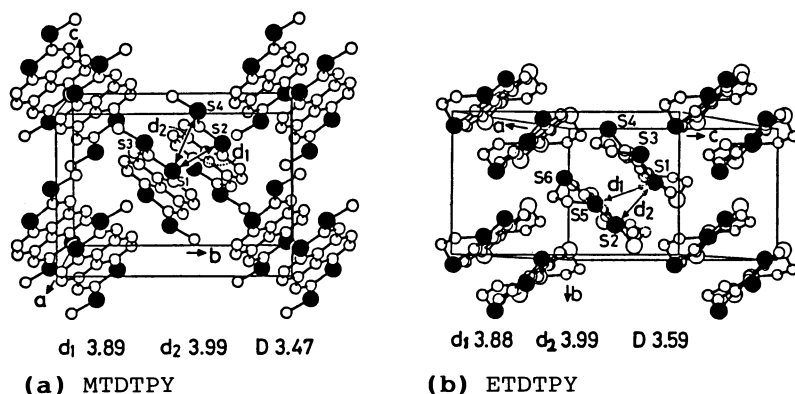


Fig. 2. Crystal structures.

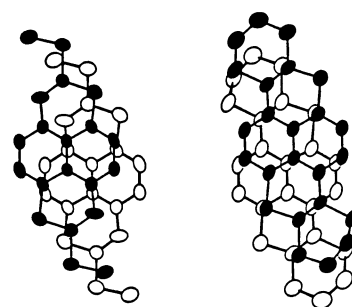


Fig. 3. Overlap modes.

The DTPY skeleton in MTDTPY is nearly planar: the maximum deviation is 0.084 Å for C(7). S(3), C(15), S(4), and C(16) of methylthio groups deviate 0.124, 0.188, 0.268, and 0.168 Å, respectively. The crystal structure (Fig. 2(a)) contains dimeric pairs of MTDTPY molecules. The overlap mode (Fig. 3(a)) is diagonal shift type. The interplanar distance is 3.47 Å. The intrapair S...S distances, $d_1 = 3.89$ and $d_2 = 3.99$ Å, are longer than the sum of van der Waals radii (3.70 Å).⁸⁾ There are found the interpair S...S distances, $d_3 = 3.63$ and $d_4 = 3.59$ slightly shorter than the van der Waals contact. These S...S contacts by d_3 and d_4 lead to one dimensional packings of the pairs along the [100] and the [101] directions, respectively. Therefore, the crystal packing is characterized as sheet-like networks of dimeric pairs of MTDTPY molecules in the (010) plane.

A similar crystal structure was found in ETDTPY (Fig. 2(b)). The planarity of the DTPY skeleton in ETDTPY is slightly decreased: the maximum deviation is 0.195 Å for C(1). The ethanedithio moieties are boat form. The interplanar distance in a pair is 3.59 Å. The overlap mode is shown in Fig. 3(b). The intrapair S...S distances, $d_1 = 3.88$ and $d_2 = 3.99$ Å, are longer than the van der Waals contact. The interpair S...S distances, d_4 : $S(3)(x,y,z) \dots S(5)(-1+x, 1.5-y, -0.5+z) = 3.41$ Å and d_5 : $S(5)(x,y,z) \dots S(3)(1+x, 1.5-y, 0.5+z) = 3.40$ Å, are shorter than the van der Waals contact (Fig. 4(b)). Therefore, the dimeric pairs form sheet-like networks parallel to the (102) plane.

Important structural features of molecular metals containing TTF type donors,

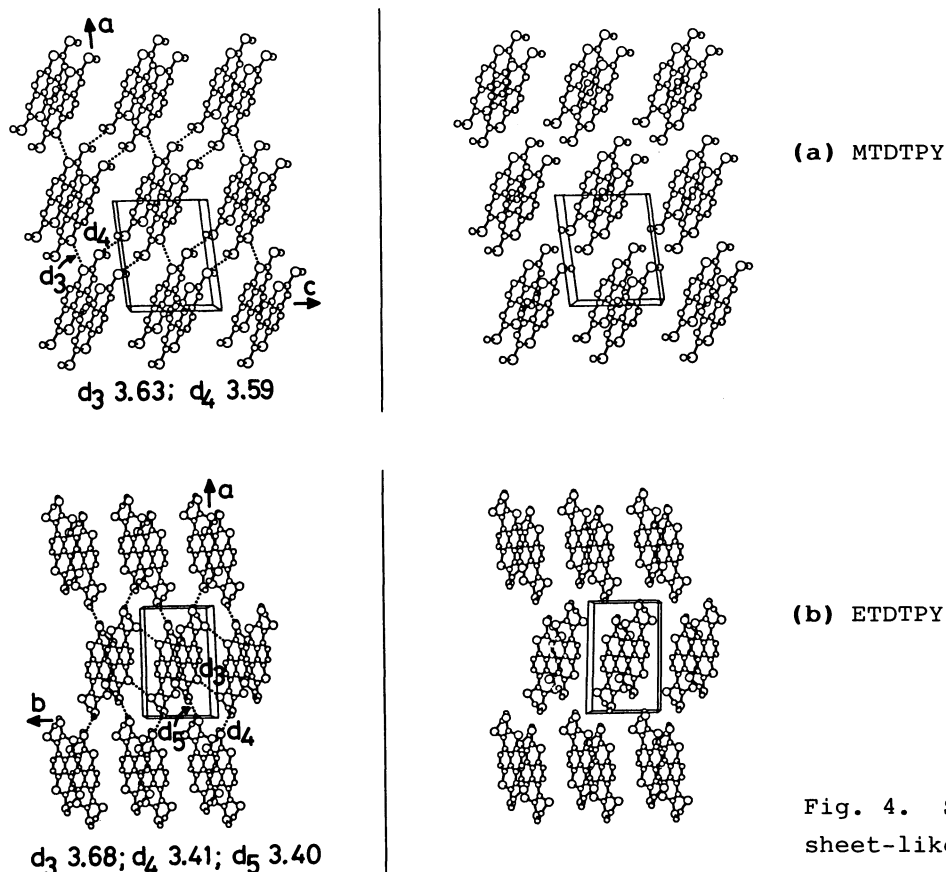


Fig. 4. Stereoviews of sheet-like networks.

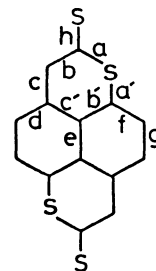
bis(ethanedithio)tetrathiafulvalene (BEDT-TTF) for example, are well characterized by two dimensional sheet-like networks of the donors with extensive intermolecular short S...S contacts.^{1e,8)} Such features are maintained even in the neutral BEDT-TTF molecules.⁹⁾ From the present studies, neutral molecules, MTDTPY and ETDTPY, were found to crystallize with unique molecular packing, though there exist only a lesser extent of the number and strength of S...S contacts. Furthermore, MTDTPY produced molecular metals with sheet-like networks of the donor molecules.³⁾ Although a finding of molecular packings of sheet-like networks is only the starting point to realize multi-dimensionality in electronic structures, for the first time, structural resemblances in crystal structures to BEDT-TTF are realized for the new donors which do not contain TTF type skeletons. This might be attributable to an effect of methylthio (MT)- and ethanedithio (ET)-substituents on DTPY. Present studies suggest a potential importance of MT- and ET-type modification on other known multi-stage redox type donors to explore new molecular solids.

Bond length differences between DTPY skeletons in MTDTPY and its charge transfer complexes with TCNQ and chloranil (CHL)³⁾ are listed in Table 1. As already reported,²⁾ the signs of expected changes of bond lengths are obtained from simple consideration of the nodal properties of HOMO of the DTPY skeleton. Negative and positive signs indicate shortening and lengthening of the bond lengths in the charge transfer complexes, respectively. Although estimation of the ionicity is difficult, the data in Table 1 are consistent with the ionic nature of MTDTPY molecules in charge transfer complexes except bonds a', b, and c.

Table 1. Bond Length Changes of DTPY Skeletons in CT Complexes^{a)}

Bond	$\alpha^b)$	$\beta^c)$	CHL ^{d)}	Sign ^{e)}	Bond	α	β	CHL	Sign
a	-15	-31	-16	-	d	+ 8	+10	+13	+
a'	+ 5	- 6	+ 2	-	e	0	+16	+ 1	+
b	-44	- 3	-60	+	f	+15	+24	+30	+
b'	-10	-21	-18	-	g	- 4	- 9	-14	-
c	-15	+13	-38	-	h	0	- 7	- 1	-
c'	+ 6	0	+ 4	+					

a) Å/10⁻³. b) α -MTDTPY-TCNQ (averaged over assumed C_{2h} molecular symmetry). c) β -MTDTPY-TCNQ. d) MTDTPY-Chloranil. e) expected changes of bond lengths, see text.



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