Syntheses, Physical Properties and X-Ray Structures of Benzocycloheptene-1,4,7-trione and its 6-Phenylthio- and 6,8-Bis(phenylthio) Derivatives.[1] Novel A, A–D and D–A–D Molecular Units Aiming at Organic Conductors

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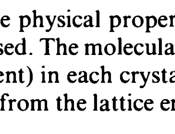
6-Phenylthio- and 6,8-bis(phenylthio)benzocycloheptene-1,4,7-triones **2** and **3** have been synthesized as prototypes for a new type of organic conductor. Their characteristic features of structures and physical properties are discussed in comparison with those of the parent trione **1** and related compounds. The single crystal X-ray analyses showed that a segregated column stacking existed in a crystal of **3** and a crystal of benzene adduct of **2**, but not in **1** and pure **2**. The pendant phenyl groups supported by sulfur atoms in **2** and **3** were found to be facing to the quinone carbonyl and may be responsible to the molecular arrangements in their crystals. Estimations of crystal structures by the crystal molecular packing analysis showed that the segregated column stacking was stable in **3**, but unstable in **1**. The derivatives of **3** seem to be potential candidates for organic conductors of D–A–D type.

It is well known that organic conductors are often made up of various combinations of acceptor (A) and donor (D) molecules. Becker *et al.*[2] proposed another type of organic conductors formed from single molecules such as D–A–D or A–D–A, in which donors and acceptors are chemically bonded *via* bridging atoms. As a prototype of this kind of compound, they synthesized 2,5-dibenzyl-TCNQ and found that it formed a slipped stacking constructed by overlaps of acceptor parts (TCNQ) A • • • A • • • A. As we have been studying the synthesis of tropone-annelated quinones aiming at efficient electron acceptors, we tried to obtain the D–A–D type of compounds with use of benzocycloheptene-1,4,7-trione (**1**) as the acceptor and synthesized 6-phenylthio- and 6,8-bis(phenylthio)-benzocycloheptene-1,4,7-triones **2** and **3**.[1]



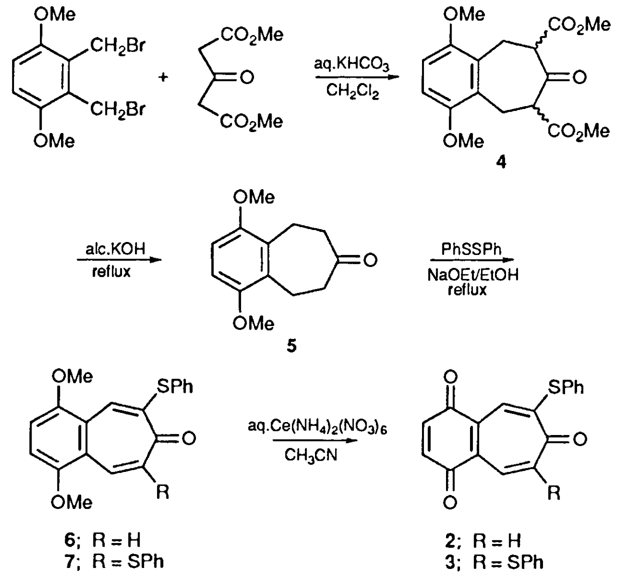
1 $R^1 = R^2 = H$
2 $R^1 = SPh; R^2 = H$
3 $R^1 = R^2 = SPh$

Structure 1

Now, single crystal X-ray analyses on 6-phenylthio- and 6,8-bis(phenylthio)-benzocycloheptene-1,4,7-triones **2** and **3** along with the parent **1** have been carried out and the results are given below. The physical properties of **1**–**3** and related compounds are discussed. The molecular structures, the packing (molecular arrangement) in each crystal, and the stabilities of the packing estimated from the lattice energies of these compounds are also discussed.

Results and Discussion

Synthesis.—Compound **1** was obtained by a method reported previously[3,4] and compounds **2** and **3** were synthesized starting from 1,4-dimethoxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-7-one **5** by a method shown in Scheme 1.



Scheme 1

Physical Data.—IR absorption spectra. The IR bands assigned to the stretching of quinone carbonyl appear at 1660–1665 in nujol and 1668–1676 cm^{-1} in chloroform as usual (9,10-anthraquinone 1670 cm^{-1}) (Table 1). The bands due to tropone appear at 1610–1638 and 1580–1596 cm^{-1},[5] among which the latter moved to lower frequencies (1565–1570 cm^{-1}) when the tropone ring is substituted with two phenylthio groups at C6 and C8. It is interesting to note that in the case of **2**, both bands (*ca.* 1590 and 1570 cm^{-1}) were observed.

^{1}H NMR spectra. The olefinic proton signals of compounds **1**–**3** are shown in Table 2 along with those of similar compounds. Signals due to 2-H and 3-H on the quinone ring appear at higher fields as usual (7.10–6.78 ppm) and the mean values of those due to α- and β-protons on tropone rings fall in a narrow range of 7.52–7.77 ppm when the tropone ring is condensed directly to quinone ring. On the other hand, when a benzene ring is spaced between quinone and tropone rings, this value moved to higher field (7.24 ppm). Unlike bromine substitution on C6,[4] for compounds **2** and **3**, α-phenylthio substitution caused higher field shift of the β-H signal (Δ + 0.2–0.4 ppm).

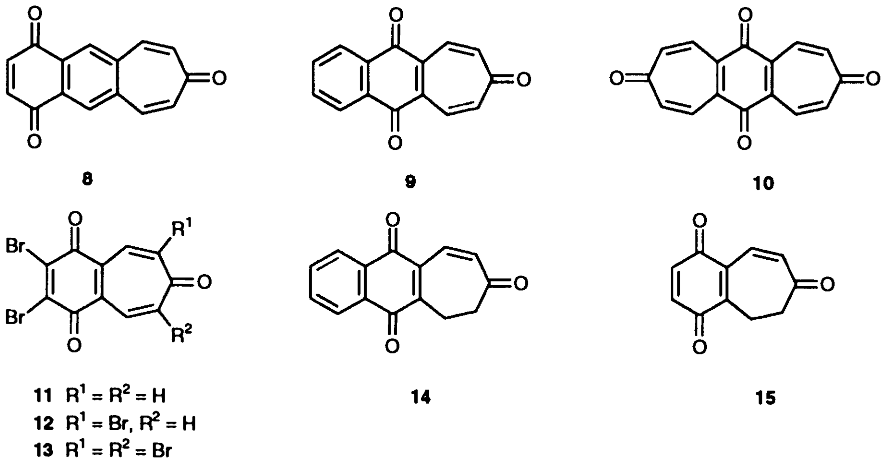
Table 1 Wavenumbers of quinone carbonyl and tropone bands in IR absorption maxima for various compounds (cm^{-1})

Compound	Medium	Quinone carbonyl	Tropone bands		
1	$CHCl_3$	1668 (vs)	1628 (s) 1615 (vs)	1590 (ms)	
2	$CHCl_3$	1670 (s)	1613 (vs)	1593 (s)	1570 (ms)
2	nujol	1660 (s)	1610 (s)	1585 (m)	1570 (s)
3	$CHCl_3$	1668 (m)	1619 (w)		1568 (vs)
3	nujol	1665 (m)	1620 (mw)		1565 (vs)
8	$CHCl_3$	1676 (vs)	1630 (s)	1596 (vs)	
9	$CHCl_3$	1668 (s)	1628 (m)	1590 (vs)	
10	nujol	1660 (s)	1635 (m)	1605 (s); 1580 (s)	
11	nujol	1668 (s)	1638 (s)	1594 (vs)	
12	nujol	1670 (s) 1660 (s)	1633 (ms)	1605 (ms) 1588 (m)	
13	KBr	1673 (s)	1626 (s)	1575 (ms)	
9,10-Anthraquinone	nujol	1670 (s)			
Tropone[a]			1638	1582	

[a] H. J. Dauben and H. J. Ringold, *J. Am. Chem. Soc.*, 1951, **73**, 876.

Table 2 ^1H NMR data for **1–3** and related compounds (ppm in $CDCl_3$; J in Hz)

Compound	$H_A(\alpha)$	$H_B(\beta)$	J_{AB}	$H_A + H_B/2$	$H_{2,3}$	$J_{2,3}$
1	7.25	7.99	12.5	7.64	7.04 (s)	—
2	7.28	8.13 7.65 (s)	12.8	7.71	6.87, 6.95	10.1
3		7.77 (s)	—	—	6.78 (s)	
8	6.93	7.54	12.5	7.24	7.10 (s)	—
9	7.28	8.25	12.6	7.77	—	—
10	7.29	8.10	12.5	7.70	—	—
11	7.14	7.90	11.9	7.52	—	—
12	7.37	8.06 8.94 (s)	12.8	7.72	—	—
14	6.55	7.65	12.8	7.10	—	—
15	6.50	7.42	12.7	6.96	6.86, 6.92	10.2



Structure 2

^{13}C *NMR spectra.* The carbonyl signals of compounds **1–3** along with those of similar compounds are given in Table 3. Quinone carbonyl signals appeared at 183–186 ppm (**1–3**, **8** and **15**) when they did not carry substituent(s) on quinone ring (C2 and/or C3). When two bromine atoms were present at these positions (**11** and **12**),[4] the signals moved to higher field (175–177 ppm) by the similar effect to that of the chlorine atom.[6] Substitution by bromine or phenylthio groups of C6 and/or C8 proton(s) also caused a higher field shift of the tropone carbonyl[6] as shown in cases, **1**: 186 (6-H, 8-H), **2**: 181.3 (6-H, 8-SPh), **3**: 173.1 (6-SPh, 8-SPh), **11**: 185.7 (6-H, 8-H) and **12**: 170.2 (6-H, 8-Br). To the best of the authors' knowledge, the higher field shift by phenylthio substitution has never been noticed.[7]

Electronic spectra. The observed spectra for compounds **1–3**, **8** and **9** in acetonitrile are shown in Fig. 1. The predicted maxima and their corresponding oscillator strengths for these compounds calculated with use of a package program PPP-PC (for NEC PC-9801)[8] are also shown in Fig. 1. In the case of **8**,[9] where a benzene ring is spacing between tropone and quinone

Table 3 ^{13}C NMR data for **1**–**3** and related compounds (ppm in $CDCl_3$)

Compound	Quinone	Tropone	Ketone
1	184.8	186.1	
2	184.8, 185.0	181.3	
3	184.9	173.1	
8	183.6	187.4	
9	182.3	185.6	
11	176.9	185.7	
12	176.1, 175.5	170.2	
14	183.0, 183.5		199.7
15	185.1, 185.6		199.3
1,4-Naphthoquinone	184.7		
Tropone		188.2	

Table 4 Electronic absorption maxima for compounds **2** and **3** in different solvents

Compound	Absorption maxima [λ_{max}/nm (log ε)]		
	Acetonitrile	Dichloromethane	Benzene
2	238 (4.32)	245 (4.33)	
	322 (4.14)	323 (4.15)	
	478 (3.91)	492 (3.95)	498
3	353 (4.32)	358 (4.35)	358
	510 (4.05)	526 (4.08)	530

rings, the calculated frequencies are quite similar to those of the observed ones, but in the cases of tropones directly attached to a quinone ring, the observed frequencies of the absorption maxima for the longest wavelengths were always found in considerably shorter wavelengths than the calculated ones. A negative solvatochromism[10] has been observed for compounds **2** and **3** (Table 4) and to a lesser extent for compound **1** (395 nm in CH_3CN, 400 nm in CH_2Cl_2).

Reduction potentials. The first reduction potential of compound **2** falls on a line representing a linear relationship between E_{LUMO} and E_1^{redox}, which has been reported in a previous paper.[4] A deviation from the line was observed in the plot of E_1^{redox}/E_{LUMO} for compound **3**. This phenomenon will be discussed in a forthcoming paper in comparison with 6,8-dibenzyl- and 6,8-diphenoxy-benzocycloheptene-1,4,7-triones. It is interesting to note that E_1^{redox} is lowered to -0.40 V but E_2^{redox} is raised to -0.73 V for compound **3** when taken in dichloromethane (reversible CV curve) compared with those taken in acetonitrile [$E_1 = -0.30$ V, $E_2 = -0.80$ V (incompletely reversible)].[4] The radical anion of **3** seems to be more stabilized in polar solvents than in non-polar solvents.

Molecular Structure.—In the crystal of **1**, two crystallographically independent molecules, Mol-1 and Mol-2, were present in a unit cell. Compound **2** gave a crystal in which a molecule of benzene was included per each four molecules of **2** [benzene adduct of **2** (**2**: benzene = 4:1)], when recrystallized from benzene. There are two crystallographically independent molecules of **2** (Mol-1 and Mol-2) in a unit cell of the adduct. When recrystallized from a mixture of hexane and dichloromethane, compound **2** gave crystals free from solvent. This crystal consists of only one crystallographically independent molecule and it is referred to Mol-3 of **2**. In the crystal of **3**, there is only one crystallographically independent molecule. The side views of Mol-1 and Mol-2 in compound **1** are shown in Fig. 2. As can be seen from Fig. 2, the quinotropone framework of **1** is approximately planar. But a detailed examination showed that the tropone rings in **1**, as well as those in **2** and **3**, formed slightly shallow boat forms (see Table 5). Similar shallow boat forms have been often observed in the crystals of a number of tropone derivatives.[11–14]

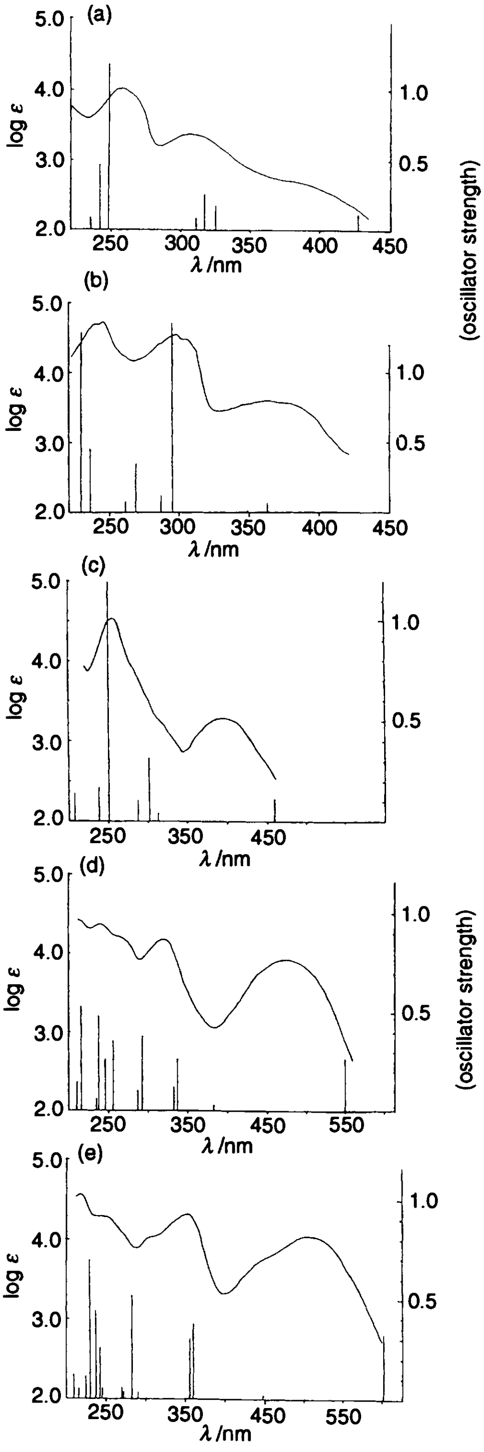


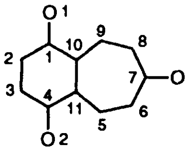
Fig. 1 Electronic spectra in acetonitrile. (a) **9**, (b) **8**, (c) **1**, (d) **2**, (e) **3**. Calculated maxima and their corresponding oscillator strengths are shown with the bar charts. Owing to the lack of the data for phenylthio group, the data for methylthio group were used for PPP-calculations of compounds **2** and **3**. The scales of oscillator strengths are shown on the right hand vertical axes.

The most stable structure of **1** suggested by molecular mechanics [MM2(87)][15] is nearly planar. On the other hand the molecular orbital (MO) calculations on **1** using the MNDO method (MOPAC Ver. 6)[16] resulted in two different structures, one nearly planar and the other slightly non-planar one. The latter ($\Delta H^f = -99.7$ kJ mol^{-1}) was obtained when the calculations were started from the observed structure of Mol-1

Table 5 Deviations of atoms from the least-squares plane of C(5)–C(6)–C(8)–C(9) (× 10^3 Å) and inter plane angles (°) for **1**, **2** and **3**

	Deviations					
	1		**2**			**3**
Atoms[a]	Mol-1	Mol-2	Mol-1	Mol-2	Mol-3	
O(3)	288(6)	−40(6)	−112(8)	347(8)	−191(4)	147(8)
C(5)	−7(4)	3(3)	17(5)	5(5)	−8(3)	0(4)
C(6)	10(4)	0(3)	−21(5)	−6(5)	9(2)	0(3)
C(7)	118(4)	−16(4)	−45(5)	154(6)	−78(3)	59(5)
C(8)	−8(4)	0(4)	19(5)	5(5)	−15(3)	—
C(9)	6(4)	−4(4)	−16(5)	−4(5)	12(3)	—
C(10)	99(5)	−10(5)	−59(6)	111(7)	−19(4)	—
C(11)	85(8)	−2(5)	−15(6)	147(7)	−33(4)	43(5)
	Inter plane angle					
(5–6–8–9)–(6–7–8)[b]	9.6(3)	1.3(4)	3.8(4)	12.8(5)	6.1(3)	4.9(4)
(5–6–8–9)–(5–9–10–11)	4.6(2)	0.3(2)	2.1(3)	6.4(3)	1.4(2)	2.2(3)
(5–9–10–11)–(1–4–10–11)	0.6(2)	0.9(2)	2.0(1)	3.0(2)	0.8(2)	0.4(3)
(1–4–10–11)–(1–2–3–4)	3.9(2)	0.8(3)	6.9(3)	1.7(3)	5.3(2)	0.0(4)

[a] For the numbering of atoms, see Structure 4. [b] (5–6–8–9)–(6–7–8) means the angle between C(5)–C(6)–C(8)–C(9) and C(6)–C(7)–C(8) planes.



Structure 4

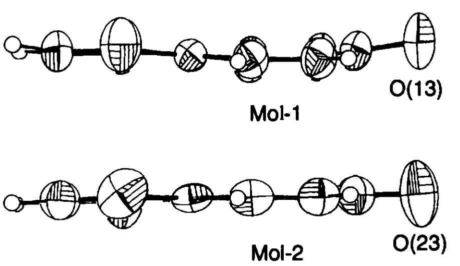
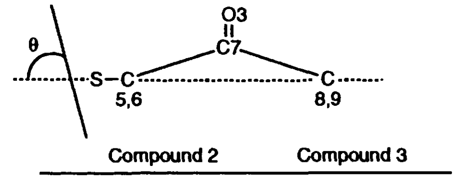


Fig. 2 Side views of the two crystallographically independent molecules (Mol-1 and Mol-2) of compound **1**



	Mol-1	Mol-2	Mol-3	
θ/°	62.8(2)	90.1(2)	71.1(1)	97.1(2)

Fig. 3 Definition of the angle (θ) between the mean plane of the phenyl group and that of C5–C6–C8–C9 moiety and the values of θ for Mol-1, Mol-2, Mol-3 of **2** and for the molecule of **3**

as the initial one for the MO calculation, while the former (ΔH^f = −98.3 kJ mol^{-1}) was derived when the calculations were started from the observed structure of Mol-2 as the initial one. This result suggests that a slightly non-planar structure could be the real structure of **1** in the gaseous state or in non-polar solvent. Therefore, the observed slight non-planarity of the tropone ring could not be attributed merely to intermolecular compression in the crystal.

The phenyl groups in **2** and **3** were found to be facing towards the quinone carbonyls. The same spatial arrangement, which had been predicted by ^1H NMR spectrum, was also found for 1,4-dimethoxy-6,8-bis(phenylthio)-7*H*-benzocyclohepten-7-one.[1] In the thiocolchicine (5,6-dihydro-6-hydroxymethyl-1,2,3-trimethoxy-9-methylthio-8*H*-cyclohepta[*a*]naphthalen-8-one),[17] the thiomethyl group attached to the carbon atom adjacent to the tropone carbonyl has the same orientation as the thiophenyl group in **3**. The angle between the mean plane of the phenyl group and that of C5–C6–C8–C9 moiety of a molecule in each crystal of **2** and **3** is given in Fig. 3. An averaged value of intramolecular O3 ··· S distance and some mean bond angles for **2** and **3** are shown in Fig. 4. The O3 ··· S distance of 2.68 Å is considerably shorter than the sum of the corresponding van der Waals radii (3.32 Å). It is noted that the angle of C7–C6–S (108.7°) is much smaller than that of C7–C6–CH_3 in 6,8-dimethyl-7*H*-benzocyclohepten-7-one (113.5°)[13] and the angle of C6–C7–O3 in each of **2** (Mol-1, Mol-2 and Mol-3) is a little smaller than that of C8–C7–O3 in spite of the short O3 ··· S contact. This fact suggests the presence of an attracting interaction between sulfur atoms and oxygen atoms of the tropone carbonyl. The small valence angle of S (*ca.* 104°) is also interesting.

The electronic charge distributions in **1**, benzoquinone and tropone calculated by the MNDO method are shown in Fig. 5. Those in the quinotropone frameworks of **2** and **3** were found to be approximately identical to that of **1**. The comparison of the charge distributions of these compounds shows that the tropone-annellation to benzoquinone caused a slight change in the charge distributions in the tropone part and left those in the enedione moiety of the quinone part (O1–C1–C2–C3–C4–O2) almost unchanged. Fig. 5(*c*) indicates a tendency that in the molecule of **1**, a small amount of electrons (*ca.* 0.06 e) is transferred from the enedione moiety to the tropone part.

The observed bond lengths in **1**–**3**, and the reported ones for benzoquinone[18] and tropone itself[19] are summarized in Table 6. The remarkably long bond lengths (*ca.* 1.50–1.51 Å) of C1–C10 and C4–C11 in **1**–**3** compared with those of the corresponding bonds (C1–C2 and C3–C4) in benzoquinone indicate that the delocalization of π-electrons is divided into two parts (the enedione moiety O1–C1–C2–C3–C4–O2 and tropone part).

The bond length of C5–C11 (or C9–C10) is longer and those of C5–C6 (or C8–C9) and C7–O3 are shorter than the corresponding ones in tropone (Table 6). This means that the contribution of the following structure to the resonance

Table 6 The observed bond lengths (in Å) for **1**, **2**, **3**, quinone and tropone (calculated ones for **1**–**3** in parentheses)

	Compounds				
Bonds[a]	**1**[b]	**2**[c]	**3**	Benzoquinone	Tropone
C1–C2	1.472 (1.483)	1.461 (1.484)	1.467 (1.484)	1.467	
C2–C3	1.319 (1.331)	1.310 (1.331)	1.313 (1.331)	1.312	
C3–C4	1.466	1.464 (1.482)		1.467	
C4–C11	1.507 (1.510)	1.507 (1.512)			
C10–C11	1.375 (1.361)	1.372 (1.360)	1.375 (1.363)		1.337
C1–C10	1.509	1.501 (1.508)	1.504 (1.508)		
C1–O1	1.212 (1.218)	1.219 (1.218)	1.213 (1.219)	1.212	
C4–O2	1.218	1.215 (1.219)			
C5–C11	1.434 (1.445)	1.417 (1.439)			1.425
C5–C6	1.343 (1.339)	1.363 (1.350)			1.357
C6–C7	1.449 (1.469)	1.477 (1.491)			1.442
C7–C8	1.457	1.434 (1.474)	1.459 (1.491)		1.455
C8–C9	1.347	1.346 (1.338)	1.365 (1.346)		1.360
C9–C10	1.438	1.425 (1.440)	1.409 (1.435)		1.431
C7–O3	1.231	1.234 (1.224)	1.227 (1.221)		1.258

[a] For numbering scheme of atoms, see footnote of Table 5. [b] Observed bond lengths are average values of Mol-1 and Mol-2. [c] Observed bond lengths are average values of Mol-1, Mol-2 and Mol-3. Numbering scheme of atoms for **2** in this Table is partially different from those in Fig. 15 and data in supplementary Tables 3 and 7 (CCDC).

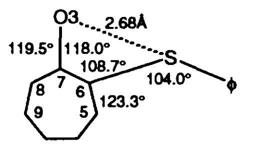


Fig. 4 Mean non-bonded O3 ··· S distance and mean values of some selected bond angles in the tropone moiety of **2** and **3**

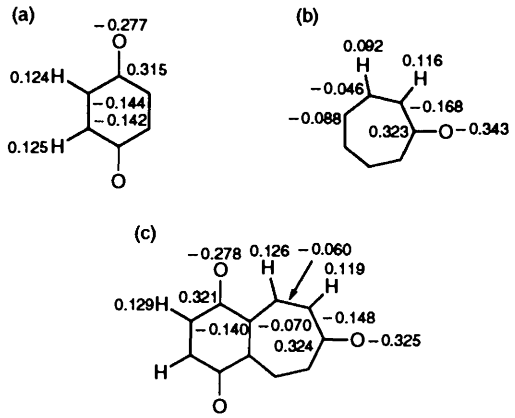
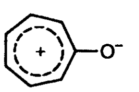


Fig. 5 Atomic charge distributions calculated by MNDO method for (a) benzoquinone, (b) tropone and (c) compound **1**



Structure 3

hybrid of **1** seems to be reduced compared to tropone itself. The existence of a phenylthio group on C6 in **2** resulted in significant elongation of C5–C6 and shortening of C5–C11 bonds, suggesting that the effect of the phenylthio group is essentially localized to the C6–C5–C11 moiety. The same tendency was reproduced by the MNDO method as shown in Table 6. The observed bond length of C6–C7 in **2** is clearly longer than the corresponding bond in **1**. The MNDO calculations also showed the similar trend (Table 6). The effect of cross conjugation by S–Ph group might retard the conjugation of C5–C6 double bond to tropone carbonyl.

Crystal Structure.—The crystal structure of **1** is characterized by an alternate packing of two types of layers extending parallel to the crystallographic *ac*-plane. The first layer is formed by Mol-1, and the second one by Mol-2 (see Fig. 6). In the first type of layer, there is a slipped overlap of molecules shown in Fig. 7(*a*), while, in the second type of layer, there is another kind of slipped overlap shown in Fig. 7(*b*), although in both cases the overlap of molecules is poor.

The crystal structure of pure **2** is constructed by a packing of complex column structures running along the crystallographic a-direction (Fig. 8). In each of the columns, they showed no segregated stackings and there is poor overlap of adjacent molecules.

In the crystal of the benzene adduct of **2**, one can see a segregated stacking of the molecules built by three kinds of molecular contacts (A ··· B, B ··· C, and C ··· D in Fig. 9). In A ··· B and C ··· D contacts, the shortest distances between carbon atoms of upper and lower molecules are 3.539(5) Å [for C(27A) ··· C(210B)] and 3.339(5) Å [for C(17C) ··· C(110D)], while that of the B ··· C contact is 3.294(5) Å [for C(16C) ··· C(24B)]. The molecules of **2** in the crystal are located on a plane which is coplanar to the molecular planes and spreading throughout the crystal as shown in Fig. 10. This fact forms a striking contrast to the case of **3** (see Fig. 12) and is interesting from the point of molecular design aiming at three dimensional organic conductors.

The molecular packing in **3** is shown in Figs. 11 and 12. Ribbon motifs extending along [10$\bar{1}$] direction (··· A·B ··· or ··· C·D ···) are piled up to form a layer which is parallel to the crystallographic *ac*-plane. The quinone rings of an upper ribbon (··· A·B ···) and the tropone rings of the adjacent lower ribbon (··· C·D ···) considerably overlap as shown in Fig. 11a and b. A ribbon motif in the layer which is adjacent sideways to the original one shown in Fig. 11b is situated at middle point between A and C (or B and D) when viewed parallel to the molecular plane. As a result, the ribbon motifs are located alternately on a plane passing throughout the crystal (see Fig. 12).

Thus, among the compounds studied, the crystal of **3** and benzene adduct of **2** showed the segregated column stacking with considerable overlap of the acceptor π-systems. But only the crystals of **3** formed the stacking structure of ribbon motifs pointing in the same direction and having the same and shorter distances between upper and lower rows of the ribbon motif.

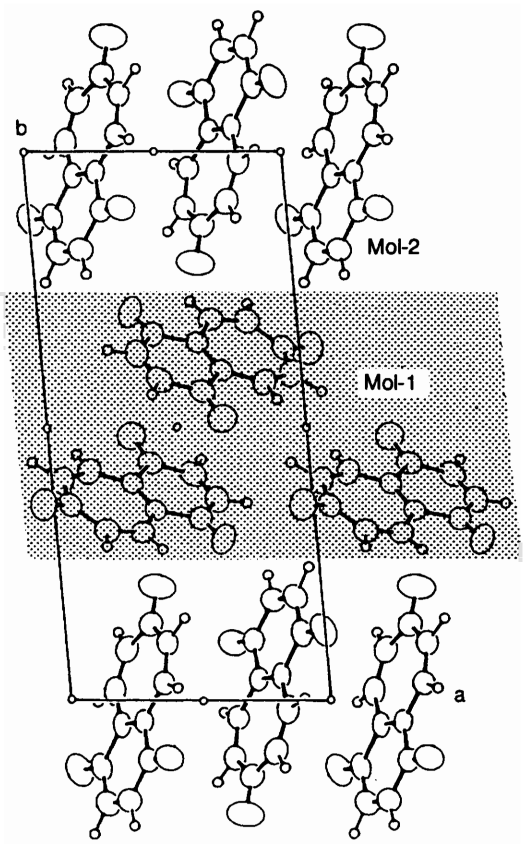


Fig. 6 Crystal structure of compound **1** projected onto *ab* plane. Shaded part corresponds to a sheet of layer which is formed by Mol-1 and extends parallel to the *ac* plane.

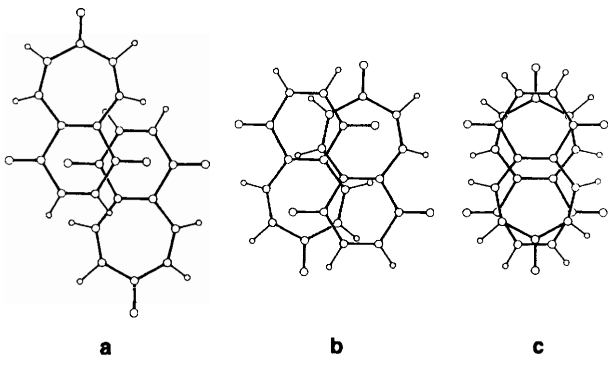


Fig. 7 Overlaps of two molecules of **1** (a and b: observed in the crystal; c, optimized structure for a cluster of two molecules)

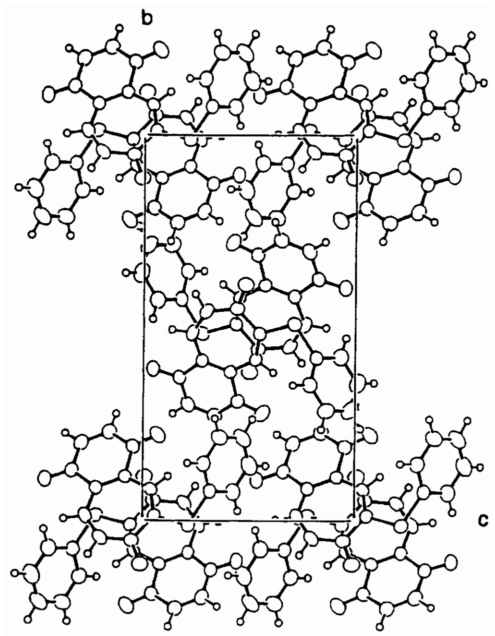


Fig. 8 Crystal structure of compound **2** (free from solvent) projected onto *bc* plane

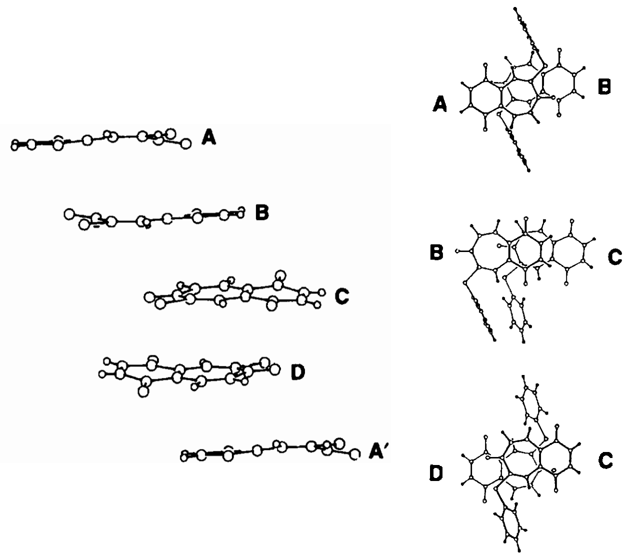


Fig. 9 Stacking of molecules of compound **2** in the benzene adduct of **2** (left: viewed parallel to molecular plane; right: perpendicular to the molecular plane). Symmetry codes; A (Mol-2), $-x + 1$, $-y + 1$, $z + 1$; B (Mol-2), x, y, z; C (Mol-1), x', y', z'; D (Mol-1), $-x'$, $-y' + 1$, $-z'$; A' (Mol-2): $-x$, $-y + 1$, $-z$.

Then, the derivatives of **3** seem to be potential candidates for organic conductors consisting of D–A–D molecular unit. It should be noted here that neither the overlap of molecules nor the segregated stacking can be seen in the crystal of a related compound, 7-(dicyanomethylene)-7*H*-benzocycloheptene-1,4-dione,[4] as well as **1** having no pendant on both sides of the ring system. In the case of the benzene adduct of **2**, the enclosed benzene molecules seem to serve as a substitute for a missing one of the phenylthio group of **3** to form the packing pattern similar to that in **3**.

In the crystal of **3**, the intermolecular O(2B)••• H(1A) distance (2.48 Å) is shorter than the sum of the van der Waals radii of the corresponding atoms (Fig. 11a), therefore, a head-to-tail interaction seems to exist. For a number of crystals of organic compounds it has been known that C–H••• O interactions stabilize ribbon motifs.[20,21] This type of electrostatic interaction seems to contribute to the stabilization of the ribbon motif in **3**. In line with this, an MO calculation by the MNDO method revealed that H(1) and H(2) carry rather large positive charges (*ca.* +0.13).

Calculations of Lattice Energy.—Table 7 lists the results of the lattice energy calculations for **1** and **3** by PCK83 program[22] under various conditions (for details of the calculations, see the footnotes for Table 7 and the Experimental section to follow). The lattice energy of Crystal-(obs) of compound **1** and that of compound **3** were calculated based on the corresponding observed crystal structures. When the lattice energy of each compound was optimized starting from the observed crystal structure, Crystal-(C1) of each compound was obtained. The unit cell parameters (lattice constants), lattice energies and packing coefficients of these artificial crystals of **1** and **3** obtained by the calculation were found to be similar to those of

Table 7 Unit cell parameters, unit cell volume (V) and lattice energy (E) obtained by crystal molecular packing analysis for **1** and **3**

Compd.	Name[a]	a/Å	b/Å	c/Å	α/°	β/°	γ/°	V/Å^3	E/kJ mol^{-1}	D[b]	C[c]
1	Crystal-(obs)	8.233	17.327	5.984	91.94	90.17	95.43	848.27	−99	0.72	obs
	Crystal-(C1)	7.939	17.177	6.179	92.02	87.95	96.11	836.94	−101	0.73	C1
	Crystal-(C2)	8.714	13.910	3.862	90	99.18	90	468.03	−91	0.65	C2
3	Crystal-(obs)	7.247	29.128	4.888	90	108.98	90	975.71	−156	0.67	obs
	Crystal-(C1)	7.376	28.936	4.764	90	110.84	90	950.24	−160	0.69	C1

[a] Crystal-(obs) and crystal-(C1) denote the observed and optimized crystal lattices, respectively. [b] Packing density (volume of molecules in the unit cell/volume of the unit cell). [c] Conditions for the calculation of lattice energy; obs: E was obtained for the observed lattice without the energy optimization. C1: Crystal system and space group were assumed to be same as the observed ones. Initial structure = observed one. C2: Monoclinic unit cell and space group *Cm* were assumed. Initial structure and cell constants were derived from those observed for **3**.

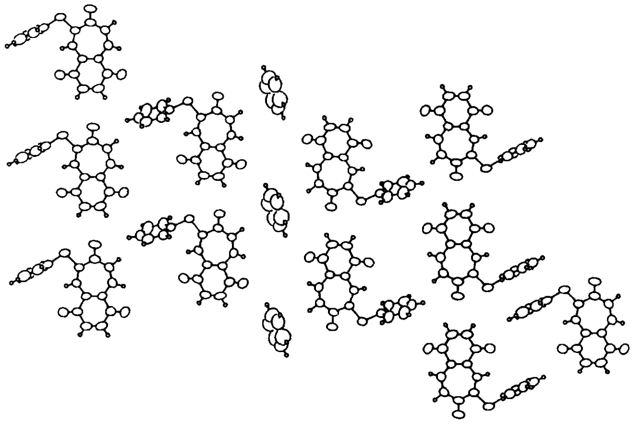


Fig. 10 The arrangement of molecules in the crystal of the benzene adduct of **2** viewed perpendicular to the quinotropone ring of compound **2**. The planes of the rings and the centres of the included benzene molecules lie in a plane.

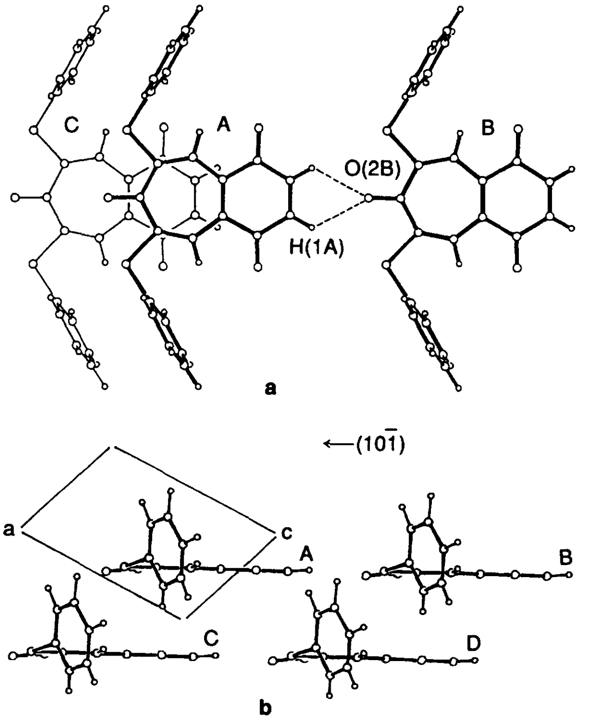


Fig. 11 Stacking of molecule **3** in the crystal (a: viewed perpendicular to molecular plane; b, parallel to the molecular plane). Symmetry codes: A, x, y, z; B, $x - 1, y, z + 1$; C, $x, y, z - 1$, D, $x - 1, y, z$.

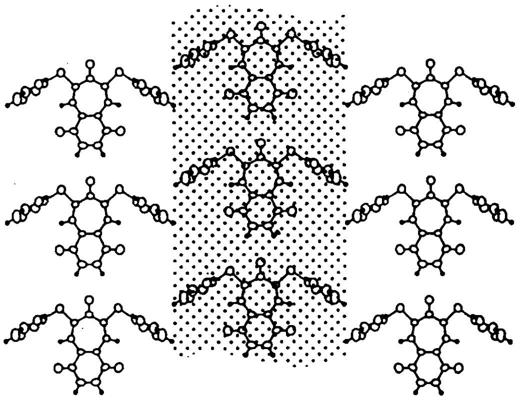


Fig. 12 Arrangement of molecules of **3** viewed perpendicular to the molecular planes. The shaded molecules are located up (or below) the plane of paper on which molecular planes of non-shaded molecules are situated.

the observed crystals (see Table 7). Since the observed crystal structures of **1** and **3** could be almost reproduced by the calculations (taking into account the repulsion, dispersion and Coulomb terms as the non-bonded intermolecular interactions), the lattice energies of these compounds seem to be explicable without assuming strong extra forces such as charge transfer interaction. Even in the case of **3** where considerable overlap of molecules can be seen, the contribution of the charge transfer interaction seems, if any, to be small. This is consistent with a preliminary measurement of electrical conductivity on a compressed disk indicating that compound **3** was an insulator.

The contribution of Coulomb term to the total lattice energy in each compound appears to be relatively small; in the case of **1**, the values for the repulsion, dispersion and Coulomb terms are obtained as 62.5, −148.2 and −13.0 kJ mol^{-1}, respectively. These values are in accord with the data reported for other ordinary organic compounds.[23]

The Stability of Molecular Overlap.—In order to examine the stability of the molecular overlap, we performed calculations of energies of molecular clusters of **1** and **3** using PCK83 program. The optimized structures of clusters consisted of two and four molecules of **3** were almost identical with the local structures of the observed crystal. For the cluster consisting of two molecules of **1**, an overlapped structure shown in Fig. 7(c) was found to be more stable than the observed slipped structures [Fig. 7(a) and (b)]. When the calculation of lattice energy optimization was carried out for compound **1** starting from an initial crystal structure containing the artificial molecular overlap shown in Fig. 7(c), it converged to a final crystal structure that has a molecular overlap similar to that shown in Fig. 7(b). This result suggests that the slipped overlap of **1** [Fig. 7(a) or (b)] is more stable than the well overlapped one [Fig. 7(c)] in the crystalline state.

An artificial crystal of compound **1** [Crystal-(C2) given in Table 7] was obtained when a parallel arrangement of molecules and space group of *Cm* were assumed. The lattice energy of this crystal (*ca.* −91 kJ mol^{-1}) is considerably higher than that of Crystal-(obs) and the packing density of crystal-(C2) was considerably low. These features seem to be unfavourable for the formation of a stable crystal[24] and it appears to be difficult for **1** to be arranged in a way of stacking similar to that found in the crystal structure of **3**.

Experimental

General.—The NMR spectra were taken on JEOL Model GX400 (^{1}H; 400 MHz, ^{13}C; 100 MHz) or FX100 (^{1}H; 100 MHz, ^{13}C; 25 MHz) FT-NMR spectrometer. *J*-values are given in Hz. Deuteriochloroform was used as solvent in every case unless otherwise specified. The IR spectra were recorded on a JASCO Model A-102 spectrometer and the UV on a Hitachi Recording spectrometer Model 323 or on a Shimadzu Model UV-160A spectrometer with a colour X-Y plotter Model P/N 206-15788. The reduction potentials were recorded on a BAS voltammetry control unit Model CV-1B in dichloromethane or acetonitrile containing tetrabutylammonium perchlorate (10^{-1} mol dm^{-3}) as the supporting electrolyte. Ferrocene was used as an internal standard (+0.40 V). A graphite rod was used as a working electrode.

Materials.—The trione **1** and **8** have been prepared by the oxidation of the corresponding hydroquinone dimethyl ethers.[4,9] The preparations of triones **2** and **3** are described below. These tropones were recrystallized from benzene or a mixture of hexane and dichloromethane. Compound **8**[9] m.p. 220 °C (decomp.); *m/z* 236 (16%, M$^+$), 209 (17), 207 (100), 180 (20), 154 (16), 153 (10), 152 (68), 151 (11) and 126 (59); δ_H(100 MHz), 6.93 (2 H, bd, *J* 12.5), 7.10 (2 H, s), 7.54 (2 H, d, *J* 12.5) and 8.37 (2 H, s); δ_C(25 MHz) 131.7(s), 132.5(d), 137.6(d), 139.4(d), 139.6(d), 139.8(d), 183.6(s) and 187.4(s); λ_{max}-(CH_3CN) 238 (log ε 4.69), 244 (4.72), 286 (infl.), 296 (4.52), 305 (4.46) and 364 (3.58).

1,4-*Dimethyl*-6,7,8,9-*tetrahydro*-5H-*benzocyclohepten*-7-*one* (**5**).—2,3-Bis(bromomethyl)-1,4-dimethoxybenzene[25] (10.0 g, 30.9 mmol), dimethyl 3-oxoglutarate (6.61 g, 38.0 mmol), benzyl triethylammonium chloride (800 mg) dissolved in dichloromethane (144 cm^3) was stirred at 45–50 °C with 20% aq. potassium hydrogen carbonate (134 cm^3). Insoluble materials were gradually dissolved and colourless solutions resulted. After 2 days stirring at the temperature, two layers were separated and the aq. solution was extracted three times with dichloromethane. All of the organic layers were combined and washed with water and saturated brine. From the dried organic layer, a pale yellow oil (11.0 g) was obtained after evaporation of the solvent under reduced pressure. The remaining oil **4** was partially crystallized by cooling. This was decarboxylated without further purification.

Thus, the crude ester **4** (11.0 g) suspended in 0.5 mol cm^{-3} 50% aq. ethanolic potassium hydroxide (178 cm^3) was refluxed overnight, during which time colourless precipitates (6.08 g) were formed. These precipitates were dissolved in benzene–ethyl acetate (95:5 v/v; 100 cm^3) and insoluble impurities were filtered off. The filtrate was chromatographed on silica gel (60 g) and eluted with the same solvent to give colourless crystals (4.78 g, 71%). Compound **5**, m.p. 118–120 °C (from hexane–dichloromethane) (Found: C, 71.0; H, 7.4. $C_{13}H_{16}O_3$ requires C, 70.89; H, 7.39%); δ_H(100 MHz) 2.53–2.56 (4 H, m), 2.99–3.02 (4 H, m), 3.79 (6 H, s) and 6.75 (2 H, s); δ_C(25 MHz) 20.6 (t, *J* 130), 43.8 (t, *J* 129), 56.2 (q, *J* 143), 109.3 (d, *J* 159), 131.0(s), 150.8(s) and 212.1(s); ν_{max}(Nujol)/cm^{-1} 1695, 1600(w), 1485, 1260, 1090, 1075, 995 and 800.

6-*Phenylthio- and* 6,8-*Bis*(*phenylthio*)-1,4-*dimethoxy*-7H-*benzocyclohepten*-6-*ones* (**6** *and* **7**) *from* 1,4-*Dimethoxy*-6,7,8,9-*tetrahydro*-5H-*benzocyclohepten*-7-*one* (**5**).—Absolute ethanol (188 cm^3) was added to an oil suspension of sodium hydride (60%, 2.01 g; 50.8 mmol) placed in a flask fitted with dropping funnel under a nitrogen atmosphere. After a clear solution has been obtained, 1,4-dimethoxy-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one **5** (1.76 g, 8.00 mmol) and diphenyldisulfide (8.73 g, 40 mmol) were added in portions and the suspension was heated at 80–90 °C under stirring. The colour of the mixture turned gradually from colourless to yellow and finally to light brown, during which period insoluble materials mostly disappeared. After heating the mixture overnight, powdered sodium methoxide (0.95 g, 17.6 mmol) was added and heated at 90 °C for a further 10 h. After cooling to room temperature, the yellow precipitates were filtered off and washed with water (1st batch, 1.09 g). The filtrate was neutralized by the addition of 1 mol dm^{-3} aq. sodium dihydrogenphosphate (200 cm^3) and water (50 cm^3), and then concentrated to a volume of 300 cm^3. The yellow insoluble materials were filtered and washed with water (2nd batch, 4.26 g). The filtrate was extracted with dichloromethane and the organic layer was washed successively with water, 1 mol dm^{-3} aq. sodium hydroxide [in the case of the formation of an intractable emulsion, the extracting mixture was filtered through a layer of Hyfrosupercel (filter aid)] and saturated brine. After drying, the organic layer was evaporated to dryness and the remaining material was washed with hexane (decantation) leaving brown crystals (3rd batch, 1.05 g). Chromatography of batches **1–3** on silica gel (benzene–ethyl acetate = 95:5 v/v) gave 6,8-bis(phenylthio) derivative **7** [602 mg, 17%; TLC (same solvent) R_f = 0.55] and 6-phenylthio derivative **6** [1.48 g, 57%; TLC (same solvent) R_f = 0.33]. Compound **6**, m.p. 161–162 °C (from hexane–dichloromethane) (Found: C, 70.0; H, 5.0%. $C_{19}H_{16}O_3S$ requires C, 70.35; H, 4.97%); δ_H(100 MHz) 3.56 (3 H, s), 3.90 (3 H, s), 6.90 (2 H, s), 6.92 (1 H, d, *J* 14), 7.40–7.68 (5 H, m), 7.84 (1 H, s) and 8.28 (1 H, d, *J* 14); δ_C(25 MHz) 56.5 (q, *J* 160), 56.9 (q, *J* 143), 110.6 (d, *J* 161), 113.1 (d, *J* 160), 124.7(s), 125.8(s), 126.3 (d, *J* 156), 129.3 (d, *J* 160), 129.8 (d, *J* 160), 130.4 (d, *J* 130), 131.9(s), 132.9 (d, *J* 157), 136.4 (d, *J* 163), 149.5(s), 151.4(s), 152.2(s) and 183.9(s); *m/z* 325 (22%, M$^+$ + 1), 324 (98, M$^+$), 281 (100) and 266 (22); ν_{max}(Nujol)/cm^{-1} 1615(w), 1595(w), 1570, 1460–1450(b), 1380, 1335, 1295, 1250, 1080 and 940. Compound **7**, m.p. 236–237 °C (from benzene) (Found: C, 69.55; H, 4.7. $C_{25}H_{20}O_3S_2$ requires C, 69.42; H, 4.66%); δ_H(100 MHz) 3.55 (6 H, s), 6.78 (2 H, s), 7.48–7.50 (6 H, m), 7.62–7.64 (4 H, m) and 7.96 (2 H, s); δ_C(25 MHz) 56.7 (q, *J* 144), 111.1 (d, *J* 161), 124.1(s), 126.8 (d, *J* 157), 129.2 (d, *J* 160), 129.8 (d, *J* 160), 132.3(s), 136.3 (d, *J* 164), 145.5(s), 151.3(s) and 179.1(s); ν_{max}(Nujol)/cm^{-1} 1580(w), 1565, 1540(w) and 1450(bs); *m/z* 433 (28%, M$^+$ + 1), 432 (74, M$^+$), 404 (48), 389 (44) and 138 (19).

6-*Phenylthiobenzocycloheptene*-1,4,7-*trione* (**2**).—To a stirred suspension of tropone **6** (0.486 g, 1.50 mmol) in acetonitrile (31 cm^3) was added dropwise an aq. solution of ammonium cerium(IV) nitrate (1.8 g, 3.3 mmol/H_2O, 33 cm^3) at 25–30 °C and the resulting suspension was stirred for 1 h, in which period the colour of the mixture turned from yellow to orange and finally to red. The red precipitates were filtered and washed with water (**2**, 338 mg). The filtrate was diluted with water and extracted several times with dichloromethane. The combined extracts were washed successively with water, 5% aq. sodium hydrogen carbonate, and saturated brine and then dried. The residual crystals (90 mg) from the extracts were chromatographed on silica gel (3 g, benzene–ethyl acetate = 95:5 v/v as an eluent). The fractions contained red material **2** [TLC (same solvent) R_f 0.45] were collected and evaporated (37 mg). After chromatography, the first batch gave pure red crystals **2**, 295 mg (total 332 mg, 75.2%). Recrystallization from a mixture of hexane–dichloromethane gave glittering red crystals (315 mg, 71.4%) **2**, m.p. 179–180 °C (decomp.) (Found: C, 69.05; H, 3.4. $C_{17}H_{10}O_3S_2$ requires C, 69.37; H, 3.42%); δ_H(400 MHz) 6.87 (1 H, d, *J* 10.1), 6.95 (1 H, d, *J* 10.1), 7.28 (1 H, d, *J* 12.8), 7.52–7.64 (5 H, m), 7.65 (1 H, s) and 8.13 (1 H, d, *J* 12.8); δ_C(100 MHz) 123.7, 129.3, 130.5, 130.8, 131.0, 132.3, 133.0, 135.8, 136.6, 137.0, 137.6, 166.0, 181.3, 184.8 and 185.0; ν_{max}(Nujol)/cm^{-1} 1660, 1610, 1585, 1570, 1490, 1380, 1310, 1300 and 850; *m/z* 295 (20%, $M^+ + 1$), 294 (100, M^+), 266 (33), 237 (20) and 184 (19); redox potentials (CH_2Cl_2) $E_1 = -0.37$, $E_2 = -0.86$ V; (CH_3CN) $E_1 = -0.25$, $E_2 = -0.73$ V.

6,8-*Bis(phenylthio)benzocycloheptene*-1,4,7-*trione* **3**.—To a yellow suspension of tropone **7** (100 mg, 0.23 mmol) in acetonitrile (6 cm^3) and chloroform (2 cm^3) was added dropwise an aqueous solution of ammonium cerium(IV) nitrate (340 mg, 0.62 mmol) in water (5.6 cm^3) at room temperature. The yellow crystals soon dissolved and red crystals appeared. After stirring for 1 h, the red suspension was concentrated to *ca.* 10 cm^3, filtered and washed well with water (batch 1: 67 mg). The filtrate was extracted with dichloromethane. The organic layer was washed with water and saturated brine, and then dried. The red residue (23 mg) from the extract was chromatographed on silica gel (2.5 g) with benzene as eluent [TLC (benzene) $R_f = 0.20$; batch 2: 13 mg]. Total (batches 1 and 2) **3** (80 mg, 86%), m.p. 258–260 °C (decomp.) (hexane–dichloromethane) [Found: C, 68.4; H, 3.2 (it was very difficult to make it burn completely). $C_{23}H_{14}O_3S_2$ requires C, 68.63; H, 3.48%]; δ_H(400 MHz) 6.779 (2 H, s), 7.57–7.62 (10 H, m), 7.765 (2 H, s); δ_C(100 MHz) 125.4 (d, *J* 159), 128.7 (s), 129.8(s), 130.5 (d, *J* 163), 130.7 (d, *J* 161), 136.0 (d, *J* 162), 137.4 (d, *J* 170), 157.2(s), 173.1(s) and 184.9(s); ν_{max}(Nujol)/cm^{-1} 1665, 1620, 1565, 1540 and 1465; *m/z* 403 (27%, $M^+ + 1$), 402 (100, M^+), 374 (28) and 110 (39); redox potentials (CH_2Cl_2) $E_1 = -0.40$, $E_2 = -0.73$ V; (CH_3CN) $E_1 = -0.30$, $E_2 = -0.80$ V.

Crystal Data for **1**.—$C_{11}H_6O_3$, $M = 186.1$. Triclinic, $a = 8.223(1)$, $b = 17.327(2)$, $c = 5.984(4)$ Å, $\alpha = 91.94(2)$, $\beta = 90.17(2)$, $\gamma = 95.42(1)°$, $V = 848.2(6)$ Å^3 (from 2θ values of 20 reflections, $16 < 2\theta < 19°$), space group $P\bar{1}$, $Z = 4$, $D_c = 1.458$, $D_m = 1.47$ g/cm^3. $F(000) = 384$. Crystal dimensions: 0.5 × 0.5 × 0.2 mm, μ(Mo-Kα) = 1.00 cm^{-1}. Black crystals were obtained from benzene.

Data Collection and Processing for **1**.—Rigaku AFC-5 diffractometer, $2\theta/\omega$ mode with scan width = 1.3 + 0.35 tanθ, scan speed 8 deg min^{-1}, graphite monochromated Mo-Kα radiations, 3879 reflections ($2 < 2\theta < 53°$, index range *h* −10 to 10, *k* −21 to 21, *l* 0 to 7), 3526 unique, giving 2489 with $F_o > 4\sigma(F_o)$. No absorption correction. At 298 K.

Structure Analysis and Refinement for **1**.—The structure was solved by the direct method (MULTAN78)[26] and refined by block-diagonal least squares (HBLS-V)[27] with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for the H atoms. Atomic scattering factors from ref. 28. All calculations were performed on an ACOS 2020 computer at the Information Processing Centre of Kobe University with the UNICS system.[29] The final refinement gave $R = 0.0450$, $R_w = 0.0766$; if $|F_o| < 10.0$, $w = 1$, if $|F_o| > 10.0$, $w^{-1} = [1 + 1.900(|F_o| - 10.0)]$; 302 parameters; max. shift/esd = 0.06, $\rho_{max} = 0.16$, $\rho_{min} = -0.20$ e Å^{-3} on final difference map.

Crystal Data for **2** (solvent free).—$C_{17}H_{10}O_3S$, $M = 294.2$. Monoclinic, $a = 8.718(8)$, $b = 16.633(6)$, $c = 9.665(4)$ Å, $\beta = 104.66(5)°$, $V = 1355.9(14)$ Å^3 (from 2θ values of 24 reflections, $20 < 2\theta < 28°$), space group $P2_1/c$, $Z = 4$, $D_c = 1.442$, $D_m = 1.42$ g cm^{-3}. $F(000) = 608$. Crystal dimensions: 0.6 × 0.3 × 0.2 mm, μ(Mo-Kα) = 2.33 cm^{-1}. Wine red crystals were obtained from a mixture of hexane and dichloromethane.

Data Collection and Procession for **2** (solvent free).—Rigaku AFC-5 diffractometer, $2\theta/\omega$ mode with scan width = 1.0 + 0.35 tanθ, scan speed 8 deg min^{-1}, graphite monochromated Mo-Kα radiations, 3442 reflections ($2 < 2\theta < 55°$, index range *h* −11 to 0, *k* −21 to 0, *l* −12 to 12), 3122 unique, giving 2455 with $F_o > 3\sigma(F_o)$. At 298 K. No absorption correction.

Structure Analysis and Refinement for **2** (solvent free).—Structure was solved by the same way as for **1** with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for the H atoms. The final refinement gave $R = 0.0403$, $R_w = 0.0462$; $w^{-1} = [\sigma^2(F_o) + 0.006\,02\,|F_o| + 0.000\,05\,|F_o|^2]$; 231 parameters; max. shift/esd = 0.00, $\rho_{max} = 0.22$, $\rho_{min} = -0.18$ e Å^{-3} on final difference map.

Crystal Data for the Benzene Adduct of **2** (**2**:benzene = 4:1).—$(C_{17}H_{10}O_3S)(C_6H_6)_{1/4}$, $M = 313.8$. Triclinic, $a = 13.909(8)$, $b = 14.429(7)$, $c = 10.166(4)$ Å, $\alpha = 96.56(5)$, $\beta = 100.10(6)$, $\gamma = 128.81(3)°$, $V = 1497.0(17)$ Å^3 (from 2θ values of 30 reflections, $20 < 2\theta < 26°$), space group $P\bar{1}$, $Z = 4$, $D_c = 1.393$, $D_m = 1.35$ g cm^{-3}. $F(000) = 650$. Crystal dimensions: 0.55 × 0.5 × 0.1 mm, μ(Mo-Kα) = 2.16 cm^{-1}. Wine red crystals were obtained from benzene.

Data Collection and Processing for the Benzene Adduct of **2**.—Rigaku AFC-5 diffractometer, $2\theta/\omega$ mode with scan width = 1.6 + 0.35 tanθ, scan speed 8 deg min^{-1}, graphite monochromated Mo-Kα radiations, 4169 reflections ($2 < 2\theta < 45°$, index range *h* −14 to 14, *k* −15 to 15, *l* 0 to 10), 3864 unique, giving 2735 with $F_o > \sigma(F_o)$. At 298 K. No absorption correction.

Structure Analysis and Refinement for the Benzene Adduct of **2**.—Structure was solved by the same way as for **1** with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for the H atoms except H(204), which was constrained. The final refinement gave $R = 0.0456$, $R_w = 0.0425$; $w^{-1} = [\sigma^2(F_o) - 0.102\,41\,|F_o| + 0.004\,98\,|F_o|^2]$; 495 parameters; max. shift/esd = 0.06, $\rho_{max} = 0.30$, $\rho_{min} = -0.24$ e Å^{-3} on final difference map.

Crystal Data for **3**.—$C_{23}H_{14}O_3S_2$, $M = 402.5$. Monoclinic, $a = 7.247(3)$, $b = 29.128(15)$, $c = 4.888(2)$ Å, $\beta = 108.98(2)°$, $V = 975.6(7)$ Å^3 (from 2θ values of 26 reflections, $20 < 2\theta < 29°$), space group C_m, $Z = 2$, $D_c = 1.371$, $D_m = 1.35$ g cm^{-3} (molecular symmetry is C_s). $F(000) = 416$. Crystal dimensions: 0.4 × 0.4 × 0.2 mm, μ(Mo-Kα) = 2.81 cm^{-1}. Wine red crystals were obtained from benzene.

Data Collection and Processing for **3**.—Rigaku AFC-5 diffractometer, $2\theta/\omega$ mode with scan width = 1.8 + 0.35 tanθ, scan speed 8 deg min^{-1}, graphite monochromated Mo-Kα radiations, 1227 reflections ($2 < 2\theta < 55°$, index range *h* 0 to 9, *k* −37 to 0, *l* −6 to 6), 1146 unique, giving 1055 with $F_o > 3\sigma(F_o)$. At 296 K. No absorption correction.

Structure Analysis and Refinement for **3**.—Structure was solved by the same way as for **1** with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for the H atoms. The final refinement gave $R = 0.0404$, $R_w = 0.0410$; $w^{-1} = [\sigma^2(F_o) - 0.256\,81\,|F_o| + 0.012\,31\,|F_o|^2]$; 165 parameters; max. shift/esd = 0.10, $\rho_{max} = 0.36$, $\rho_{min} = -0.58$ e Å^{-3} on final difference map.

Results of Crystal Structure Determinations.—The molecular structure and numbering scheme of atoms for **1** are shown in Fig. 13 (ORTEP drawing).[30] Those for **2** (free from solvent) are shown in Fig. 14. For the benzene adduct of **2**, the molecular structure and the numbering schemes for atoms in **2** and benzene are given in Fig. 15. The molecular symmetry of **3** in the crystalline state was found to be C_s. Fig. 16 illustrates thermal ellipsoid plots (ORTEP drawing) of the molecule of **3** with the numbering scheme of atoms.

Atomic coordinates for the crystals of **1**, **2** (solvent free), the benzene adduct of **2**, and **3** are given in Supplementary Tables 1–4, respectively. Their selected bond lengths and angles are listed in Supplementary Tables 5–8.* The deviations of atoms from each mean plane and the inter-plane angles indicative of the degree of non-planarity are listed in Table 5 for the compounds studied.

Computational Method for the Lattice Energy and the Potential Energy of Cluster of Molecules.—Estimations of the lattice energies and the potential energies of molecular clusters were carried out with the use of a crystal molecular packing analysis program (PCK83) developed by Williams.[22] In the calculation, repulsion, dispersion and Coulomb terms are taken

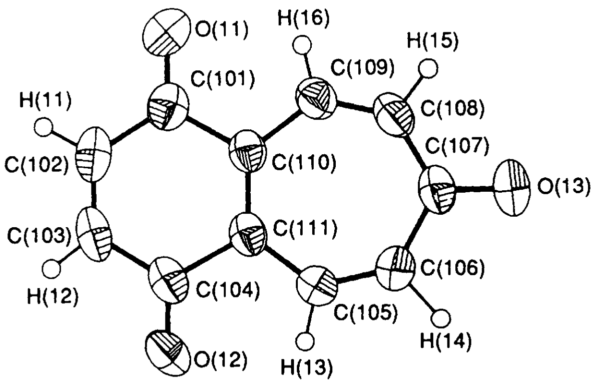


Fig. 13 X-Ray structure (ORTEP drawing) and numbering scheme of atoms for compound **1**

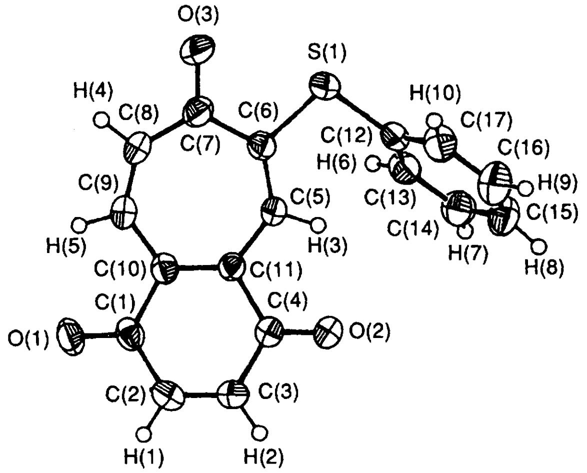


Fig. 14 X-Ray structure (ORTEP drawing) and numbering scheme of atoms for the molecule of **2** in the crystal (solvent free)

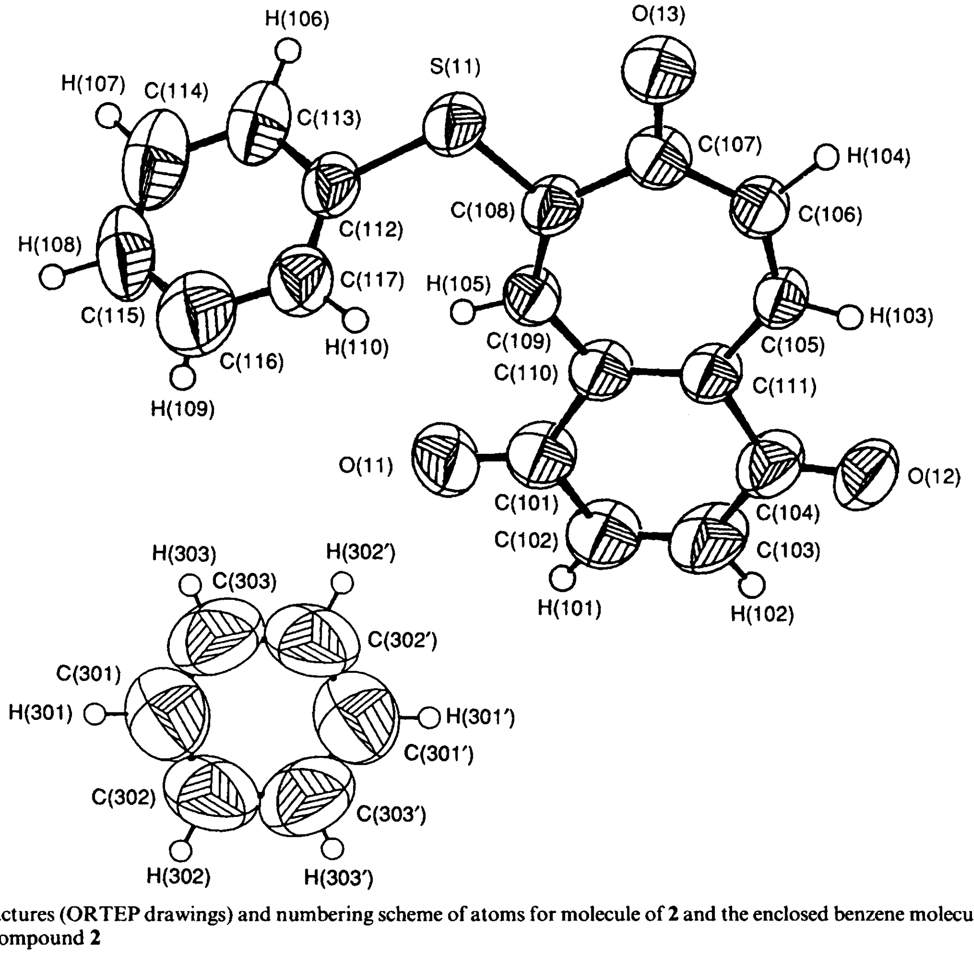


Fig. 15 X-Ray structures (ORTEP drawings) and numbering scheme of atoms for molecule of **2** and the enclosed benzene molecule in the crystal of benzene adduct of compound **2**

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* Lists of bond lengths and bond angles, and fractional atomic coordinates have been deposited at CCDC. For details of the deposition scheme please see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, Issue 1, 1993.

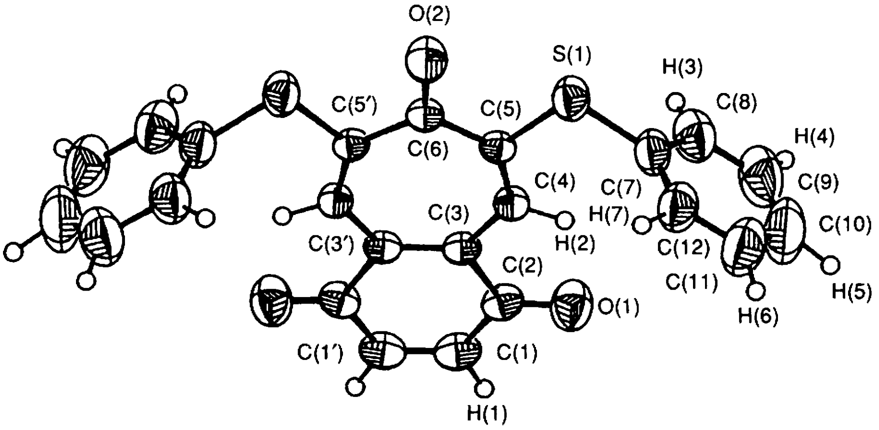

Fig. 16 X-Ray structure (ORTEP drawing) and numbering scheme of atoms for compound 3 (molecular symmetry in the crystal is *Cs*)

into account as non-bonded, intermolecular interactions.[31] Total atomic charges obtained by the MNDO method were used for the calculations of Coulomb terms. Since the parameters for sulfur atom is absent in the program, we used those for the oxygen atom as substitutes for sulfur when needed. Molecular volumes, which were needed to calculate the packing densities of the crystals studied, were estimated by the method reported by Nagao.[32]

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