X-Ray Structures and Physical Properties of Tropone-annelated *p*-Benzoquinones Substituted with X–Ar Groups α to Tropone Carbonyls and First Examples of the Trione Substituted with an Electron-withdrawing Group

Kimiaki Furuichi,*[a] Hitoshi Tada,[a] Akira Itoh,[a] Yasuyo Takeuchi,[a] Masashi Mitoori,[a] Masahiko Kato,*[a] Shuji Matsumoto[b] and Masao Hashimoto*[b]
[a] *Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, Japan*
[b] *Faculty of Science, Kobe University, Nada-ku, Kobe, Japan*

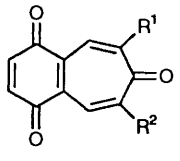
6,8-Dibenzyl-, 6,8-bis(*p*-dimethylaminobenzyl)- and 6,8-diphenoxy-benzocycloheptene-1,4,7-triones have been synthesized and their physical properties (IR, UV, NMR spectra and redox potentials) compared with those of 6,8-bis(phenylthio)benzocycloheptene-1,4,7-trione. The first redox potentials fall in the order OPh > CH_2Ph > SPh > $CH_2C_6H_4NMe_2$-(*p*) but the second fall in the order OPh > SPh > CH_2Ph > $CH_2C_6H_4NMe_2$-(*p*), the latter order is in accord with that of their σ_I values. The molecular structures of the first three compounds, determined by the single crystal X-ray analyses, were found to be very similar, except for the bond angle at the atom connecting tropone with the phenyl rings. The crystal structures of compounds **4** and **5** were almost identical, but were quite different from that of the SPh analogue **3**. Success in the synthesis of benzocycloheptene-1,4,7-triones substituted with an electron withdrawing group on C-6 is also described. Electron transfer was not appreciable in a crystal of the complex of benzo[1,2;4,5]dicycloheptene-3,6,9,12-tetrone with TTF according to the crystal structure analysis.

In a previous paper,[1] we have described the synthesis and X-ray structures of 6-phenylthio- and 6,8-bis(phenylthio)-benzocycloheptene-1,4,7-triones **2** and **3** as D–A and D–A–D molecular units, aiming at the prototypes of organic conductors, and discussed their structures and physical properties compared with those of the unsubstituted trione **1**. The crystal structure of **3** revealed the formation of a segregated column stacking with a head to tail arrangement of the molecules pointing in one direction, one of the required arrangements to form organic conductors. In addition, it has been shown that this compound exhibited an intense second harmonic generation at *ca.* 500 nm by irradiation with a laser at 1060 nm,†[2] though the compound had absorption covered up to 500 nm and longer.[1] Therefore, it is interesting to synthesize the benzyl and phenoxy analogues of **3** in order to exploit their potential physical properties. Further, in order to obtain hitherto unknown quinotropones substituted with electron-withdrawing groups such as cyano or sulfinyl groups on C-6, oxidations of appropriate precursors have been studied.

In an attempt to study charge-transfer complexes containing tropone-annelated quinones, we have prepared a complex of benzo[1,2;4,5]dicycloheptene-3,6,9,12-tetraone with TTF and investigated its X-ray crystal structure.

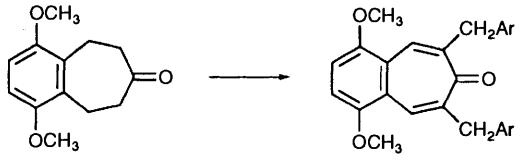
Results and Discussion

Syntheses of 6,8-*Dibenzylbenzocycloheptene*-1,4,7-*trione* **4** *and its Substituted Derivatives* **6**, **8** *and* **9**.—The precursors, 6,8-



1 $R^1 = R^2 = H$
2 R^1 = SPh, $R^2 = H$
3 $R^1 = R^2$ = SPh
4 $R^1 = R^2 = CH_2Ph$
5 $R^1 = R^2$ = OPh
6 $R^1 = R^2 = CH_2C_6H_4$-*p*-$N(CH_3)_2$
7 $R^1 = R^2$ = Br

† We are greatly indebted to Professor K. Nakatsu of Kwansei Gakuin University for observing the second harmonic generation of compound **3**.



12

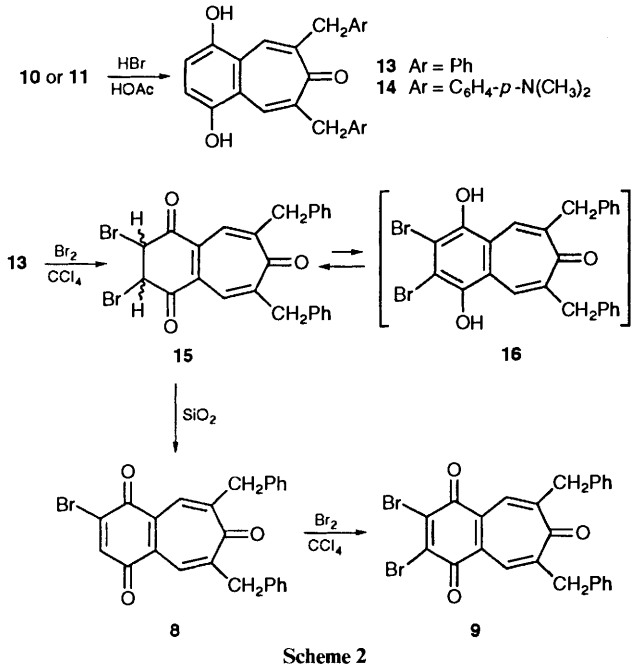
10 Ar = Ph
11 Ar = C_6H_4-*p*-$N(CH_3)_2$

Scheme 1 *Reagents and conditions:* i, ArCHO, Bu^{t}OK/Bu^{t}OH or C_2H_5ONa/C_2H_5OH

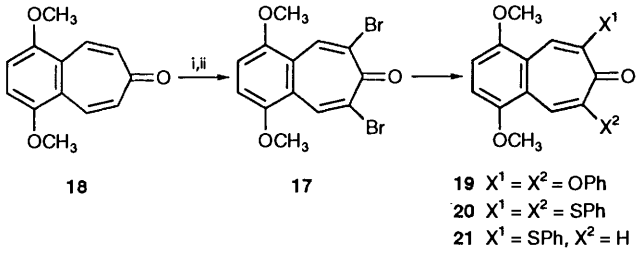
dibenzyl- and 6,8-bis(*p*-dimethylaminobenzyl)-1,4-dimethoxybenzocyclohepten-7-ones **10** and **11** were prepared from 1,4-dimethoxy-5,6,8,9-tetrahydrobenzocycloheptene-7-one **12**[3] by reaction with appropriate benzaldehydes in the presence of potassium *tert*-butoxide. Quinone **4** was easily obtained by the CAN [ammonium cerium(IV) nitrate] oxidation of the corresponding hydroquinone dimethyl ether **10** (Scheme 1).

2-Bromo- and 2,3-dibromo-6,8-dibenzylbenzocycloheptene-1,4,7-triones **8** and **9** were obtained by bromination of the hydroquinone **13**, prepared by demethylation of **10**. It is interesting to note that even with excess of bromine, the hydroquinone **13** did not give the dibromide **9** directly, instead, it gave monobromide **8** after silica gel chromatography, which was transformed into **9** by further bromination. Examination of the NMR spectra of the intermediate of the initial bromination of **13** revealed that it existed in the dihydroquinone structure **15** rather than the hydroquinone structure **16** (Scheme 2). Hydroquinone **14** was smoothly transformed into the corresponding quinone **6** by oxidation.

Synthesis of 6,8-*Dibromo*-1,4-*dimethoxybenzocyclohepten*-7-*one* **17**: *a Versatile Intermediate*.—Because the bromine atoms of compound **17** should be easily replaceable by nucleophiles, as was observed in the case of 2-bromotropone,[4] compound **17** seems to be a useful intermediate for the synthesis of 6,8-disubstituted quinotropones. The dibromide **17** was obtained from 1,4-dimethoxybenzocyclohepten-7-one **18**[3] by bromination[5] followed by dehydrobromination (Scheme 3).



Scheme 2



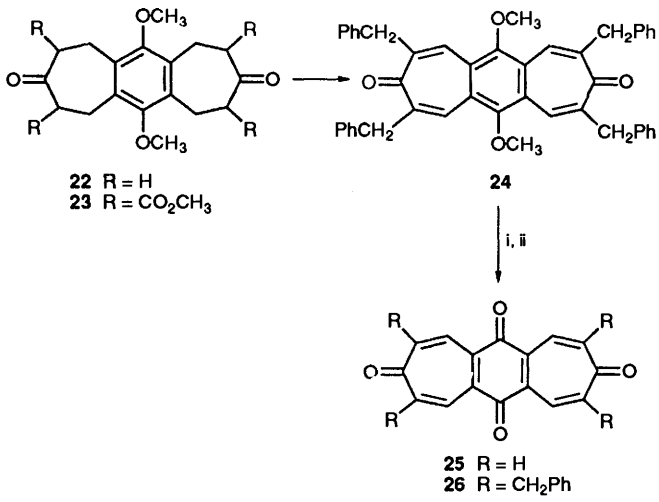
Scheme 3 *Reagents:* i, $2Br_2$; ii, Et_3N

Nucleophilic Substitution of the Bromide **17**.—(*a*) *Synthesis of* 6,8-*diphenoxybenzocycloheptene*-1,4,7-*trione* **5**. The bromide **17** was treated with sodium phenoxide in DMF[4] (80 °C, overnight) to give 1,4-dimethoxy-6,8-diphenoxybenzocyclohepten-7-one **19**. Usual oxidation of **19** with CAN gave the corresponding trione **5**.

(*b*) *Synthesis of* 6,8-*bis*(*phenylthio*)*benzocycloheptene*-1,4,7-*trione* **3**. The bis(phenylthio) analogue **20** of compound **19** was obtained quantitatively from **17**. The reaction was found to proceed more smoothly (80 °C, 1 h) than in the case of compound **19**. The yield of compound **20** was considerably improved with this route *via* the dibromide **17** (previous method; less than 15% from **12**).[1] Oxidation of **20** gave **3** in high yield.[1]

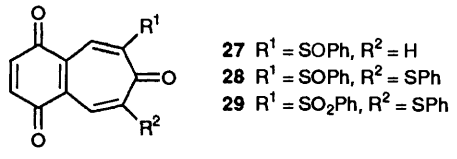
Synthesis of 2,4,8,10-*Tetrabenzylbenzo*[1,2;4,5]*dicycloheptene*-3,6,9,12-*tetraone* **26**.—The reaction of 6,12-dimethoxy-1,2,4,5,7,8,10,11-octahydrobenzo[1,2;4,5]dicycloheptene-3,9-dione **22**,[6] prepared from 2,4,8,10-tetramethoxycarbonyl derivative **23**,[3] with a large excess of benzaldehyde gave 6,12-dimethoxy-2,4,8,9-tetrabenzylbenzo[1,2:4,5]dicycloheptene-3,9-dione **24** in low yield. Ether-cleavages of **24**, followed by nitric acid oxidation[1] gave tetraone **26** in a moderate yield. (Scheme 4).

First Examples of the Synthesis of Benzocycloheptene-1,4,7-*trione Substituted with a Strong Electron-withdrawing Group on* C-6.—As we have already uncovered, benzocyclohepten-7-one substituted with electron-withdrawing groups on C-6 and C-8 easily underwent ring contraction under aqueous oxidation



Scheme 4 *Reagents and conditions:* i, HBr/HOAc; ii, HNO_3 (*d* 1.38)

conditions.[3] Therefore, we examined the oxidation of the sulfides **2** and **3** under anhydrous conditions and also performed the work-up process with protection from contact with water. Thus, the triones **2** and **3** were treated with purified mCPBA (*m*-chloroperbenzoic acid) in anhydrous chloroform in the presence of powdered dipotassium hydrogen phosphate. When the reaction was complete, the reaction mixtures were filtered and the filtrates were chromatographed directly on silica gel to give pure monosulfoxides **27** and **28** in moderate yields, respectively. In the case of oxidation of the sulfide **3**, even with use of an excess of mCPBA the product was the monosulfone **29** rather than the disulfoxide.

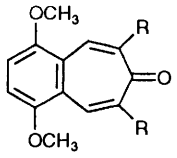


In an attempt to synthesize 6-cyanobenzocycloheptene-1,4,7-trione, which has been estimated by MNDO calculations[3] to give a reduction potential of −0.076 V based on the energy level of the LUMO (−2.43 eV),[3] we used the Dieckmann condensation technique on 2,3-bis(2-cyanoethyl)-1,4-dimethoxybenzene **30**[7] shown in Scheme 5. Acid hydrolysis of the condensation product gave 6-cyano-1,4-dimethoxy-5,6,8,9-tetrahydrobenzocyclohepten-7-one **31**. The precursor **34** was obtained through phenylselenylation of an active hydrogen on **31**, followed by oxidative elimination of the phenylselenoxide and then dehydrogenation. Attempted direct dehydrogenation of **31** with excess of NBS followed by triethylamine gave, in addition to the expected compound **34**, 6-bromo-8-cyano-1,4-dimethoxybenzocyclohepten-7-one **35** in almost the same amount.

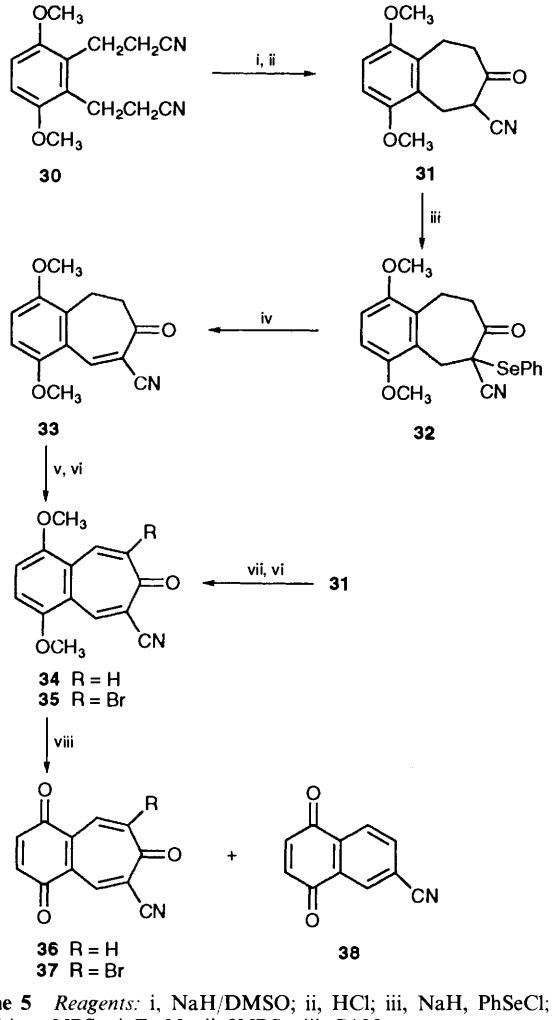
The solid state oxidation described earlier for the synthesis of 7-dicyanomethylenebenzocycloheptene-1,4-dione[3] was performed on the 6-cyano precursor **34** and gave a product thought to be a mixture composed of 6-cyano-1,4-naphthoquinone **38** and the expected quinotropone **36**, from which the latter could not be isolated in a pure state. On the contrary, 6-bromo-8-cyanobenzocycloheptene-1,4,7-trione **37** was isolated in poor yield by the solid state oxidation of the corresponding hydroquinone dimethyl ether **35**.

Physical Properties.—^1H *NMR Spectra of hydroquinone dimethyl ethers; the quinone precursors.* The ^1H NMR signals due to the methoxy protons of the hydroquinone dimethyl

Table 1 Proton signals (ppm) for the ^{1}H NMR spectra of hydroquinone dimethyl ethers



	δ_H					
	18 (R = H)	**10** (R = CH_2Ph)	**11** (R = CH_2PhNMe_2)	**19** (R = OPh)	**20** (R = SPh)	**17** (R = Br)
OMe	3.92	3.78	3.80	3.87	3.54	3.97
5-H, 9-H	8.21d	8.22	8.18	8.45	7.96	9.21
2-H, 3-H	7.06	6.89	6.89	7.02	6.78	7.14
Angles (°) at X in XPh		117.8		119.2	103.1	



Scheme 5 *Reagents:* i, NaH/DMSO; ii, HCl; iii, NaH, PhSeCl; iv, mCPBA; v, NBS; vi, Et_3N; vii, 2NBS; viii, CAN

ethers substituted with benzyl, phenoxy or phenylthio groups at position(s) 6 and/or 8 are found at a higher magnetic field than those without substituents or with bromine atoms at these positions (Table 1).

The bond angles at the atoms connecting the tropone ring with the phenyl group obtained from the X-ray structure of the corresponding quinones[1] are shown at the bottom of Table 1. From the table, it can be seen that the signals due to the methoxy groups have a tendency to move to higher field as the angles decrease. This means that the chemical shifts of the methoxy group must have been affected by the ring current on the benzene ring(s)[8] in the substituents on C-6 and C-8. The signals due to the protons on C-5 and C-9 of benzyl derivatives **10** and **11** do not shift much from those of the unsubstituted one, therefore it seems reasonable to assume that they are not affected by the ring current on benzene ring(s). The reason that the signals due to the protons at positions 5 and 9 shift to lower field when the compound had substituents such as a bromine or phenoxy group on C-6 (and C-8) and shift to higher field when it is substituted with phenylthio groups, is mainly attributed to the electron-withdrawing abilities (σ_I Br, 0.42; OPh, 0.38; H, 0.0; CH_2Ph, 0.03) of the bromine and phenoxy groups in the former case and to a balance between the resonance and inductive effects of the phenylthio group in the latter case.

The unusually large downfield shift caused by bromine substitution at C-6 and C-8 may be partly attributed to a deformation[9] of the electron cloud of the protons pressed by the neighbouring bromine atom. The ^{1}H NMR signals for the quinotropones are given in Table 3.

^{13}C *NMR Spectra.* The higher field-shifts of signals due to the quinone-carbonyl caused by substitution on C-6 and C-8 are less than 3 ppm. The shifted values are in the order: bromine (the largest), phenylsulfonyl, phenoxy, phenylthio and benzyl groups. On the contrary, as discussed earlier,[10] the higher-field shift of the signals due to the tropone-carbonyl was also observed in the case of substitution with phenoxy groups (**5**) and bromine atoms (**7**) to the same extent (12–13 ppm) as that with phenylthio substitution **3** (**5**, 172.6; **7**, 173.9; **3**, 173.1 ppm) on C-6 and C-8 compared with that of unsubstituted (**1**) or benzyl substituted (**4**) derivatives (**1**, 184.8; **4**, 185.8 ppm) (see Table 3).[1]

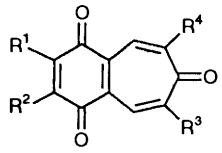
IR Spectra. In addition to the signals due to the quinone carbonyl at 1665–1680 cm^{-1},[1] the strongest of the tropone signals[1] appears at 1600–1665 cm^{-1} both with or without symmetrical benzyl substitution on C-6 and C-8, and appears at 1582–1596 cm^{-1} with phenoxy and bromine substitutions, and at 1570 cm^{-1} with phenylthio substitution (see Table 4).

Electronic spectra.[1] The longest wavelength absorption maxima for quinotropones are moved to longer wavelengths by 6,8-disubstitution as follows (Table 5): unsubstituted, 400 nm; dibenzyl, 420 nm; dibromo, 422 nm; diphenoxy, 459 nm; bis(phenylthio), 526 nm. Substitution with one phenylthio group, gives the shift marked as +92 nm but the second substitution causes only +34 nm shift.

In the case of phenylsulfinyl group, the spectra were very similar to the unsubstituted ones as shown by the maxima of the longest wavelength: R^4 = SOPh, R^3 = SPh (495 nm) nearly equal to R^4 = H, R^3 = SPh (492 nm); R^3 = SOPh, R^4 = H (405 nm) nearly equal to R^3 = R^4 = H (400 nm).

In the case of substitution with *p*-dimethylaminobenzyl

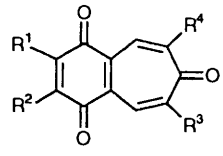
Table 2 Proton signals (ppm) for the ^{1}H NMR spectra of quinotropones



	δ_H					
Compound	**1**	**4**	**6**	**5**	**3**	**7**
R^1,R^2=	H	H	H	H	H	H
R^3,R^4=	H	CH_2Ph	CH_2PhNMe_2	OPh	SPh	Br
5-H. 9-H	7.99	7.97	7.94	7.83	7.77	8.93
2-H, 3-H	7.04	6.88	6.83	6.91	6.78	7.09

	δ_H						
Compound	**1**	**2**	**27**	**28**	**29**	**8**	**9**
R^1=	H	H	H	H	H	H	Br
R^2=	H	H	H	H	H	Br	Br
R^3=	H	SPh	SOPh	SOPh	SO_2Ph	CH_2Ph	CH_2Ph
R^4=	H	H	H	SPh	SPh	CH_2Ph	CH_2Ph
5-H	7.99	7.65	8.94	9.12	9.53	7.90	7.94
8-H	7.25	7.28	7.17	—	—	—	—
9-H	7.99	8.13	8.11	7.95	7.64	7.96	7.94
$J_{8,9}$ (Hz)	12.5	12.8	12.8	—	—	—	—

Table 3 ^{13}C NMR Carbonyl signals (ppm) for the quinotropones



	δ_C					
Compound	**1**	**4**	**6**	**5**	**3**	**7**
R^1,R^2=	H	H	H	H	H	H
R^3,R^4=	H	CH_2Ph	CH_2PhNMe_2	OPh	SPh	Br
Quinone (C=O)	186.1	185.1* (185.2)	185.3* (185.8)	183.9	184.9	183.3
Tropone (C=O)	184.8	185.2* (185.1)	185.8* (185.3)	172.6	173.1	173.9

	δ_C						
Compound	**2**	**27**	**28**	**29**	**8**	**9**	**26**
R^1=	H	H	H	H	H	Br	
R^2=	H	H	H	H	Br	Br	
R^3=	SPh	SOPh	SOPh	SO_2Ph	CH_2Ph	CH_2Ph	
R^4=	H	H	SPh	SPh	CH_2Ph	CH_2Ph	
Quinone (C=O)	185.0	184.2	184.6	184.1	178.5	176.0	—
	184.8	183.7	183.8	183.3	182.5	—	183.9
Tropone (C=O)	181.3	181.7	177.1	175.7	185.1	185.1	185.3

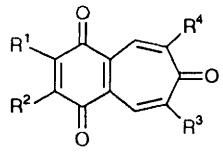
* These signals are reversible.

groups on C-6 and C-8, though the maxima seemed to show a little hypsochromic shift compared with that of the dibenzyl substitution, a new absorption maximum appeared at 578 nm. This new absorption has not been observed in the spectra of the other quinotropones substituted with simple benzyl groups, therefore, it seems to be an intramolecular CT band[11] between dimethylaminophenyl and the quinone moieties in **6**.

The shape of the electronic spectrum of the tetrabenzyl derivative **26** was very similar to that of the parent tetraone **25**, but every maximum had moved to longer wavelength by *ca.* 20–50 nm (Fig. 1).

Redox potentials. Entries 1–11 and 12–15 of Table 6 are separately arranged in the decreasing order of the first redox potentials. Comparing these data, the following general rules are drawn. The substitution of hydrogens on C-2 and C-3 with bromine atoms causes the elevation of E_1^{redox} by 0.17–0.24 V (compare entry 2 with 4, 3 with 7, and 5 with 9). On the other hand, the substitution of hydrogens on C-6 and C-8 with bromine atoms causes the elevation of E_1^{redox} by *ca.* 0.19 V

Table 4 Quinone and tropone carbonyl IR absorption bands



	ν/cm^{-1}						
Compound	**1**	**4**	**6**	**5**	**3**	**7**	
R^1,R^2=	H	H	H	H	H	H	
R^3,R^4=	H	CH_2Ph	CH_2PhNMe_2	OPh	SPh	Br	
Quinone	1668vs	1670	1665m	1678m	1668m	1673vs	
	1628s			1642m		1638m	
Tropone	1615vs	1610	1610vs	1630s	1619w		
	1590ms			1596vs	1568vs	1582s	
	ν/cm^{-1}						
Compound	**2**	**27**	**28**	**29**	**8**	**9**	**26**
R^1=	H	H	H	H	H	Br	
R^2=	H	H	H	H	Br	Br	
R^3=	SPh	SOPh	SOPh	SO_2Ph	CH_2Ph	CH_2Ph	
R^4=	H	H	SPh	SPh	CH_2Ph	CH_2Ph	
Quinone	1670s	1670s	1676s	1670s	1670s	1689s	1670m
Tropone	1610s	1610s	1598s	1610s	1650s		
	1593ms	1590m	1570m	1585m	1600vs	1600s	1604vs

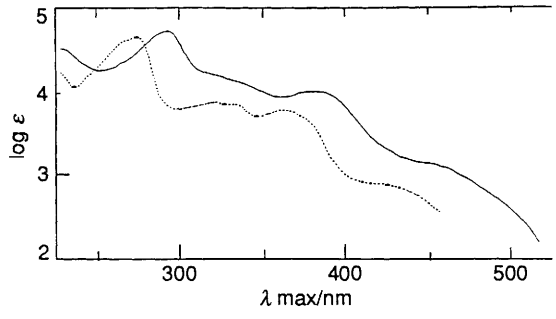
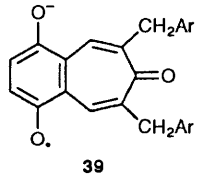


Fig. 1 Electronic spectra in dichloromethane, **25**; dotted line, **26**; solid line

(compare entry 4 with 7). When a bromine atom of **7** was substituted with a cyano group, the E_1^{redox} is raised by *ca.* 0.17 V (compare entry 1 and 4), therefore, the E_1^{redox}-elevation ability of cyano substitution for 6-H may be estimated to be 0.27 V when we assume the elevation ability of a bromine as 0.1 V (=0.19 V/2). On the other hand, substitution with a phenylsulfinyl group for 6-H caused the elevation of E_1^{redox} by 0.15 V (compare entry 13 with 7) and the substitution of phenylsulfinyl on C-6 with phenylsulfonyl group gave an elevation of E_1^{redox} of 0.09 V (compare entry 12 with 14). Therefore, the E_1^{redox}-elevation ability of phenylsulfonyl substitution for 6-H may be estimated at 0.24 V (0.15 V + 0.09 V). Thus, the order of the elevation abilities of E_1^{redox} for substitution on C-6 will be as follows: CN (0.27 V), SO_2Ph (0.24 V), SOPh (0.15 V), Br (0.10 V). This order is the same as that for the Hammett[12] σ_I values; CN (0.57), SO_2Ph (0.55 for SO_2Me), SOPh (0.50 for SOMe), Br (0.47). Therefore, the E_1^{redox}-elevation of substituents which do not have electron-donating character was found to be parallel to the strength of the inductive effect of the substituents.

In the case of the disubstitution with electron-donating groups such as phenoxy, phenylthio and benzyl groups, ΔE_1^{redox} values decrease in the order: SPh (−0.09 V), CH_2Ph (−0.07 V) and OPh (−0.03 V). The Hammett's σ_I values (OPh, 0.38; SMe, 0.23; CH_2Ph, 0.03) and also (σ_I + σ_R) values (OPh, 0.04; SMe, 0.03; SPh, −0.09) are not in line with this order.[13] From the knowledge of single crystal X-ray analysis of these quinotropones, the phenyl rings of the phenylthio groups in **3** exist in nearer and facing position to the quinone carbonyls compared with those of phenoxy or benzyl derivatives. Therefore, some part of the electron on the phenyl ring may be attracted to the quinone moiety of the quinotropone. As a result, the phenylthio group may cause a decreasing electron affinity of the quinotropone part.

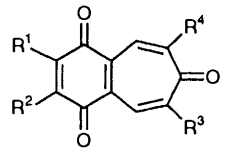
On the contrary, the second redox potentials of the disubstituted quinotropones, which correspond to the reduction of the anion radicals, increase in the increasing order of σ_I values of these substituents: H (E_2^{redox} = −0.90 V, σ_I = 0.00); CH_2Ph (E_2^{redox} = −0.78 V, σ_I = 0.03); SPh (E_2^{redox} = −0.73 V, σ_I = 0.23 as SMe); OPh (E_2^{redox} = −0.71 V, σ_I = 0.38); Br (E_2^{redox} = −0.59 V, σ_I = 0.42).[14] It is interesting to note that the dimethylamino substitution on the benzyl groups resulted in lowering of the 1st redox potential by *ca.* 0.04 V but did not affect the 2nd redox potential (compare entry 11 with 9). The former may be caused by partial electron transfer from the electron-rich dimethylaminophenyl group to the quinone moiety of **6**. The corresponding anion radical **39**, however, which had already an excess electron on the quinone moiety, has no ability to attract any electron from the dimethylaminophenyl group, therefore, the E_2^{redox} (−0.78 V) for bis(dimethylaminobenzyl)benzocycloheptene-1,4,7-trione could become the same as that of the dibenzyl derivative because they are corresponding to the reduction of the same anion radical (**39**).



39

The decrease in the reduction potential of 2,4,8,10-tetrabenzylbenzo[1,2;4,5]dicycloheptene-3,6,9,12-tetraone **26** is *ca.* 0.2 V

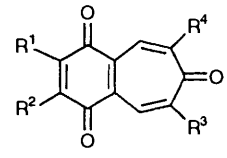
Table 5 Electronic absorption maxima [$\lambda_{max}(CH_2Cl_2)$/nm (log ε)] of the quinotropones



	λ_{max}/nm					
Compound	**1**	**5**	**3**	**28**	**27**	**2**
R^1=	H	H	H	H	H	H
R^2=	H	H	H	H	H	H
R^3=	H	OPh	SPh	SPh	SOPh	SPh
R^4=	H	OPh	SPh	SOPh	H	H
	255	—	—	230(4.42)	261(4.42)	245(4.33)
	—	289(4.34)	358(4.35)	320(4.12)	283(4.17)	323(4.15)
	400	459(3.71)	526(4.08)	495(4.01)	405(3.51)	492(3.95)

	λ_{max}/nm				
Compound	**4**	**6**	**8**	**9**	**7**
R^1=	H	H	Br	Br	H
R^2=	H	H	H	Br	H
R^3=	CH_2Ph	CH_2PhNMe_2	CH_2Ph	CH_2Ph	Br
R^4=	CH_2Ph	CH_2PhNMe_2	CH_2Ph	CH_2Ph	Br
	275(4.50)	263	278(4.61)	280(4.44)	—
	—	300	310(4.12)	332(4.00)	293(4.53)
	420(3.54)	400	438(3.40)	450(3.23)	422(3.68)

Table 6 Redox potentials[a] for the quinotropones (V in CH_2Cl_2)



Entry	R^1	R^2	R^3	R^4	E_1^{redox}	E_2^{redox}	log *K*sem
1	H	H	Br	CN	+0.05		
2	Br	Br	Br	Br	+0.045	−0.62	11.4[b]
3	Br	Br	H	H	−0.085	−0.73	11.1[b]
4	H	H	Br	Br	−0.12	−0.59	8.0
5	Br	Br	CH_2Ph	CH_2Ph	−0.15	−0.66	8.6
6	H	Br	CH_2Ph	CH_2Ph	−0.26	−0.73	8.0
7	H	H	H	H	−0.31	−0.90	10.2
8	H	H	OPh	OPh	−0.34	−0.71	6.4
9	H	H	CH_2Ph	CH_2Ph	−0.38	−0.78	6.8
10	H	H	SPh	SPh	−0.40	−0.73	5.6[c]
11	H	H	$C_6H_4PhNMe_2$	$C_6H_4PhNMe_2$	−0.42	−0.78	6.1
12	H	H	SPh	SO_2Ph	−0.14	−0.59	7.8
13	H	H	H	SOPh	−0.16	−0.64	8.5
14	H	H	SPh	SOPh	−0.23	−0.63	7.0
15	H	H	H	SPh	−0.37	−0.86	8.5

[a] The cyclic voltammograms were run on a potentiometer, Model CV-1B (B.S.S. Inc.) using platinum wire electrodes (Ag/AgCl) at room temperature. A solution of each substrate was made in dichloromethane containing tetrabutylammonium perchlorate (10^{-1} mol dm^{-3}) as the supporting electrolyte. Ferrocene was added after several runs as an internal standard (+0.4V). Graphite rod was used as a working electrode. [b] See ref. 3. [c] See ref. 6.

compared with that of the unsubstituted analogue **25** (Table 7) which is more than double (Δ 0.14 V) the difference (ΔE_1) between the E_1 of compound **4** and that of **1**.

Molecular Structure.—The molecular structures of **4**, **5** and **9** with the numbering schemes for atoms are shown in Figs. 2–4, respectively.

The bond lengths in the quinotropone frameworks in compounds **4**, **5** and **9** along with those in **3** and benzoquinone[15] are summarized in Table 8. The bond lengths of C-1–C-10 and C-4–C-11 in **4**, **5** and **9** are in the range 1.49–1.51 Å. They are remarkably long compared with those of the corresponding bonds in benzoquinone (1.467 Å) as shown in Table 8.

The results of the MNDO[16] calculations also showed the same trend. These facts indicate that the delocalization of π-electrons over the quinotropone ring is divided into two parts (the enedione moiety O1–C1–C2–C3–C4–O2 and tropone part). The same tendency has been found for a few quinotropones investigated previously.[1]

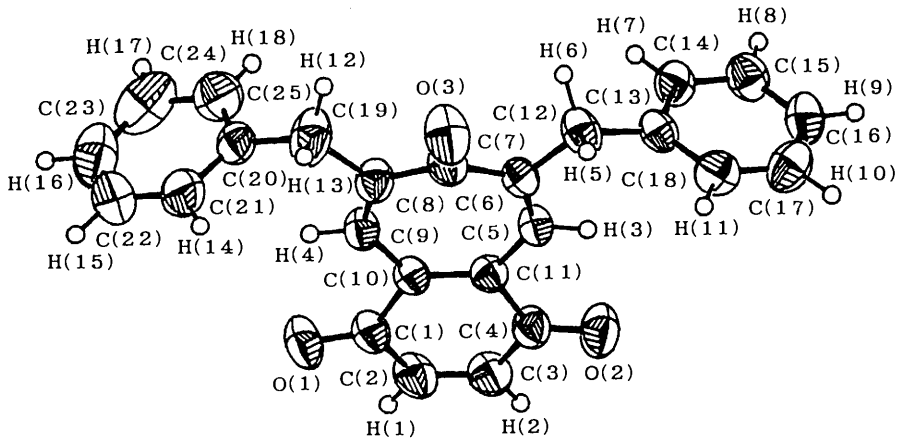


Fig. 2 Molecular structure and numbering scheme of atoms in compound **4** (ORTEP[24] drawings)

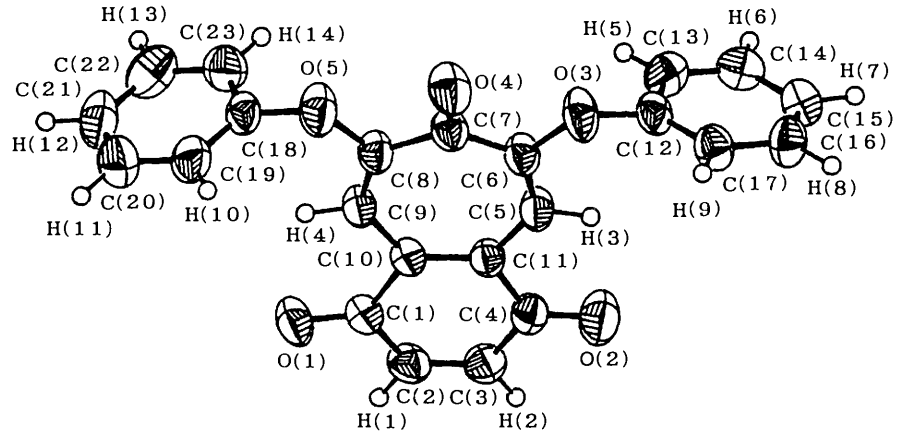


Fig. 3 Molecular structure and numbering scheme of atoms in compound **5** (ORTEP[24] drawings)

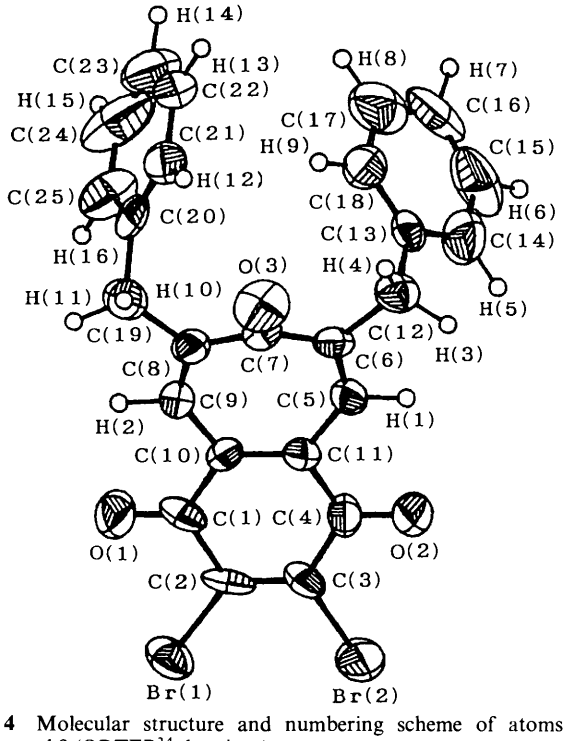


Fig. 4 Molecular structure and numbering scheme of atoms in compound **9** (ORTEP[24] drawings)

The side and top views of the molecules of **4**, **5** and **9** are shown in Fig. 5. Quantitative measures of the non-planarity of the quinotropone rings shown in Fig. 5 are provided in Table 9.

It should be noted that the phenyl groups in **9** are not facing towards the quinone carbonyls (the dihedral angle of C-5–C-6–C-12–C-13 = *ca.* 90°), while the phenyl groups in **4** and **5**, as well as those in other quinotropone derivatives reported previously,[1] are facing the quinone carbonyls (for example, the dihedral angle for compound **4** = *ca.* 0°). For the convenience of discussion, we define here two types (type A and B) of conformations concerning the orientation of the phenyl groups as shown in Fig. 5. The MNDO calculation on **5** started from the observed conformation (type A) as an initial structure was performed by changing the coordinates of all atoms to optimize the energy. This calculation gave the structure of type A. The calculation on **9** also started from the observed structure (type B) converged to a structure of the type B. For compound **9**, we also examined the calculations starting from a structure of type A derived from the observed conformation of **4** by replacing the hydrogen atoms on C-2 and C-3 by two bromine atoms. In this case, a molecular structure of type B was the optimized one at the final stage of the MNDO calculation. These results suggest that the molecular conformations of **5** and **9** found in the crystalline state are the same as those expected to be stable in the gaseous state. In the case of compound **4**, however, the MNDO calculation started from the observed conformation (type A) converged to a type B molecule, indicating that the

Table 7 Redox potentials for benzo[1,2;4,5]dicycloheptene-3,6,9,12-tetraones (V in CH_2Cl_2)

Entry	Compound	E_1^{redox}	E_2^{redox}	log *K*sem
1	**25**	−0.14	−0.78	10.3[a]
2	**26**	−0.34	−0.76	7.9

[a] See ref. 3.

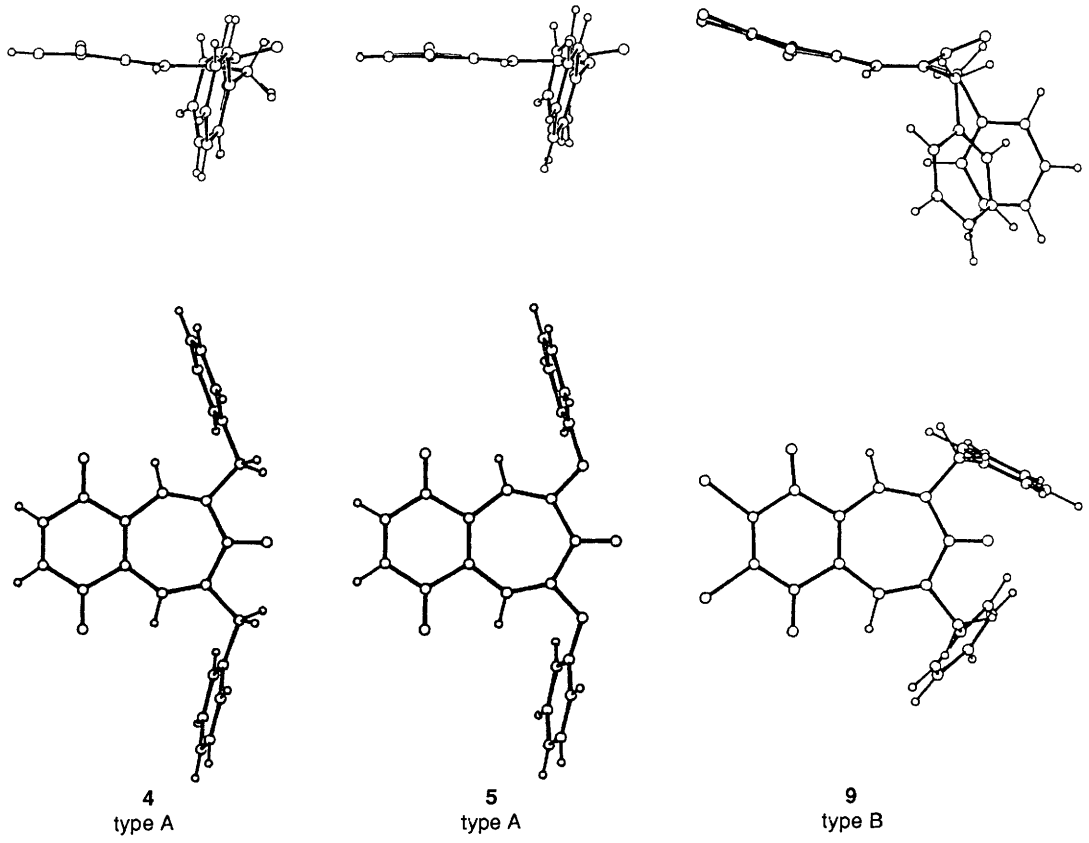


Fig. 5 Side and top views of the molecules of **4**, **5** and **9**

Table 8 Observed bond lengths (Å) for **3**, **4**, **5**, **9** and benzoquinone

	Bond length/Å				
Bond[a]	3	4	5	9	Benzoquinone[b]
C(1)–C(2)	1.467	1.467	1.467	1.525[c]	1.467
C(2)–C(3)	1.313	1.323	1.321	1.346	1.312
C(3)–C(4)		1.456	1.465	1.444	1.467
C(4)–C(11)		1.507	1.504	1.500	
C(10)–C(11)	1.375	1.368	1.375	1.361	
C(1)–C(10)	1.504	1.509	1.507	1.490	
C(1)–O(1)	1.213	1.213	1.219	1.216	1.212
C(4)–O(2)		1.224	1.219	1.210	
C(5)–C(11)		1.425	1.418	1.418	
C(5)–C(6)		1.356	1.353	1.367	
C(6)–C(7)	1.466	1.467	1.459		
C(7)–C(8)	1.459	1.464	1.469	1.462	
C(8)–C(9)	1.365	1.355	1.353	1.358	
C(9)–C(10)	1.409	1.434	1.419	1.417	
C(7)–O(3)	1.227	1.236	1.221	1.209	

[a] For numbering of the atoms, see Figs. 2–4. [b] See ref. 15. [c] This bond length is unusually long.

Table 9 Deviations of atoms from the least-squares plane of C(5)–C(6)–C(8)–C(9) ($\times 10^3$ Å) and inter plane angles (°) for **3**, **4**, **5** and **9**

	Deviation ($\times 10^3$ Å)			
Atom	3	4	5	9
O(3)	147(8)	541(5)	334(4)	815(16)
C(5)	0(4)	0(3)	−2(3)	7(11)
C(6)	0(3)	0(3)	2(3)	−9(11)
C(7)	59(5)	220(3)	148(3)	350(12)
C(8)		0(3)	−2(3)	8(10)
C(9)		2(5)	2(3)	−8(11)
C(10)		171(6)	92(3)	253(14)
C(11)	43(5)	159(5)	78(3)	291(14)
	Inter plane angles (°)			
(5-6-8-9)-(6-7-8)[a]	4.9(4)	18.5(3)	11.6(2)	28.4(10)
(5-6-8-9)-(5-9-10-11)	2.2(3)	8.3(2)	4.3(2)	13.7(7)
(5-9-10-11)-(1-4-10-11)	0.4(3)	0.7(2)	1.2(2)	3.8(7)
(1-4-10-11)-(1-2-3-4)	0.0(4)	7.7(2)	6.1(2)	9.3(7)

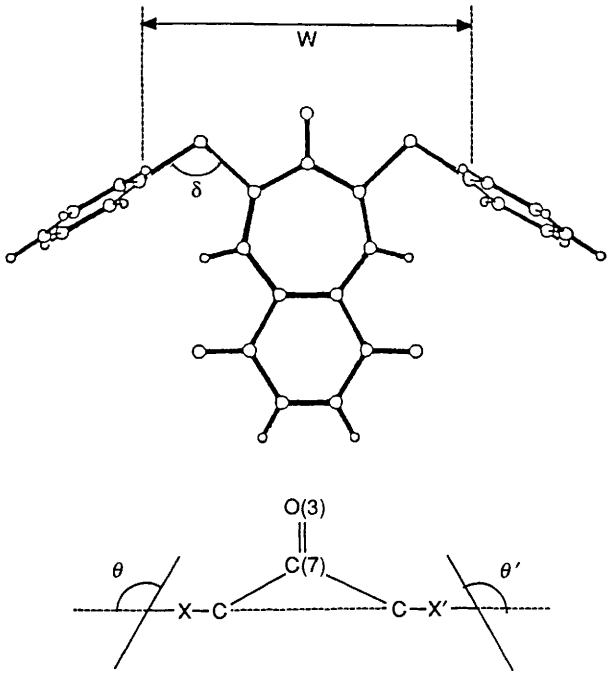
[a] (5-6-8-9)-(6-7-8) means the angle between C(5)–C(6)–C(8)–C(9) and C(6)–C(7)–C(8) planes.

stable form of the free molecule of **4** in the gaseous state may be different from that found in the crystal.

A few important geometric features of the molecular structures of compounds **3**–**5** to characterize the differences between them are summarized in Fig. 6. The major difference comes from the spatial arrangement of the phenyl groups against the quinotropone ring. The bond angles (δ) at the bridging methylene group (-CH_2-) and the oxygen atom (-O-) in compounds **4** and **5** in the crystal (*ca.* 119° and *ca.* 118°) are considerably larger than an sp^3 angle. The steric repulsion between the quinone ring and the phenyl groups seems to be a possible factor to determine the angle δ as judged from the following facts: (1) the length of the bridging group in compound **3** (-S-) is considerably longer than those in the compounds **4** or **5** (-CH_2- or -O-) and therefore, the repulsive interaction in **3** is weak enough to tolerate the small values of δ (103°); (2) in the case of compound **9**, where the above repulsive interaction between the quinone ring and the phenyl groups is absent, δ is 112°. The loss of the total molecular energy due to the deviation of δ from *ca.* 112° for **9** to *ca.* 119° for **4** was estimated by the MNDO method to be the order of 10 kJ mol^{-1}. Therefore the relatively large covalent angle found for **4** (*ca.* 119°) is not surprising.

Crystal Structure of 6,8-*Bis*(*RX*)-*benzocycloheptene*-1,4,7-*triones* **4**, **5** *and* **9**.—It may be expected from the similarity of the molecular structures of **3**, **4** and **5** that these compounds have similar crystal structures. In fact, the crystal structures of compounds **4** and **5** are essentially identical and they may be regarded as pseudo-isomorphic because the unit cell parameters of **4** are almost the same as those of **5** (see Table 10 below). The crystal structure of **4** (or **5**) is characterized by a type of layer structure; namely, as can be seen from Fig. 7, a layer of quinotropone moieties is sandwiched by those of phenyl groups which are almost parallel to the crystallographic *bc* plane. On the other hand, the present X-ray work revealed that the crystal structure of **4** (or **5**) is quite different from that of the compound **3**. Thus in a crystal of **4** (or **5**), there unfortunately exists no segregated stacking which is one of the fundamental requirements for organic conductors. The crystal of compound **9** has neither the local overlap of quinotropone ring nor the segregated stacking. This observation seems to be consistent with the molecular structure of **9** having the phenyl groups oriented almost perpendicular to the quinotropone ring (see Fig. 5).

The Stability of Molecular Overlap.—The overlaps of molecules found in the crystals of **3** and **5** are shown in Fig. 8. Compound **4** exhibits an overlap similar to that of compound **5**, but not to **3**. The overlap of molecules of **5** (or **4**) is poorer than that of **3** and the interplanar distances are considerably longer (3.70 and 3.85 Å for **5** and **4**, respectively) than that for compound **3** (3.30 Å). It is interesting to note that the arrangement of overlapping of molecules of **3** is parallel, while that of **5** antiparallel. In order to examine the stability of a



	C(6)–X (Å) C(8)–X (Å)	δ (°) δ′ (°)	W (Å)	θ(°) θ′(°)
3	1.759	103.1	8.0	97.0
4	1.513	118.8	7.5	99.2
	1.518	116.8		97.2
5	1.372	119.5	7.1	103.7
	1.367	118.8		95.8

Fig. 6 A few important geometric data of the molecular structures of compounds **3**–**5** to characterize the differences between them

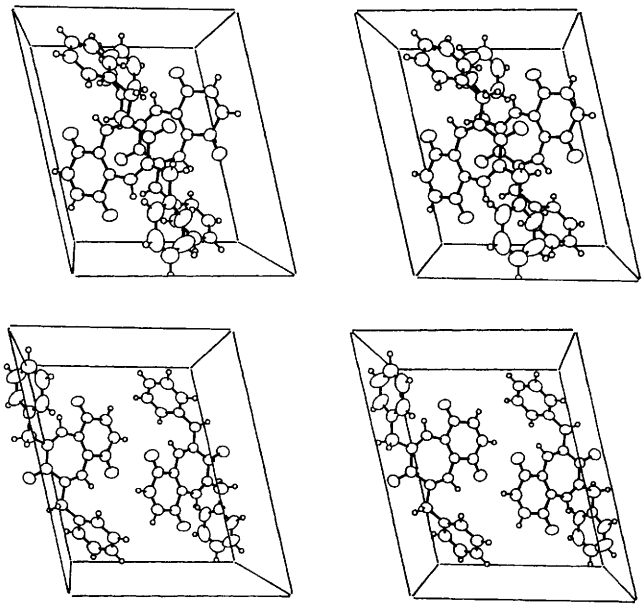


Fig. 7 Packing of molecules in the crystal of **4** (the crystal structure is shown by two separate figures for simplicity)

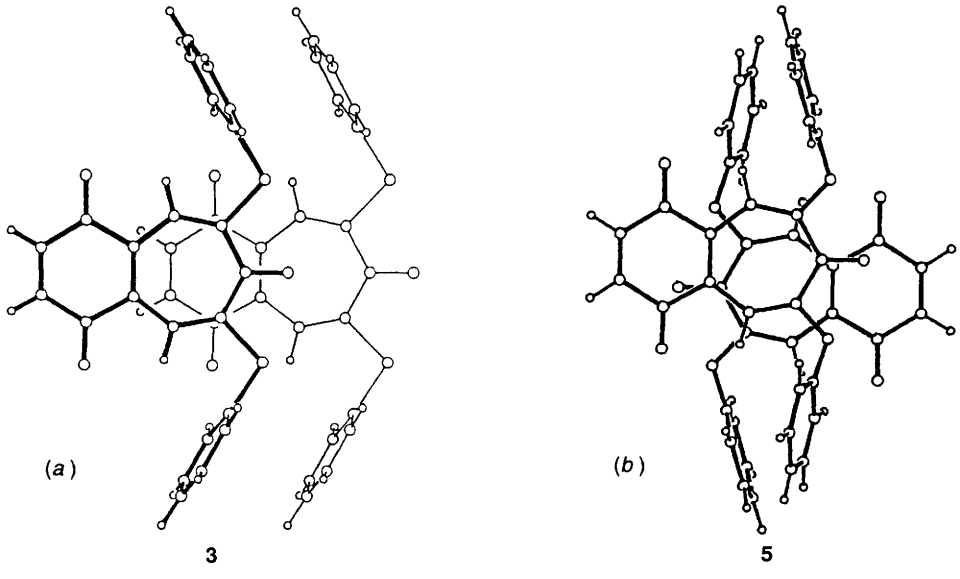


Fig. 8 Overlap of molecules in the crystal: (*a*) for compound **3**; (*b*) for compound **5**

Table 10 Lattice constants, unit cell volume (V) and lattice energies (E) obtained by crystal molecular packing analysis for compounds **4** and **5**

Compound	Name[a]	Space group	a/Å	b/Å	c/Å	β/°	V/Å^3	E/kJ mol^{-1}
4	Crystal-(obs)	$P2_1/c$	13.089	13.943	10.530	103.19	1871.1	−178.5
	Crystal-P-(**4**obs)	$P2_1/c$	13.055	13.647	10.442	102.77	1814.3	−180.4
5	Crystal-(obs)	$P2_1/c$	12.943	13.269	10.472	100.47	1767.0	−170.9
	Crystal-P-(**5**obs)	$P2_1/c$	12.928	12.968	10.440	99.82	1724.6	−173.6
	Crystal-C-(**5**obs)	*Cm*	7.451	27.002	5.036	106.99	969.0	−144.7
	Crystal-P-(**5i**)	$P2_1/c$	13.494	15.328	9.847	102.73	1986.7	−136.4
	Crystal-C-(**5i**)	*Cm*	7.376	28.936	4.764	110.84	950.2	−160.5
	Crystal-P-(**5i'**)	$P2_1/c$	13.198	13.280	10.322	102.76	1764.5	−172.4
	Crystal-C-(**5i'**)	*Cm*	7.439	28.445	4.925	110.42	976.7	−144.8

[a] For the meanings of obs, **4**obs, **5**obs, **5i** and **5i'**, see text.

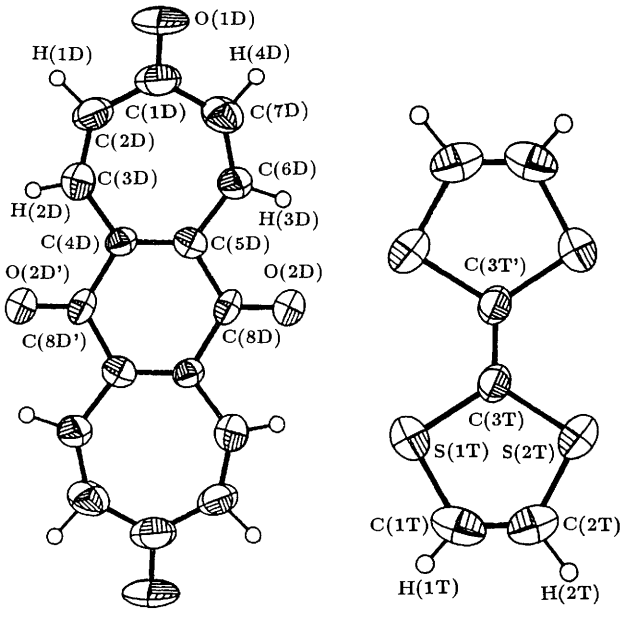


Fig. 9 Molecular structure and the numbering scheme of atoms in the **25**-TTF complex (ORTEP[24] drawings)

parallel arrangement of the molecules of **5**, we estimated the energy of a molecular cluster consisting of two molecules of **5** with use of PCK83 program[17] (for the program, see Experimental section below). When the potential energy of a model cluster was optimized starting from an initial arrangement similar to that of **3** shown in Fig. 5(*a*), the calculation converged to a final structure almost identical to the initial one, indicating that the parallel arrangement of molecules **5** could also exist in the cluster. In practice, this type of molecular arrangement of **5** has not been found in the crystalline state (see below).

Calculations of Lattice Energy.—Table 10 lists the lattice energies of compound **4** and **5** estimated by calculations using PCK83 program.[17] The lattice energies of Crystal-(obs) of compounds **4** and **5** were calculated, without optimization, on the basis of the observed crystal structures. When the lattice energy of each compound was optimized starting from the observed crystal structure, Crystal-P-(**4**obs) and Crystal-P-(**5**obs) were obtained. As can be seen from Table 10, the lattice constants, unit cell volumes and the lattice energies of these artificial crystals obtained by the calculation are in fairly good agreement with those for the observed crystals [Crystal-(obs) of compounds **4** and **5**], indicating that the crystal structures of these compounds can almost be reproduced by the calculation. In order to check the contribution of Coulomb term to the lattice energy, the lattice energy calculation for **5** was repeated by setting the electrical charges on the atoms to be zero. The structure obtained without Coulomb term was in good agreement with Crystal-P-(**5**obs), although the lattice becomes less stable by about 12 kJ mol^{-1}. This observation suggests that the dominant factor effective to the packing of molecules is the geometry of the molecule.

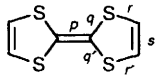
The packing of molecules in the crystal of **5** (or **4**) (space group $P2_1/c$) is completely different from that of compound **3** (space group *Cm*). As can be seen from Fig. 6, there are slight but appreciable differences between the molecular structures of **3** and **5** (or **4**), although their overall geometries bear great resemblance to each other. Thus, as an attempt to examine the effect of molecular geometry on the crystal structure, lattice energies of several artificial crystals of **5** were estimated by using PCK83 program. When an optimization of lattice energy was performed for an initial structure including the observed molecules of **5** (**5**obs) packed into an artificial crystal lattice derived from that of compound **3** (space group *Cm*), the optimized structure [Crystal-C-(**5**obs) in Table 10] had a lattice energy of *ca.* −145 kJ mol^{-1} compared to −171 kJ mol^{-1} for Crystal-(obs) of **5** [or −174 kJ mol^{-1} for Crystal-P-(**5**obs)]. For further examination, lattice energies were calculated for a few artificial crystals composed of two kinds of imaginary molecules of compound **5** (**5i** and **5i'**): they were derived from the observed molecules of **3** and **4** by replacing the S atoms and CH_2 groups with O atoms, respectively. When the molecules of **5i** were packed into the crystal lattices of $P2_1/c$ and *Cm*, the optimized crystal structures showed the lattice energies of *ca.* −136 kJ mol^{-1} [Crystal-P-(**5i**)] and *ca.* −161 kJ mol^{-1} [Crystal-C-(**5i**)], respectively. On the contrary, in the case of the molecule of **5i'**, the crystal of $P2_1/c$ obtained by the calculation [Crystal-P-(**5i'**)] was found to be more stable than that having *Cm* symmetry [Crystal-C-(**5i'**)]. The results of these calculations suggest that a crystal lattice of space group $P2_1/c$ is more favourable for the packing of molecules having structures similar to the observed molecules of **5** (or **4**).

Complex Formation of Benzo[1,2;4,5]*dicycloheptene*-3,6,9,12-*tetraone* **25** *with TTF.*—Among the tropone-annelated quinones we have studied, benzo[1,2;4,5]dicycloheptene-3,6,9,12-tetraone **25**, which has no substituent, showed the highest reduction potential. Therefore we examined the complex formation of this compound with TTF,[18] which has been known to give complexes of metallic character with some electron acceptors, and obtained a complex as black needles. In order to determine the extent of the electron transfer between the donor and acceptor, and the molecular packing in the crystal, single crystal X-ray analysis was performed.

X-Ray Crystal Structure of the **25**–*TTF Complex.*—The molecular structures of **25** and TTF in the **25**–TTF complex are shown in Fig. 9.

The atom numbering scheme is also given in the figure. The crystal structure of the **25**–TTF complex is characterized by the closed packing of the columns formed by an alternate stacking

Table 11 Bond lengths in the TTF molecule found in the pure material and in the **25**–TTF complex



40

Compound	Bonds[a]					
	p	*q*	*q'*	*r*	*r'*	*s*
TTF	1.349(3)	1.756(2)	1.758(2)	1.732(2)	1.729(2)	1.314(3)
25–TTF	1.346(10)	1.745(8)	1.757(8)	1.743(9)	1.727(9)	1.310(12)

[a] For definition of the bonds, see structure **40**.

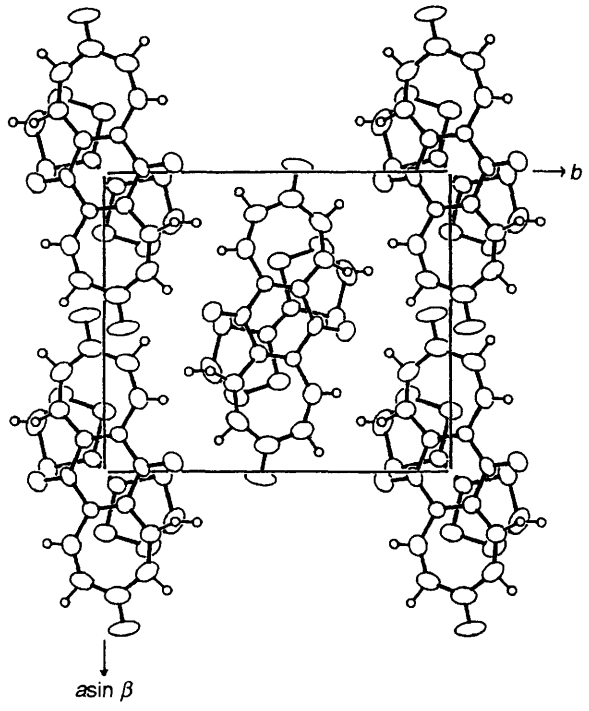


Fig. 10 Crystal structure of the **25**–TTF complex projected along the crystal *b* axis onto the (*ab*) plane

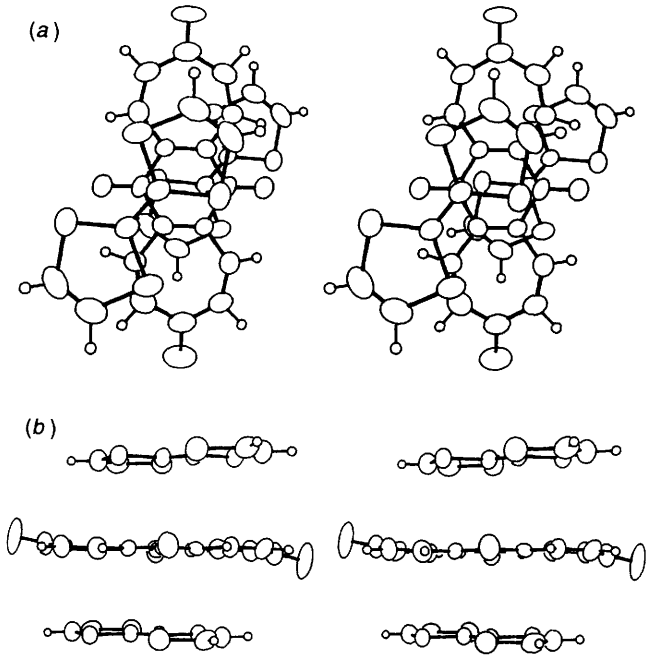


Fig. 11 Overlap of molecules in a column found for the **25**–TTF complex. (*a*) Top view, (*b*) side view (stereo drawings)

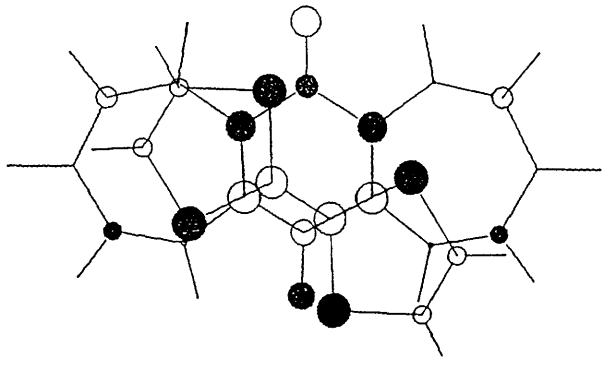


Fig. 12 The signs of LUMO of acceptor molecule and those of HOMO of the donor molecule in the arrangement of the molecules found in **25**–TTF complex

of compound **25** and TTF (see Fig. 10). The overlap of molecules in a column is illustrated in Fig. 11.

The bond lengths of the TTF molecules found in pure TTF [19] and in the **25**–TTF complex are given in Table 11.

The overlapping of the donor and the acceptor seems favourable for charge-transfer interaction as judged by the signs of the LUMO of the acceptor and the HOMO of the donor molecules as shown in Fig. 12.

However, though the bond lengths of *q* and *r* found in the TTF molecule in the **25**–TTF complex exhibited slight differences from those of the corresponding pure TTF, the bond length of *p* did not show any change. This fact indicates that there is little electron transfer between **25** and TTF. The distance between the molecular planes of TTF and **25** (*ca.* 3.4 Å) is comparable with the van der Waals contact, in accord with the small amount of charge transfer just mentioned.

For a discussion on the charge transfer between **25** and TTF, it is relevant to compare the molecular structures of **25** in its pure crystal and in the **25**–TTF complex. Unfortunately the crystal structure of **25** has not been determined because the quality of the single crystal of **25** was poor.

Experimental

General.—Melting points were determined with a Yanagimoto melting-point apparatus and are uncorrected. NMR spectra were taken on JEOL Model GX400 or FX100 FT-NMR spectrometers. *J*-Values are expressed in Hz. IR spectra were recorded on a JASCO Model A-102 spectrometer or a Shimadzu Model FTIR-8500 spectrometer, UV spectra on a Hitachi recording spectrometer 323 or a Shimadzu Model UV-160A spectrometer with colour *X*–*Y* plotter Model P/N 206-15788, and mass spectra on a JEOL Model AX-500. In preparations, extracts containing organic solvents were dried

over sodium sulfate. Preparative column chromatography was carried out on silica gel (Merck, Kieselgel 60). Analytical TLC was performed with silica gel (Merck, Kieselgel 60 PF_{245}, TLC Plates).

6,8-*Dibenzyl*-1,4-*dimethoxybenzocyclohepten*-7-*one* **10**.—To a hot solution of 1,4-dimethoxy-5,6,8,9-tetrahydrobenzocyclohepten-7-one **12** (2.30 g, 10.4 mmol) in anhydrous *tert*-butanol (40 cm^3) were added benzaldehyde (3.74 g, 35.2 mmol) and potassium *tert*-butoxide (3.90 g, 34.8 mmol) each in one portion, under a nitrogen atmosphere. After refluxing the reaction mixture for 45 min, yellow crystals separated. After cooling, the mixture was diluted with water (20 cm^3) and filtered. The crude crystals formed were dissolved in chloroform, washed with water and brine, and then dried. Evaporation of the solvent, followed by recrystallization of the residual solid from ethyl acetate gave yellow crystals of the *title compound* **10** (2.48 g, 60%), m.p. 142–144 °C (Found: C, 81.7; H, 6.15. $C_{27}H_{24}O_3$ requires C, 81.78; H, 6.11%); δ_H(400 MHz; $CDCl_3$) 3.78 (6 H, s), 4.05 (4 H, s), 6.89 (2 H, s), 7.15 (2 H, m), 7.21 (8 H, m) and 8.22 (2 H, s); δ_C(100 MHz; $CDCl_3$) 41.8 (t), 56.7 (q), 111.6 (d), 125.9 (s), 125.9 (d), 128.2 (d), 129.1 (d), 131.2 (d), 140.4 (s), 144.4 (s), 144.5 (s), 151.9(s) and 187.2 (s); $\nu_{max}(CHCl_3)/cm^{-1}$ 1595, 1460, 1455, 1415, 1260 and 1090; $\lambda_{max}(CH_2Cl_2)/nm$ 233 (log ε 4.52), 303 (4.53) and 380 (3.62); *m*/*z* (Found: M^+ 396.1702. $C_{27}H_{24}O_3$ requires *M*, 396.172 54) 396 (100), 368 (95), 353 (65), 191 (30), 138 (30) and 91 (35).

1,4-*Dimethoxy*-6,8-*bis*(p-*dimethylaminobenzyl*)*benzocyclohepten*-7-*one* **11**.—Compound **11** was obtained in 70% yield with use of *p*-dimethylaminobenzaldehyde in place of benzaldehyde under similar condition to that described above for the preparation of **10**. *Compound* **11** m.p. 182–183 °C (Found: C, 77.05; H, 7.2; N, 5.95. $C_{31}H_{34}N_2O_3$ requires C, 77.15; H, 7.10; N, 5.80%); δ_H(400 MHz; $CDCl_3$) 2.87 (12 H, s), 3.80 (6 H, s), 3.96 (4 H, s), 6.64 (4 H, d, *J* 8.8), 6.89 (2 H, s), 7.09 (4 H, d, *J* 8.8) and 8.18 (2 H, s); δ_C(100 MHz; $CDCl_3$) 40.8 (t), 40.9 (q), 56.8 (q), 111.3 (d), 113.1 (d), 126.1 (s), 128.8 (s), 129.8 (d), 130.5 (d), 145.4 (s), 149.3 (s), 151.9 (s) and 187.7 (s); $\nu_{max}(CHCl_3)/cm^{-1}$ 1610, 1595, 1515, 1455, 1405 and 1085; *m*/*z* (Found: M^+ 482.2560. $C_{31}H_{34}N_2O_3$ requires *M* 482.2569), 482 (38), 361 (100), 332 (15) and 318 (32).

6,8-*Dibenzylbenzocycloheptene*-1,4,7-*trione* **4**.—To a solution of **10** (370 mg, 0.93 mmol) in a mixture of chloroform (5 cm^3) and acetonitrile (5 cm^3) was added dropwise an aqueous solution of CAN (1.27 g, 2.30 mmol; 4 cm^3) at room temperature. After stirring for 1.5 h, the reaction mixture was diluted with chloroform (100 cm^3) and washed with water and brine, and then dried. Evaporation of the solvent, followed by chromatographic separation on silica gel (benzene) gave orange crystals **4** (300 mg, 88%), m.p. 133.5–135 °C (from benzene) (Found: C, 81.8; H, 4.9. $C_{25}H_{18}O_3$ requires C, 81.94; H, 4.95%); δ_H(400 MHz; $CDCl_3$) 4.06 (4 H, s), 6.88 (2 H, s), 7.12–7.25 (10 H, m) and 7.97 (2 H, s); δ_C(400 MHz; $CDCl_3$) 42.1 (t), 126.6 (d), 128.6 (d), 129.2 (d), 129.4 (d), 133.9 (s), 137.1 (d), 138.3 (s), 154.9 (s), 185.1 (s) and 185.2 (s); $\nu_{max}(CHCl_3)/cm^{-1}$ 1670, 1610, 1290 and 850; *m*/*z* (Found: M^+ 366.1240. $C_{25}H_{18}O_3$ requires *M* 366.1256) 366 (100), 338 (10), 275 (40), 247 (55) and 91 (70). For other spectral data, see the text.

6,8-*Bis*(p-*dimethylaminobenzyl*)*benzocycloheptene*-1,4,7-*trione* **6**.—To a solution of **11** (480 mg, 0.10 mmol) dissolved in hot acetic acid (5 cm^3) was added 47% hydrobromic acid (3 cm^3). The mixture was heated overnight at 125 °C, and then cooled to room temperature. After evaporating off the acetic acid under reduced pressure, the residue was neutralized with 5% aqueous sodium hydrogen carbonate, and then extracted with ethyl acetate (20 cm^3 × 3). The combined organic layer was washed with water and brine, and then dried. Evaporation of the solvent left a green powder **16** (332 mg 71%). To a solution of the green powder (103 mg, 0.23 mmol) in 1 mol dm^{-3} aqueous hydrochloric acid (3 cm^3) was added powdered $FeCl_3 \cdot 6H_2O$ (130 mg, 0.48 mmol) and the mixture was stirred for 40 min at room temperature. The reaction mixture was neutralized with 5% aqueous sodium hydrogen carbonate and then extracted with dichloromethane (10 cm^3 × 3). The combined organic layer was washed with water and brine, and then dried. Evaporation of the solvent gave a black powder **6** (70 mg, 65%). The physical data were measured immediately after isolation, because this product seemed to be unstable and decomposed easily on standing even in a freezer under nitrogen atmosphere. δ_H(400 MHz; $CDCl_3$) 2.87 (12 H, s), 3.97 (4 H, s), 6.60 (4 H, d, *J* 8.3), 6.83 (2 H, s), 7.02 (4 H, d, *J* 8.3) and 7.97 (2 H, s); δ_C(100 MHz; $CDCl_3$) 40.6 (q), 41.2 (t), 113.0 (d), 126.2 (d), 128.9 (d), 129.9 (d), 133.7 (s), 137.1 (s), 149.4 (s), 155.6 (s), 185.3 (s) and 185.8 (s); $\nu_{max}(CHCl_3)/cm^{-1}$ 1665, 1610, 1515, 1290 and 1165. For other spectral data, see the text.

2-*Bromo*-6,8-*dibenzylbenzocycloheptene*-1,4,7-*trione* **8**.—To a solution of **10** (397 mg, 0.10 mmol) dissolved in hot acetic acid (6 cm^3) was added 47% hydrobromic acid (3 cm^3) and the mixture was heated overnight at 125 °C and then cooled to room temperature. After dilution with water (5 cm^3) the mixture was cooled to give crystals which were collected by filtration and were again dissolved in ethyl acetate. The solution was washed with 5% aqueous sodium hydrogen carbonate and brine, and then dried. Evaporation of the solvent gave compound **13** as a yellow powder, which was used without purification. To a suspension of the yellow powder in chloroform (30 cm^3) was added dropwise a solution of bromine (350 mg, 2.2 mmol) in chloroform (2 cm^3). After the colour of the mixture had changed from red to light brown, the reaction mixture was washed with 1 mol dm^{-3} aqueous sodium thiosulfate and brine, and then dried. Evaporation of the solvent gave an oil **15**; δ_H(100 MHz; $CDCl_3$) 4.06 (4 H, s), 4.94 (2 H, s), 7.08–7.26 (10 H, m) and 7.80 (2 H, s); ν_{max}(film)/cm^{-1} 1695, 1600, 1495, 1270 and 1220.

The oily product **15** was transformed into monobromoquinotropone **8** (an oil) during chromatographic purification with silica gel (benzene–hexanes 2:1 v/v). Compound **8** (335 mg, 75% from **10**) δ_H(400 MHz; $CDCl_3$) 4.04 (2 H, s), 4.05 (2 H, s), 7.10–7.14 (4 H, m), 7.15–7.24 (6 H, m), 7.39 (H, s), 7.91 (H, s) and 7.96 (s); δ_C(100 MHz; $CDCl_3$) 42.0 (t), 42.1 (t), 126.7 (d), 126.8 (d), 128.6 (d × 2), 128.7 (d × 2), 128.9 (d), 129.15 (d × 2), 129.19 (d × 2), 129.6 (d), 133.7 (s), 133.1 (s), 137.98 (s × 2), 138.01 (s), 138.8 (d), 154.9 (s), 155.4 (s), 178.5 (s), 182.5 (s) and 185.1 (s); ν_{max}(film)/cm^{-1} 1670, 1650, 1600, 1490, 1290 and 1230; *m*/*z* (Found: M^+ + 2, 446.0370. $C_{25}H_{17}{}^{81}BrO_3$ requires *M* 446.0328. Found: M^+, 444.0320. $C_{25}H_{17}{}^{79}BrO_3$ requires *M* 444.0361) *m*/*z* 446 (M^+ + 2, 28), 444 (M^+, 30) and 91 (100). For other spectral data, see the text.

2,3-*Dibromo*-6,8-*dibenzylbenzocycloheptene*-1,4,7-*trione* **9**.—To a stirred solution of **8** (280 mg, 0.93 mmol) in tetrachloromethane (4 cm^3) was added a solution of bromine (140 mg, 0.88 mmol) in tetrachloromethane (2 cm^3) at room temperature. After stirring for 3 h at 45 °C, the reaction mixture was diluted with chloroform (50 cm^3). The chloroform layer was separated off and washed with 1 mol dm^{-3} aqueous sodium thiosulfate and brine, and then dried. Evaporation of the solvent, followed by chromatographic purification on silica gel (benzene–hexanes, 2:1 v/v), gave an orange oil which soon solidified. Recrystallization of the solid from ethyl acetate gave pure compound **9** (200 mg, 61%), m.p. 129–131 °C (Found: C, 57.35; H, 3.15. $C_{25}H_{16}Br_2O_3$ requires C, 57.27; H, 3.08%);

δ_H(400 MHz; $CDCl_3$) 4.06 (4 H, s), 7.05–7.15 (4 H, m), 7.17–7.26 (6 H, m) and 7.94 (2 H, s); δ_C(100 MHz; $CDCl_3$) 42.1 (t), 126.9 (d), 128.8 (d), 129.3 (d), 129.4 (d), 133.8 (s), 137.9 (s), 140.5 (s), 155.4 (s), 176.6 (s) and 185.1 (s); ν_{max}($CHCl_3$)/cm^{-1} 1680, 1600, 1575 and 1235; *m/z* (Found: M^+ + 4, 525.9404. $C_{25}H_{16}{}^{81}Br_2O_3$ requires *M* + 4, 525.9503. Found: M^+ + 2 523.9384. $C_{25}H_{16}{}^{79}Br^{81}BrO_3$ requires *M* + 2 523.9446. Found: M^+ 521.9485. $C_{25}H_{16}{}^{79}Br_2O_3$ requires *M* 521.9466) 526 (M^+ + 4, 25), 524 (M^+ + 2, 38), 522 (M^+, 20) and 91(100). For other spectral data, see the text.

6,8-*Dibromo*-1,4-*dimethoxybenzocyclohepten*-7-*one* **17**.—To a stirred solution of 1,4-dimethoxybenzocyclohepten-7-one **18** (745 mg, 3.45 mmol) in chloroform (70 cm^3) was added bromine (2.0 g, 12 mmol) and the mixture was stirred for 1 h. Triethylamine (20 cm^3) was added and the mixture was stirred for a further 20 min. After filtration, the separated precipitates were washed thoroughly with water and dried. Recrystallization from chloroform gave yellow crystals **17** (931 mg, 72%), m.p. > 300 °C (Found: C, 41.55; H, 2.7. $C_{13}H_{10}Br_2O_3$ requires C, 41.74; H, 2.69%); ν_{max}(Nujol)/cm^{-1} 1622, 1590, 1282, 1238, 1204, 1080, 928 and 826; λ_{max}(CH_2Cl_2)/nm 322 (log ε 4.05) and 401 (4.61). For other spectral data, see the text.

6,8-*Dibromobenzocycloheptene*-1,4,7-*trione* **7**.—To an ice-cooled solution of compound **17** (99 mg, 0.27 mmol) dissolved in conc. sulfuric acid (10 cm^3) was added dropwise nitric acid (*d* 1.42, 1 cm^3) and the mixture was stirred for 5 min at the same temperature. The mixture was poured onto water, and the crystals which formed were filtered off. After drying, the product was recrystallized from ethyl acetate to give orange needles **7** (217 mg, 70%), m.p. 238 °C (decomp.) (Found: C, 38.4; H, 1.05. $C_{11}H_4Br_2O_3$ requires C, 38.41; H, 1.17%); δ_C(100 MHz; $CDCl_3$) 132.1, 134.7, 137.5, 141.4, 173.9 and 183.3; ν_{max}(Nujol)/cm^{-1} 1673, 1638, 1620, 1610, 1582, 1298, 1113, 1032, 952, 848 and 700. For other spectral data, see the text.

1,4-*Dimethoxy*-6,8-*diphenoxybenzocyclohepten*-7-*one* **19**.—To a solution of compound **17** (204 mg, 0.546 mmol) in DMF (10 cm^3) were added successively phenol (311 mg, 3.31 mmol) and sodium hydride (60% in oil, 135 mg, 3.32 mmol) and the mixture was heated overnight at 80 °C. After addition of water, the precipitated crystals were filtered off and dried. Recrystallization from chloroform gave yellow crystals **19** (177 mg, 72%), m.p. 277–278 °C; δ_H(400 MHz; $CDCl_3$) 3.87 (6 H, s), 6.99 (4 H, d, *J* 8.9), 7.02 (2 H, s), 7.04 (2 H, t, *J* 8.9), 7.27 (4 H, t, *J* 8.9) and 8.45 (2 H, s); ν_{max}(Nujol)/cm^{-1} 1610, 1590, 1490, 1285, 1248, 1230, 1212, 1093, 1077, 1023, 1013, 758 and 698; λ_{max}(CH_2Cl_2)/nm 317 (log ε 4.57), 388 (3.67) and 407 (3.61).

6,8-*Diphenoxybenzocycloheptene*-1,4,7-*trione* **5**.—To a stirred solution of compound **19** (54 mg, 0.14 mmol) in a mixture of chloroform (20 cm^3) and acetonitrile (20 cm^3) was added a solution of CAN (150 mg, 0.28 mmol) in water (2 cm^3) at room temperature. After stirring for 3 h, the reaction mixture was diluted with chloroform (100 cm^3) and the solution was washed with water and brine, and then dried. Evaporation of the solvent, followed by chromatographic separation of the residue on silica gel (benzene–AcOEt, 9:1 v/v) gave orange crystals **5** (33 mg, 66%), m.p. 218–219 °C; δ_H(400 MHz; $CDCl_3$) 6.91 (2 H, s), 7.12 (4 H, d, *J* 7.3), 7.30 (2 H, t, *J* 7.3), 7.47 (4 H, t, *J* 7.3) and 7.83 (2 H, s); δ_C(100 MHz; $CDCl_3$) 115.0 (d), 120.5 (d), 125.9 (d), 130.4 (d), 130.5 (s), 137.6 (d), 154.1 (s), 163.1 (s), 172.6 (s) and 183.9 (s × 2); ν_{max}($CHCl_3$)/cm^{-1} 1678, 1642, 1630, 1596, 1496, 1298, 992 and 852; *m/z* (Found: M^+ 370.0844. $C_{23}H_{14}O_5$ requires *M* 370.0841), 371 (M^+ + 1, 27), 370 (88), 342 (51), 277 (100), 249 (26), 221 (36), 94 (66) and 77 (89). For other spectral data, see the text.

6,8-*Bis*(*phenylthio*)-1,4-*dimethoxybenzocyclohepten*-7-*one* **20**.—To a solution of compound **17** (100 mg, 0.27 mmol) in DMF (3 cm^3) was added sodium thiophenolate (177 mg, 1.34 mmol) and the mixture was heated at 85 °C for 1 h. After addition of water, the separated product was filtered off, and then dried. Recrystallization from benzene gave yellow crystals **20** (115 mg quantitative yield, m.p. 236–237 °C), which showed identical m.p. and NMR spectra with those of the authentic sample.[1]

2,4,8,10-*Tetrabenzyl*-6,12-*dimethoxybenzo*[1,2;4,5]*dicycloheptene*-3,9-*dione* **24**.—A solution of 6,12-dimethoxy-1,2,4,5,7,8,10,11-octahydrobenzo[1,2;4,5]dicycloheptene-3,9-dione **22** (1.57 g, 5.21 mmol) and benzaldehyde (3.40 g, 31.9 mmol) in absolute ethanol (60 cm^3) was added sodium hydride (60% in oil, 1.28 g, 32.0 mmol), which had been freshly washed with dry hexane. The reaction mixture was refluxed for 5 h and then cooled to room temperature. This mixture was diluted with water and the separated crude crystals were filtered off and dried. Chromatographic separation of the product on silica gel (benzene) gave yellow crystals **24** (618 mg, 18%), m.p. 146–147 °C (from ethanol) (Found: C, 84.4; H, 5.85. $C_{46}H_{38}O_4$ requires C, 84.38; H, 5.85%); δ_H(400 MHz; $CDCl_3$) 3.33 (6 H, s), 4.04 (8 H, s), 7.20–7.31 (20 H, m) and 7.83 (4 H, s); δ_C(100 MHz; $CDCl_3$) 41.2, 63.0, 126.4, 128.5, 128.8, 129.5, 131.0, 139.6, 146.2, 154.0 and 187.3; ν_{max}($CHCl_3$)/cm^{-1} 1602, 1500, 1460, 1365, 1077 and 700; λ_{max}(CH_2Cl_2)/nm 248 (log ε 4.36), 326 (5.05) and 368 sh (4.25); *m/z* 654 (M^+, 28), 626 (6), 583 (30) and 91 (100).

2,4,8,10-*Tetrabenzylbenzo*[1,2;4,5]*dicycloheptene*-3,6,9,12-*tetrone* **26**.—To a solution of compound **24** (404 mg, 0.614 mmol) in acetic acid (20 cm^3) was added 47% hydrobromic acid (5 cm^3) and the mixture was refluxed overnight, then diluted with water to separate a solid. After filtration, washing with water and drying, the product was dissolved in chloroform (40 cm^3) and oxidized with nitric acid (*d* 1.38, 1 cm^3) with stirring for 5 min at room temperature. After dilution with water, the chloroform layer which separated was washed with brine, and then dried. Evaporation of the solvent, followed by chromatographic purification on silica gel (benzene) gave orange crystals **26** (146 mg, 37%), m.p. 167–169 °C (from ethyl acetate) (Found: C, 84.7; H, 4.8. $C_{44}H_{32}O_4$ requires C, 84.59; H, 5.16%); δ_H(400 MHz; $CDCl_3$) 4.06 (8 H, s), 7.12–7.28 (20 H, m) and 8.02 (4 H, s); δ_C(100 MHz; $CDCl_3$) 42.1 (t), 126.8 (d), 128.7 (d), 129.3 (d), 129.5 (d), 134.6 (s), 138.1 (s), 155.2 (s), 183.9 (s) and 185.3 (s); ν_{max}($CHCl_3$)/cm^{-1} 1670, 1604 and 1260; λ_{max}(CH_2Cl_2)/nm 291 (log ε 4.73) and 381 (4.00); *m/z* 624 (M^+, 19), 596 (9), 505 (7) and 91 (100).

Oxidation of 6-*Phenylthiobenzocycloheptene*-1,4,7-*trione* **2**.—To an ice-cooled solution of 6-phenylthiobenzocycloheptene-1,4,7-trione **2** (50 mg, 0.17 mmol) and dipotassium hydrogen phosphate (33 mg, 0.17 mmol) in dried dichloromethane (4 cm^3) was added purified *m*-chloroperbenzoic acid (32 mg, 0.19 mmol) and the mixture was stirred for 2 h. After filtration, the filtrate was chromatographed directly on silica gel (benzene–AcOEt 95:5 v/v) to give orange crystals **27** (25 mg, 48%), m.p. 147–152 °C (from dichloromethane–hexanes) (Found: C, 65.75; H, 3.1. $C_{17}H_{10}O_4S$ requires C, 65.80; H, 3.25%); δ_H(400 MHz; $CDCl_3$) 7.09 (1 H, d, *J* 10.4), 7.14 (1 H, d, *J* 10.4), 7.17 (1 H, d, *J* 12.8), 7.42–7.45 (3 H, m), 7.82–7.84 (2 H, m), 8.11 (1 H, d, *J* 12.8) and 8.94 (1 H, s); δ_C(100 MHz; $CDCl_3$) 126.1, 128.4, 129.2, 131.6, 132.7, 134.5, 136.2, 137.3, 137.5, 142.9, 143.1, 162.5, 181.7, 183.8 and 184.2; ν_{max}($CHCl_3$)/cm^{-1} 1674, 1613, 1593, 1480, 1443, 1115, 1080, 1050 and 845; *m/z* 310 (M^+, 6), 294 (3), 250 (13), 217 (28), 125 (88), 109 (38), 97 (22) and 77 (100). For other spectral data, see the text.

Oxidation of 6,8-*Bis(phenylthio)benzocycloheptene*-1,4,7-*trione* **3**.—A similar oxidation to that described above for compound **2** was carried out on 6,8-bis(phenylthio)benzocycloheptene-1,4,7-trione **3** (50 mg, 0.12 mmol) with use of dried dichloromethane (4 cm^3), dipotassium hydrogen phosphate (33 mg, 0.17 mmol) and purified *m*-chloroperbenzoic acid (32 mg, 0.19 mmol) to give a solid (71 mg). Chromatographic separation on silica gel (benzene–AcOEt, 95:5 v/v) gave orange crystals **28** (30 mg, 58%), m.p. 213–214 °C and compound **29** (3 mg, 4%), m.p. 202–204 °C. Compound **28** (Found: C, 66.15; H, 3.3. $C_{23}H_{14}O_4S_2$ requires C, 66.01; H, 3.37%); δ_H(400 MHz; $CDCl_3$) 6.91 (1 H, d, *J* 10.4), 7.41 (1 H, d, *J* 10.4), 7.42–7.45 (3 H, m), 7.51–7.56 (3 H, m), 7.56–7.66 (2 H, m), 7.95 (1 H, s), 7.90–7.94 (2 H, m) and 9.12 (1 H, s); δ_C(100 MHz; $CDCl_3$) 125.0, 126.1, 128.3, 129.1, 129.3, 129.6, 130.7, 131.2, 131.5, 133.3, 135.7, 137.1, 137.9, 145.3, 153.9, 165.2, 177.1, 183.8 and 184.6; ν_{max}($CHCl_3$)/cm^{-1} 1676, 1600, 1570, 1480, 1295, 1125, 1080, 1055, 980 and 855; *m/z* 418 (M^+, 24), 402 (18), 325 (89), 281 (19), 208 (32), 183 (25), 139 (19), 125 (89), 109 (46) and 77 (100); compound **29** δ_H(400 MHz; $CDCl_3$) 6.93 (1 H, d, *J* 10.4), 7.07 (1 H, d, *J* 10.4), 7.51–7.65 (8 H, m), 7.64 (1 H, s), 8.14–8.16 (2 H, m) and 9.53 (1 H, s); δ_C(100 MHz; $CDCl_3$) 123.6, 127.6, 128.8, 129.6, 130.8, 131.3, 133.6, 133.8, 135.1, 135.7, 136.3, 137.2, 138.1, 139.7, 143.5, 170.0, 175.7, 183.3 and 184.1; ν_{max}($CHCl_3$)/cm^{-1} 1670, 1610, 1585, 1475, 1280, 1150, 1120, 1080 and 840.

6-*Cyano*-1,4-*dimethoxy*-5,6,8,9-*tetrahydrobenzocyclohepten*-7-*one* **31**.—To a suspension of sodium hydride (60% in oil, 321 mg, 8.0 mmol) in hexanes (3 cm^3), was added a solution of 2,3-bis(2-cyanoethyl)-1,4-dimethoxybenzene **30** (1.44 g, 5.9 mmol) in anhydrous dimethyl sulfoxide (15 cm^3) under nitrogen atmosphere. The mixture was heated at 85 °C for 1 h and then cooled to room temperature. The cooled mixture was poured into ice–water and acidified carefully with 2 mol dm^{-3} hydrochloric acid keeping the temperature below 5 °C and extracted with benzene. The organic layer was re-extracted with 5% aqueous sodium hydroxide, which was immediately acidified below 5 °C. After extraction of the aqueous solution with benzene, the organic layer was dried and concentrated. Recrystallization of the residue gave pure **31** (669 mg, 48%), m.p. 165–166 °C (Found: C, 68.55; H, 6.15; N, 5.65. $C_{14}H_{15}NO_3$ requires C, 68.55; H, 6.16; N, 5.71%); δ_H(400 MHz; $CDCl_3$) 2.50 (1 H, dd, *J* 10.0, 3.2), 2.83 (1 H, ddd, *J* 9.0, 2.7, 2.2), 2.95 (1 H, ddd, *J* 10.0, 2.9, 2.7), 3.09 (1 H, ddd, *J* 9.0, 3.2, 2.9), 3.23 (1 H, dd, *J* 14.7, 9.5), 3.46 (1 H, dd, *J* 14.7, 2.7), 3.60 (1 H, dd, *J* 9.5, 2.7), 3.80 (3 H, s), 3.82 (3 H, s), 6.80 (1 H, d, *J* 12.9) and 6.82 (1 H, d, *J* 12.9); δ_C(100 MHz; $CDCl_3$) 20.8 (t), 25.4 (t), 42.3 (t), 45.2 (d), 56.2 (q), 56.3 (q), 109.9 (d), 110.9 (d), 116.5 (s), 126.1 (s), 130.4 (s), 150.7 (s), 151.3 (s) and 201.1 (s); ν_{max}($CHCl_3$)/cm^{-1} 2250, 1720, 1600, 1485, 1465, 1250 and 1073.

6-*Cyano*-1,4-*dimethoxy*-6-*phenylseleno*-5,6,8,9-*tetrahydrobenzocyclohepten*-7-*one* **32**.—To a suspension of sodium hydride (60% in oil, 105 mg, 2.63 mmol) in THF (1 cm^3), was added a solution of **31** (423 mg, 1.72 mmol) in THF (16 cm^3) at room temperature under nitrogen atmosphere. To this mixture was added dropwise a solution of phenylselenyl chloride (370 mg, 1.93 mmol) in THF (6 cm^3) and the reaction mixture was stirred for 15 min and then quenched with aqueous ammonium chloride. After evaporating off the THF under reduced pressure, the remaining liquid was extracted with benzene (10 cm^3 × 3). The combined benzene extracts were washed with brine and then dried. After evaporation of the solvent, the residue was chromatographed on silica gel (benzene–AcOEt, 100:3 v/v) to give **32** (630 mg, 91%), m.p. 131–133 °C (from methanol) (Found: C, 59.95; H, 4.8; N, 3.50. $C_{20}H_{19}NO_3Se$ requires C, 60.00; H, 4.78; N, 3.50%); δ_H(100 MHz; $CDCl_3$) 2.52–3.52 (4 H, m), 3.64 (2 H, s), 3.76 (6 H, s), 6.76 (2 H, s) and 7.22–7.64 (5 H, m); δ_C(25 MHz; $CDCl_3$) 20.7, 30.5, 37.8, 50.7, 56.0, 56.3, 109.9, 111.1, 117.8, 123.9, 125.4, 129.4, 129.6, 130.5, 137.5, 150.1 151.6 and 198.4; ν_{max}($CHCl_3$)/cm^{-1} 2250, 1700, 1490, 1460, 1440, 1255 and 1075; λ_{max}(CH_2Cl_2)/nm 232 (log ε 4.38) and 306 (3.88).

6-*Cyano*-8,9-*dihydro*-1,4-*dimethoxybenzocyclohepten*-7-*one* **33**.—To an ice-cooled solution of **32** (100 mg, 0.26 mmol) in dichloromethane (3 cm^3) was added a solution of *m*-chloroperbenzoic acid (70%, 64 mg, 0.26 mmol) in dichloromethane (2 cm^3). After stirring for 40 min at room temperature, the reaction mixture was washed successively with 5% aqueous sodium thiosulfate solution, 5% aqueous sodium hydrogen carbonate solution and brine, and then dried. Evaporation of dichloromethane gave compound **33** (60 mg, 95% from benzene), m.p. 214–215 °C (Found: C, 69.25; H, 5.35; N, 5.7. $C_{14}H_{13}NO_3$ requires C, 69.12; H, 5.39; N, 5.76%); δ_H(400 MHz; $CDCl_3$) 2.73 (2 H, m), 3.07 (2 H, m), 3.83 (3 H, s), 3.89 (3 H, s), 6.83 (1 H, d, *J* 9.3), 7.09 (1 H, d, *J* 9.3) and 8.38 (1 H, s); δ_C(100 MHz; $CDCl_3$) 19.0 (t), 41.5 (t), 56.2 (q), 56.7 (q), 109.6 (d), 114.4 (s), 117.3 (s), 117.7 (d), 122.7 (s), 133.2 (s), 146.7 (d), 150.0 (s), 154.0 (s) and 195.3 (s); ν_{max}($CHCl_3$)/cm^{-1} 2250, 1680, 1595, 1480, 1460, 1440, 1270 and 1080; λ_{max}(CH_2Cl_2)/nm 228 (log ε 4.16), 319 (4.18) and 401 (3.84).

6-*Cyano*-1,4-*dimethoxybenzocyclohepten*-7-*one* **34**.—To a solution of **33** (53 mg, 0.22 mmol) dissolved in tetrachloromethane (80 cm^3) were added NBS (38 mg, 0.22 mmol) and a small amount of AIBN. The reaction mixture was refluxed for 45 min and then cooled to room temperature. Triethylamine (0.04 cm^3, 0.29 mmol) was added to the stirring mixture and the separated crystals were filtered off. The crystals were dissolved in chloroform and the solution was washed with water and brine, and then dried. Evaporation of the solvent gave compound **34** (45 mg, 86%), m.p. 262–264 °C (from chloroform) (Found: C, 69.45; H, 4.5; N, 5.85. $C_{14}H_{11}NO_3$ requires C, 69.70; H, 4.60; N, 5.80%); δ_H(400 MHz; $CDCl_3$) 3.95 (3 H, s), 3.98 (3 H, s), 6.84 (1 H, d, *J* 13.4), 7.14 (1 H, d, *J* 9.0), 7.25 (1 H, *J* 9.0), 8.22 (1 H, d, *J* 13.4) and 8.87 (1 H, s); ν_{max}($CHCl_3$)/cm^{-1} 2200, 1710, 1630, 1600, 1580 and 1360; λ_{max}(CH_2Cl_2)/nm 237 (log ε 3.40), 302 (3.29) and 417 (4.31); *m/z* (Found: M^+ 241.0745. $C_{14}H_{11}NO_3$ requires *M* 241.0739) 241 (M^+, 61) 213 (59), 198 (100), 170 (21), 155 (9) and 127 (14).

Bromination and Dehydrobromination of 6-*Cyano*-1,4-*dimethoxy*-5,6,8,9-*tetrahydrobenzocyclohepten*-7-*one* **31**.—*Formation of* **34** *and* 6-*bromo*-8-*cyano*-1,4-*dimethoxybenzocyclohepten*-7-*one* **35**.—To a solution of compound **31** (97 mg, 0.40 mmol) dissolved in tetrachloromethane (35 cm^3) were added NBS (167 mg, 0.94 mmol) and a small amount of AIBN and the reaction mixture was refluxed for 2 h. After cooling to room temperature, the separated succinimide was filtered off. To the filtrate was added triethylamine (0.14 cm^3, 1.0 mmol) and the mixture was refluxed for 30 min to separate triethylammonium bromide, which was filtered off. The crude product, obtained from the filtrate, was separated by repeated recrystallizations from ethanol to give compounds **34** (14.5 mg, 15%) and **35** (20.4 mg, 15%), m.p. > 300 °C; δ_H(400 MHz; $CDCl_3$) 3.99 (3 H, s), 4.00 (3 H, s), 7.17 (1 H, d, *J* 10.0), 7.29 (1 H, d, *J* 10.0), 8.91 (1 H, s) and 9.19 (1 H, s); ν_{max}(KBr)/cm^{-1} 2245, 1620, 1445, 1295 and 1080; λ_{max}(CH_2Cl_2)/nm 257 (log ε 4.11). 313 (3.85) and 426 (4.47); *m/z* (Found: M^+ 318.9844. $C_{14}H_{10}{}^{79}BrNO_3$ requires *M* 318.9831. Found: M^+ 320.9818. $C_{14}H_{10}{}^{81}BrNO_3$ requires *M* 320.9823) 321 (48), 319 (48), 293 (60), 291 (60), 280 (100), 278 (100), 240 (18), 141 (28) and 126 (22). These compounds are slightly soluble in common organic solvents.

Oxidation of 6-*Cyano*-1,4-*dimethoxybenzocyclohepten*-7-*one* **34** *with CAN*.—Compound **34** (10 mg, 0.044 mmol), powdered

CAN (39 mg, 0.44 mmol) and water (8 mm^3, 0.44 mmol) were thoroughly mixed in an agate mortar with an agate pestle. The progress of the reaction was monitored by TLC. After dilution with chloroform (15 cm^3), the reaction mixture was filtered. Evaporation of the solvent gave a mixture (8 mg) thought to be 6-cyanobenzocycloheptene-1,4,7-trione **36**, δ_H(400 MHz; $CDCl_3$) 7.13 (2 H, s), 7.39 (1 H, d, *J* 13), 8.07 (1 H, d, *J* 13) and 8.60 (1 H, s); and 6-cyano-1,4-naphthoquinone **38**, δ_H(400 MHz; $CDCl_3$) 7.09 (2 H, s), 8.02 (1 H, dd, *J* 8.1, 2.6), 8.22 (1 H, dd, *J* 8.1) and 8.39 (1 H, d, *J* 2.6); *m/z* (Found: M^+ 183.0294. $C_{11}H_5NO_2$ requires *M* 183.0320), 183 (100), 155 (51), 129 (44), 127 (53) and 101 (41).

Oxidation of 6-*Bromo*-8-*cyano*-1,4-*dimethoxybenzocycloheptene*-7-*one* **35** *to* 6-*Bromo*-8-*cyanobenzocycloheptene*-1,4,7-*trione* **37**.—Compound **35** (9 mg, 0.028 mmol), powdered CAN (156 mg, 0.28 mmol) and water (1 mm^3, 0.056 mmol), were thoroughly mixed in an agate mortar with an agate pestle for 40 min under TLC monitoring. The mixture was extracted with hot chloroform by trituration and then the chloroform solution was dried and concentrated. Chromatographic separation of the residue on silica gel (benzene–AcOEt, 5 : 1 v/v) gave quinone **37** and starting material (6.2 mg, 18%). Compound **37** (1.5 mg, 18%) as a deep purple powder, δ_H(400 MHz; $CDCl_3$) 7.13 (2 H, s), 8.60 (1 H, s) and 8.94 (1 H, s); *m/z* 291 (M^+ + 2, 41), 289 (M^+, 41), 263 (23), 261 (23) and 210 (83).

Crystal Data for **4**.—$C_{25}H_{18}O_3$, *M* = 366.3. Monoclinic, a = 13.089(3), b = 13.943(4), c = 10.530(3) Å, β = 103.19(4)°, V = 1871.1(9) Å^3 (from 2θ values of 24 reflections, 21 < 2θ < 25°). Space group $P2_1/c$, Z = 4, D_c = 1.301, D_m = 1.28 g cm^{-3}. F(000) = 768. Crystal dimensions: 0.6 × 0.5 × 0.45 mm, μ(Mo-$K\alpha$) = 0.079 mm^{-1}. Orange crystals were obtained from benzene.

Data collection and processing for **4**. Rigaku AFC-5 diffractometer, $2\theta/\omega$ mode with scan width = 1.2 + 0.35 tan θ, scan speed 8 deg min^{-1}, graphite-monochromated Mo-$K\alpha$ radiation (the same experimental method and conditions were applied to the X-ray work on compounds **5**, **9** and **25**–THF). 4472 Reflections (2 < 2θ < 54°, index range h − 16 to 0, k 0 to 17, l −13 to 13), 4108 unique, giving 3035 with $F_o > 3\sigma(F_o)$. At 298 K. No absorption correction.

Structure analysis and refinement for **4**. The structure was solved by the direct method (MULTAN78)[20] and refined by block-diagonal least squares (HBLS-V)[21] with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for the H atoms except H(15) which was constrained. Atomic scattering factors were taken from ref. 22. All calculations were performed on an ACOS 2020 computer at the Information Processing Center of Kobe University with the UNICS system.[23] The final refinement gave R = 0.0593, R_w = 0.0641; $w^{-1} = [\sigma^2(F_o) - 0.668\,07\ F_o + 0.037\,28\ F_o^2]$; 322 parameters; max. shift/e.s.d. = 0.07, ρ_{max} = 0.22, ρ_{min} = −0.34 e Å^{-3} on final difference map.

Crystal Data for **5**.—$C_{23}H_{14}O_5$, *M* = 370.2. Monoclinic, a = 12.943(5), b = 13.269(3), c = 10.472(9) Å, β = 100.47(4)°, V = 1767.0(29) Å^3 (from 2θ values of 22 reflections, 20 < 2θ < 25°). Space group $P2_1/c$, Z = 4, D_c = 1.391, D_m = 1.40 g cm^{-3}. F(000) = 768. Crystal dimensions: 0.6 × 0.6 × 0.1 mm, μ(Mo-$K\alpha$) = 0.092 mm^{-1}. Orange crystals were obtained from hexane–dichloromethane.

Data collection and processing for **5**. 4482 Reflections (2 < 2θ < 55°, index range h −16 to 16, k − 17 to 0, l − 13 to 0), 4069 unique, giving 2792 with $F_o > 3\sigma(F_o)$. At 293 K. No absorption correction.

Structure analysis and refinement for **5**. By the same method as for **4**. The final refinement gave R = 0.0509, R_w = 0.0461; $w^{-1} = [\sigma^2(F_o) - 0.023\,18\ F_o + 0.001\,57\ F_o^2]$; 310 parameters; max. shift/esd = 0.05, ρ_{max} = 0.18, ρ_{min} = −0.20 e Å^{-3} on final difference map.

Crystal data for **9**.—$C_{25}H_{16}Br_2O_3$, *M* = 524.1. Orthorhombic, a = 22.010(6), b = 19.585(8), c = 9.899(1) Å, V = 4267.2(22) Å^3 (from 2θ values of 21 reflections, 23 < 2θ < 26°). Space group *Pbca*, Z = 8, D_c = 1.632, D_m = 1.60 g cm^{-3}. F(000) = 2080. Crystal dimensions: 0.4 × 0.4 × 0.4 mm, μ(Mo-$K\alpha$) = 3.785 mm^{-1}. Orange crystals were obtained from hexane–dichloromethane.

Data collection and processing for **9**. 3169 Reflections (2 < 2θ < 45°, index range h 0 to 16, k 0 to 23, l 0 to 11), 2771 unique, giving 2069 with $F_o > \sigma(F_o)$. At 298 K. No absorption correction.

Structure analysis and refinement for **9**. By the same method as for **4**. All of the H atoms were constrained. The final refinement gave R = 0.0780, R_w = 0.0546; $w^{-1} = [\sigma^2(F_o) - 0.428\,38\ F_c + 0.004\,62\ F_o^2]$; 272 parameters; max. shift/esd = 0.05, ρ_{max} = 0.56, ρ_{min} = −0.66 e Å^{-3} on final difference map.

Crystal Data for **25**–*TTF*.—$(C_{16}H_8O_4)\cdot(C_6H_4S_4)$, *M* = 486.3. Monoclinic, a = 11.195(7), b = 12.412(3), c = 7.381(2) Å, β = 105.63(2)°, V = 987.6(7) Å^3 (from 2θ values of 32 reflections, 20 < 2θ < 27°), Space group $P2_1/n$, Z = 2, D_c = 1.575, D_m = 1.57 g cm^{-3}. F(000) = 480. Crystal dimensions: 0.3 × 0.2 × 0.05 mm, μ(Mo-$K\alpha$) = 0.489 mm^{-1}. Black crystals were obtained from chloroform.

Data collection and processing for **25**–*TTF*. 2559 Reflections (2 < 2θ < 55°, index range h −14 to 14, k 8 to 16, l 0 to 9), 2270 unique, giving 960 with $F_o > 4\sigma(F_o)$. At 298 K. No absorption correction.

Structure analysis and refinement for **25**–*TTF*. By the same method as for **4**. H(1D) and H(4D) were constrained. The final refinement gave R = 0.0790, R_w = 0.0601; $w^{-1} = [\sigma^2(F_o) + 0.092\,50\ F_o - 0.006\,62\ F_o^2]$; 246 parameters; max. shift/esd = 0.02, ρ_{max} = 0.58, ρ_{min} = −0.40 e Å^{-3} on final difference map.

Results of Crystal Structure Determinations.—The molecular structures and numbering schemes of atoms in **4**, **5**, **9** and the complex **25**–TTF are shown in Figs. 2–4 and 9 (ORTEP[24] drawings), respectively. Both of the molecules of **25** and TTF in the crystal of the complex (**25**–TTF) have a centre of symmetry.

Atomic coordinates and temperature factors for crystals of **4**, **5**, **9** and the complex **25**-TTF are given in Supplementary Tables 1–8, respectively. Their selected bond lengths and bond angles are listed in Supplementary Tables 9–12.*

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.[17] In the calculation, repulsion, dispersion and Coulomb terms are taken into account as non-bonded, intermolecular interactions.[25] The repulsion and dispersion are assumed to be isotropic and the former term is expressed by an exponential function. Total atomic charges obtained by the MNDO method were used for the calculation of Coulomb terms.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific

* Lists of bond lengths and bond angles, and fractional coordinates have been deposited at CCDC. For details of the deposition scheme please see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1994, Issue 1.

Research on Priority Areas No. 03214103 from the Ministry of Education, Science and Culture of Japan.

References

1 H. Tada, Y. Takeuchi, Y. Amatatsu, K. Furuichi, M. Kato, S. Matsumoto and M. Hashimoto, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1305.
2 J. F. Nicoud and R. J. Twieg, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, D. S. Chemla and J. Zyss (ed.), vol. 1, Academic Press, London, 1987, p. 227.
3 K. Furuichi, H. Tada, A. Kanehira, M. Lee, M. Kato, M. Hashimoto and S. Matsumoto, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2169.
4 T. Nozoe, K. Takase and H. Matsumura, in *Daiyuukikagaku*, M. Kotake (ed.), vol. 13, Hirokawa Book Co., 1960, p. 179.
5 F. G. Baldwell and M. Winn, *J. Org. Chem.*, 1967, **32**, 42.
6 M. Kato, M. Mitsuda, T. Tatsumoto, R. Uchida and A. Ichimura, *Chem. Lett.*, 1989, 1789.
7 (*a*) K. Tamoto and S. Terashima, *Chem. Pharm. Bull.*, 1984, **32**, 4340; (*b*) S. Terashima and K. Tamoto, *Tetrahedron Lett.*, 1983, 2589.
8 L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd. edn., Pergamon Press, London, 1969, p. 95.
9 Ref. 8, p. 202.
10 M. Kato, Y. Amatatsu, H. Tada, S. Tanaka, K. Furuichi, H. Hashimoto and S. Matsumoto, *Chem. Lett.*, 1991, 1973.
11 J. Zyss and D. S. Chemla, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, D. S. Chemla and J. Zyss (eds.), vol. 1, Academic Press, London, 1987, p. 23.
12 N. S. Isaacs, *Physical Organic Chemistry*, Wiley, New York, 1987, pp. 134–135.
13 T. Kitagawa, J. Toyoda, K. Nakasuji, H. Yamamoto and I. Murata, *Chem. Lett.*, 1990, 897.
14 A. Aumuller and S. Hunig, *Ann. Chem.*, 1986, 165.
15 J. Trotter, *Acta Crystallogr.*, 1960, **13**, 86.
16 MOPAC Ver. 6, J. J. P. Stewart, *QCPE Bull.* 9, 10 (1989); Revised by H. Chawannya for VAX machine.
17 PCK83, D. E. Williams, QCPE No 481, University of Indiana, Bloomington, Indiana, USA, 1983.
18 M. R. Bryce, *Chem. Soc. Rev.*, 1991, **20**, 355.
19 W. F. Cooper, N. C. Kenny, J. W. Edmonds, A. Nagel, F. Wudl and P. Coppens, *J. Chem. Soc., Chem. Commun.*, 1971, 889.
20 P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, A system of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, MULTAN78, University of York.
21 T. Ashida, The Universal Crystallographic Computing Systems-Osaka, HBLS-V, The Computation Center, Osaka University, 1979, p. 53.
22 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, vol. 4.
23 T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, 1979, **55**, 69 (*in Japanese*).
24 C. K. Johnson, 'ORTEP-II. Report ORNL-5138', March, Oak Ridge National Laboratory, Tennessee, USA (1976).
25 D. E. Williams, *Topics in Current Physics*, 1981, **26**, 3.

Paper 3/06898F
Received 18*th November* 1993
Accepted 13*th January* 1994