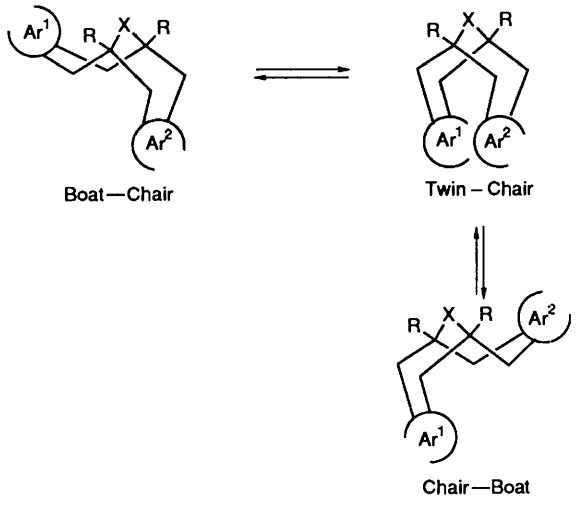
Effect of 1,4-Naphthoquinone Annelation on the Conformational Behaviour of Carbonyl- and Methano-bridged Cyclodecadiene Derivatives

Shuntaro Mataka,*[a] Seung Taeg Lee,[b] Yuriko Tamura,[b] Akihiko Tsuge[a] and Masashi Tashiro[a]
[a] *Institute of Advanced Material Study, Graduate School of Engineering Sciences, 6-1, Kasuga-koh-en, Kasuga-shi, Fukuoka 816, Japan*
[b] *Department of Molecular Science and Technology, Graduate School of Engineering Sciences, 6-1, Kasuga-koh-en, Kasuga-shi, Fukuoka 816, Japan*

The $Na_2Cr_2O_7$ oxidation of hexahydro-7,16-methanodinaphtho[2,3-*a*:2′,3′-*f*] cyclodecene derivative **2**, produced two bis-(1,4-naphthoquinone)s, **7** and **9**, and monoquinone compound **8**. Benzonaphtho derivative **3** gave two 1,4-naphthoquinone derivatives, **10** and **11**, on oxidation.

Flexible compounds **7**–**11** showed temperature-dependent ^{1}H NMR spectra due to equilibria among chair–boat, twin-chair, and boat–chair conformers, which were ^{1}H NMR spectroscopically characterized. A twin-chair conformer was detected in products **8**, **9** and **10**, but not in compounds **7** and **11**. A broad absorption band due to an intramolecular C–T interaction in the twin-chair conformer was observed at $\lambda \sim 400$ nm in the electronic spectra of the monoquinones, **8** and **10**, but not in the bis(quinone) **9**. Population of the twin-chair conformer increased with removal of the ester group on the bridgehead position. Reduction of the carbonyl group on the bridge also favoured the twin-chair conformation, indicating a repulsive interaction between the ester and the carbonyl group of the 1,4-naphthoquinone moiety. Upon irradiation with sunlight, compound **7** gave the [2 + 2]-photoadduct **15**.

It was previously reported[1,2] that benzo-, naphtho- and quinoxalino-annelated compounds, **1**–**6**, invert among their chair–boat, twin-chair, and boat–chair conformers [these conformers are abbreviated (C–B), (T–C) and (B–C), respectively] (Scheme 1). For the quinoxalino derivatives, **4** and **5**, the corresponding (T–C)s were detected by ^{1}H NMR spectroscopy, together with (C–B) and (B–C),[1] but not in the dibenzo-, dinaphtho-, and benzonaphtho-annelated analogues, **1**, **2**, and **3**.[2] This is tentatively explained by assuming that by replacing the electron-rich benzene and naphthlene ring of compounds **1**–**3** with electron-deficient quinoxalines, the π–π electronic repulsion between two facing aromatic rings would be reduced, stabilizing (T–C) in compounds **4** and **5**.



Scheme 1 **1**: $Ar^1 = Ar^2$ = B **2**; $Ar^1 = Ar^2$ = 2,3-N **3**; Ar^1 = B, Ar^2 = 2,3-N **4**; $Ar^1 = Ar^2$ = 2,3-QX **5**; Ar^1 = 2,3-QX, Ar^2 = B **6**; Ar^1 = 2,3-QX. Ar^2 = 2,3-N **7**; $Ar^1 = Ar^2$ = 2,3-(1,4-NQ) **8**; Ar^1 = 2.3-(1.4-NQ). Ar^2 = 2,3-N **9**; Ar^1 = 2,3-(1,4-NQ), Ar^2 = 6,7-(1,4-NQ) **10**; Ar^1 = 2.3-(1,4-NQ), Ar^2 = B **11**; Ar^1 = 6,7-(1,4-NQ), Ar^2 = B

Letters B, N. QX, and NQ mean benzo, naphtho, quinoxalino, and naphthoquinono, respectively.

It seemed of interest to investigate the conformational behaviour of methanocyclodecadiene systems annexed by an electron-deficient 1,4-quinone and an electron-rich aromatic ring, since the expected charge-transfer interaction[3] between them might be helpful in stabilizing a T–C conformation.

We report here the preparation, by oxidation, of naphtho-annelated derivatives **2** and **3**, and the conformation of the 1,4-naphthoquinone-annelated products **7**–**11**.

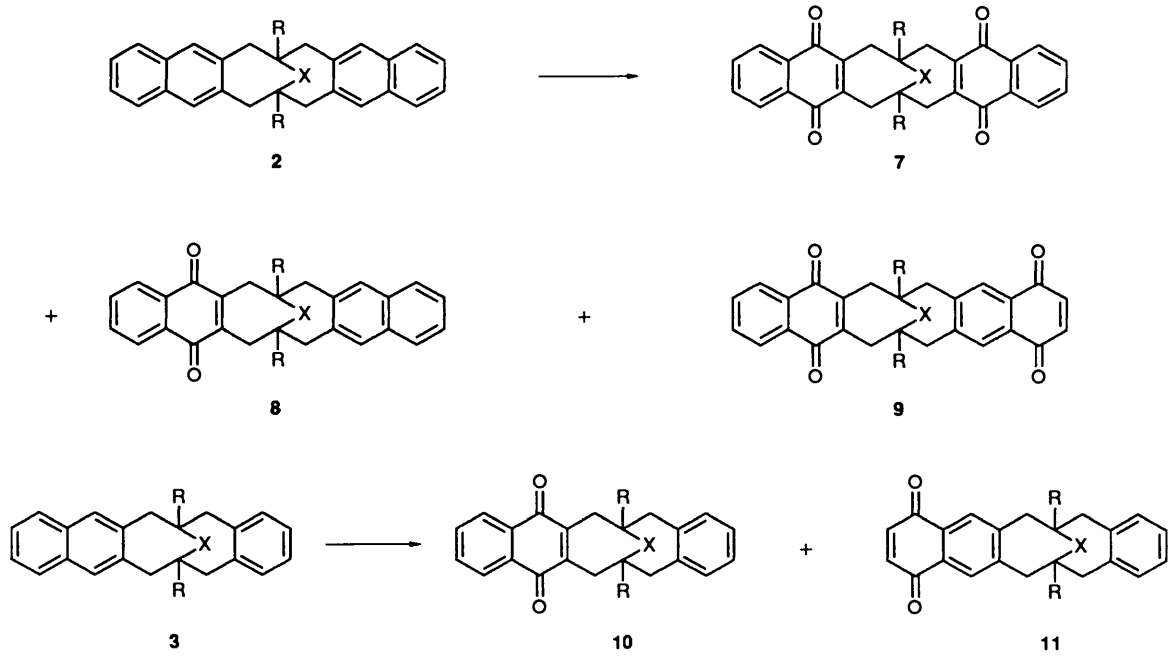
Results and Discussion

Oxidation of Compounds **2** *and* **3**.—Dinaphtho[2,3-*a*; 2′,3′-*f*]-cyclodecenes **2**, and the benzonaphtho analogues **3**, were oxidized by Na_2CrO_7 in the usual manner[5] (Scheme 2).

It is well documented that during oxidation of a naphthalene ring with dichromate, the more alkylated benzene ring is preferentially oxidized.[6] the oxidation of compounds **2a**–**c** afforded bis-(1,4-quinone)s, **7a**–**c**, and monoquinones, **8a**–**c**, in low yield. In addition, bis-(1,4-quinone)s, **9a**–**c**, were produced in comparable yield to that of isomers **7a**–**c**. Similarly, substrates **3a**–**c** gave the expected monoquinones, **10a**–**c**, and the anomalous oxidation products, **11a**–**c**. Though the innermost and dialkylated benzene ring seems more prone to oxidation than does the outside ring, the oxidizing agent avoided the sterically crowded environment of the inside ring and attacked the outside ring, giving products **9** and **11**.

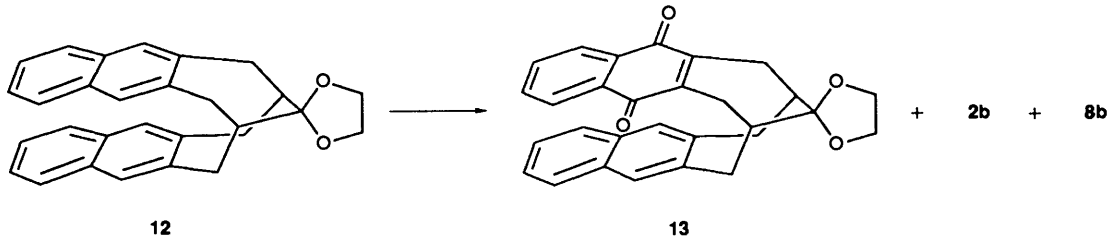
The layered *ortho*-naphthaleno[3.3] *ortho*-1,4-naphthoquinonophane **13** was prepared by the oxidation of *ortho*-[3.3]naphthalenophane **12**, in 8% yield, accompanied by formation of compounds **2b** and **8b** in 10 and 4% yield, respectively (Scheme 3).

Characterization of Conformers by ^{1}H *NMR Spectroscopy*.—Naphthoquinones **7**–**11** are flexible and exhibit temperature-dependent spectra due to the stereodynamic equilibrium among (C–B), (T–C) and (B–C) conformations (Scheme 1). The



a ; R = CO_2Me, X = CO **b** ; R = H, X = CO **c** ; R = H, X = CH_2

Scheme 2 *Reagent:* $Na_2Cr_2O_7$



Scheme 3 *Reagents:* CrO_3, AcOH

Table 1 Observed ^1H NMR data of aromatic proton signals[a] of (T–C) conformer in compounds **8**, **9** and **10**

Compound	δ
8a[b]	6.95–7.05 (2 H), 7.20 (2 H, s)
8b[c]	6.94–7.07 (2 H), 7.24 (2 H, s)
8c[d]	6.80–6.98 (2 H, 7.04 (2 H, s), 7.10–7.29 (4 H), 7.29–7.52 (2 H)
9a[b]	6.58 (2 H, s), 7.47 (2 H, s)
9b[c]	6.56 (2 H, s), 7.46 (2 H, s)
9c[e]	6.45 (2 H, s), 7.22 (2 H, s), 7.43–7.57 (2 H, 7.57–7.71 (2 H)
10a[b]	6.42–6.57 (2 H), 6.73–6.89 (2 H), 7.50–7.60 (2H), 7.84–7.91 (2 H)
10b[c]	6.34–6.53 (2 H), 6.72–6.90 (2 H), 7.66–7.84 (2H), 7.84–7.99 (2 H)
10c[f]	6.15–6.44 (2 H), 6.54–6.79 (2 H)

[a] Observed as a multiplet unless otherwise stated. [b] In $CDCl_3$ at −60 °C. [c] In a 1:2 mixture of $CDCl_3$ and CD_2Cl_2 at −80 °C. [d] In a 1:2 mixture of CS_2 and CD_2Cl_2 at −80 °C. [e] In a 1:2 mixture of CS_2 and CD_2Cl_2 at −100 °C. [f] In a 1:2 mixture of CD_2Cl_2 and CS_2 at −80 °C.

resolved ^1H NMR spectra of compounds **7a**, **8**, **9**, **10** and **11** were obtained at temperatures from −60 to −100 °C.

As represented by layered compound **13**, the upfield shift of the aromatic and quinone signals in the ^1H NMR spectrum is a characteristic feature of the T–C conformation.[7–11] Thus conformation (T–C) is easily distinguishable from (B–C) and (C–B) (Table 1).

Characterization of conformations (B–C) and (C–B) was also carried out using ^1H NMR spectroscopy. The δ-values of the benzylic protons of the major conformer of compounds **8a**, **10a**, and **11a** are tabulated together with those of the (B–C) and (C–B) conformers of **9a** and the equivalent (B–C) and (C–B) conformers of the symmetric compounds **2a** and **7a** in Table 2. The following deductions were made; (1) owing to the shielding effect of the 1,4-naphthoquinone or naphthalene ring fused on the chair-shaped ring, the benzylic protons of the boat ring appear at higher field than those on the chair ring,[2] and (2) the carbonyl groups of the 1,4-naphthoquinone deshield the equatorial protons in (B–C) and (C–B) conformations, resulting in the 1.1 and 1.6 ppm differences in the δ-values between axial and equatorial protons in the bis(naphthoquinone) **7a**. The differences in δ-values for the dinaphtho derivative **2a** are 0.1 and 0.5 ppm.

From these findings, of the four doublets of the benzylic protons of the major conformer of compound **8a**, those at δ 2.31 and 3.37 were assigned to the benzylic protons of the quinone-annelated ring, while the other set of doublets (δ 3.46 and 3.53) was due to those of the naphthalene-fused cycloheptenone. Thus, the major conformer of compound **8a** takes the B–C form, a composite of the quinone-fused boat and the naphthalene-fused chair. The preferred conformer of compound **10a** is similarly believed to take the B–C conformation.

In the ^1H NMR spectrum of compound **9a**, fifteen of the sixteen peaks of eight doublets due to (B–C) and (C–B) conformations were separately observed (Fig. 1). Each of the peaks was characterized on the basis of coupling constants and relative intensities of peaks, and confirmed by a decoupling

Table 2 Observed ^{1}H NMR data of benzylic protons of (B–C) and (C–B) conformers of compounds **2a**, **7a**, **8a**, **9a**, **10a** and **11a**

	δ				
	Major conformer		Minor conformer		Quotient major/minor conformers
Quinone	Boat	Chair	Chair	Boat	
2a[a]	(2.92, 3.03) (*J* 14.5)	(3.33, 3.80) (*J* 15.4)			
7a[b]	(2.58, 3.70) (*J* 14.6)	(2.77, 4.35) (*J* 15.6)			
8a[b]	(2.31, 3.37) (*J* 14.6)	(3.46, 3.53) (*J* 15.6)			84/6
9a[b]	(2.37, 3.55) (*J* 14.8)	(3.47, 3.67) (*J* 15.3)	(3.07, 4.15) (*J* 15.3)	(3.07, 3.33) (*J* 13.9)	56/37
10a[b]	(2.44, 3.43) (*J* 14.7)	(3.26–3.55)[c]			92/4
11a[b]	(2.94, 3.07) (*J* 14.5)	(3.24, 3.65) (*J* 15.2)			92/8

[a] In $CDCl_3$ at −20 °C. [b] In $CDCl_3$ at −60 °C. [c] Observed as a multiplet.

Table 3 ^{1}H NMR data of aromatic proton signals in compounds **2a** and **7a**

	δ	
Compound	Boat	Chair
2a[a]	7.34–7.43 (2 H, m)	7.48–7.57 (2 H, m)
	7.67 (2 H, s)	7.80 (2 H, s)
	7.67–7.77 (2 H, m)	7.81–7.90 (2 H, m)
7a[b]	7.73–7.83 (2 H, m)	7.83–7.94 (2 H, m)
	8.06–8.16 (2 H, m)	8.16–8.17 (2 H, m)

[a] In $CDCl_3$ at −20 °C. [b] In $CDCl_3$ at −60 °C.

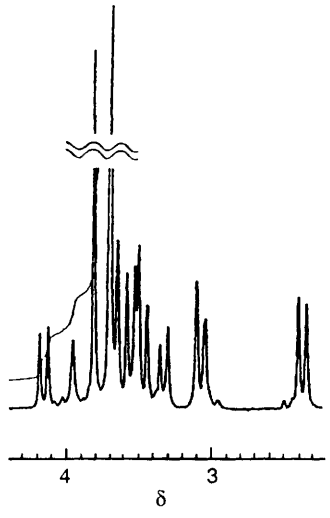


Fig. 1 ^{1}H NMR spectrum of benzylic protons of compound **9a** (at −60 °C in $CDCl_3$)

experiment. Reasoning that the outer 1,4-quinone moiety in compounds **9a** influences the δ-values of the benzylic signals less than does the inner quinone, we assigned the major conformer of compound **9a** as (B–C) and the minor as (C–B).

In Tables 3 and 4, ^{1}H NMR data for the aromatic protons of compounds **2a** and **7a**–**11a** are summarized. A characteristic feature observed in the spectra of compounds **8a** and **10a** is the *ca.* 0.2 ppm upfield shift of protons at the *peri*-position of the 1,4-naphthoquinone moiety in conformer (B–C), compared with those in conformer (C–B). In the ^{1}H NMR spectrum of bisquinone **9a**, the upfield shift of the two kinds of *peri*-proton in conformer (B–C) was also observed; the proton of the outer quinone appeared as two singlets at δ 8.01 and 8.08, each assignable to (C–B) and (B–C) conformers, respectively, while the protons of the inner quinone gave two multiplets, at δ 8.11 and 8.25 for (B–C) and (C–B) conformers (Fig. 2). Characterization of conformers (B–C) and (C–B) of compounds **8b**, **9b**, **10b**, **11a**, **11b** and **11c** were similarly carried out on the basis of the upfield-shifted *peri*-proton signals of conformers (B–C) (Table 4) in the ^{1}H NMR spectra. The reason for the upfield shift is not known.

Bisquinones **7b** and **7c** did not afford well resolved spectra even at −100 °C. We were unable to differentiate the conformers (B–C) and (C–B) of compounds **8c**, **9c**, and **10c** on the basis of their broadened ^{1}H NMR spectra.

Factors Controlling the Conformations of compounds **7**–**11**.—The ratios of the three conformers of the 1,4-naphthoquinone-annelated compounds **7**–**11** are given in Table 5.

In the bisquinones **7**, the (T–C) conformer was expected to be favoured because of the reduced repulsive interaction between two electron-deficient 1,4-naphthoquinone moieties, but it was not detected in the ^{1}H NMR spectrum of compound **7a**. Electronic repulsion among the four quinone-carbonyl groups in close proximity is unfavourable in compounds **7**.

In the naphtho–1,4-naphthoquinone compound **8a**, the (T–C) conformer was detected as only a minor fraction. Removal of the ester function on the bridgehead position made the T–C conformation more favoured, and in compound **8b** the relative content of conformer (T–C) is significantly increased to 54%. Reduction of the bridging sp^2-carbon of the carbonyl group of compound **8b** to sp^3 further benefited the (T–C) conformer, which increased to 82% of compound **8c**. The (T–C) conformer of the ester derivative **9a** exists as 7% of the compound, which increased, on removal of the two ester groups, to 56% in compound **9b** (^{1}H NMR) (Fig. 2). With the following reduction of the bridging carbonyl function to methylene, 91% of compound **9c** was in the (T–C) conformation. The (T–C) fraction of benzo–naphthoquinone compounds **10** also increased from 4% in compound **10a** to 25% in compound **10b**, and to 70% in compound **10c**. On the other hand, conformer (T–C) was not detected in compounds **11a**–**c**.

From these results we deduced that in 1,4-naphthoquinone-annelated compounds, **8a**–**c**, **9a**–**c**, and **10a**–**c**, the ester group on the bridgehead position plays a crucial role, though reduced repulsion of the two fused rings and charge-transfer attractive interactions are also important. The effect of the ester substituent seems to suggest the presence of the steric repulsion

Table 4 Observed ^{1}H NMR data of aromatic proton signals[a] of (B–C) and (C–B) conformers in compounds **8**, **9**, **10** and **11**

Compound	δ (B–C)		δ (C–B)	
8a[b]	7.47–7.60 (2 H)	7.66–7.77 (2 H)		
	7.80 (2 H, s)	7.82–7.92 (2 H)		
	8.00–8.11 (2 H)		8.22–8.30 (2 H)	
8b[c]	7.46–7.52 (2 H)	7.68–7.79 (2 H)	7.37–7.45 (2 H)	
	7.84 (2 H, s)	7.85–7.94 (2 H)		
	7.98–8.10 (2 H)		8.18–8.26 (2 H)	
9a[b]	7.10 (2 H, s)	7.72–7.85 (2 H)	7.00 (2 H, s)	7.85–7.96 (2 H)
	8.04–8.19 (2 H)	8.08 (2 H, s)	8.01 (2 H, s)	8.19–8.30 (2 H)
9b[c]	7.08 (2 H, s)	7.73–7.83 (2 H)	7.00 (2 H, s)	7.85–7.93 (2 H)
	8.00–8.12 (2 H)		8.15–8.25 (2 H)	
10a[b]	7.29–7.49 (4 H)	7.74–7.84 (2 H)	7.09–7.22 (4 H)	7.84–7.91 (2 H)
	8.01–8.17 (2 H)		8.17–8.26 (2 H)	
10b[c]	7.26–7.48 (4 H)	7.66–7.84 (2 H)	7.08–7.23 (4 H)	7.84–7.99 (2 H)
	7.99–8.13 (2 H)		8.13–8.27 (2 H)	
11a[b]	6.99 (2 H, s)	7.43 (4 H, s)	7.08 (2 H, s)	
	7.98 (2 H, s)		8.04 (2 H, s)	
11b[b]	6.97 (2 H, s)	7.34 (4 H, s)	7.08 (2 H, s)	7.13 (4 H, s)
	7.98 (2 H, s)		8.04 (2 H, s)	
11c[d]	6.86 (2 H, s)	7.08–7.26 (4 H)	6.91 (2 H, s)	6.90–7.09 (4 H)
	7.63 (2 H, s)		7.81 (2 H, s)	

[a] Observed as a multiplet unless otherwise stated. [b] In $CDCl_3$ at −60 °C. [c] In a 1:2 mixture of $CDCl_3$ and CD_2Cl_2 at −80 °C. [d] In a 1:2 mixture CS_2 and $CDCl_3$ at −80 °C.

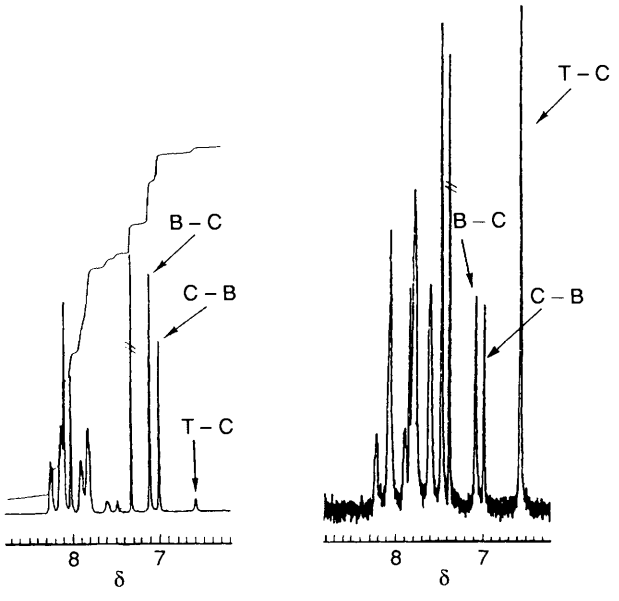


Fig. 2 ^{1}H NMR spectra of aromatic protons of compounds **9a** (at −60 °C in $CDCl_3$) and **9b** (at −80 °C in a mixture of $CDCl_3$ and CD_2Cl_2)

between the benzylic hydrogen and the ester group on the bridgehead position in conformer (T–C) of compounds **8a**, **9a** and **10a**. Previously, the similar but very slight increase in the (T–C) fraction was observed in the benzoquinoxalino derivative **5**:[1] from 6 to 8% with removal of the ester group. Therefore, the drastic increase in the (T–C) fraction in compounds **8**, **9** and **10** cannot be reasoned only in terms of steric factors, though they might be one of the major reasons for the increase. Electronic repulsion between the carbonyl groups of the 1,4-quinone moiety and the ester groups on the bridgehead position might be more important than steric crowding.

Compounds **8**, **9** and **10** showed a similar increase in conformer (T–C) with removal of the ester group followed by reduction of the carbonyl group, thus the attractive charge-transfer interaction was considered to have a secondary effect for stabilizing the (T–C) conformer. As previously mentioned,

Table 5 Quotients of conformers (T–C)/[(B–C) + (C–B)] in compounds **7a** and **8–11**

Compound	Quotient	Compound	Quotient
7a[a]	0/100	**10a**[a]	4/(4 + 92)
8a[a]	10//(4 + 86)	**10b**[c]	25/(14 + 61)
8a[b]	11/(5 + 84)	**10c**[f]	70/(30)
8b[c]	54/(11 + 35)	**10c**[c]	70/(30)
8c[d]	82/(18)	**10c**[g]	73/(27)
9a[a]	7/(37 + 56)	**11a**[a]	0/(8 + 92)
9b[c]	56/(16 + 28)	**11b**[a]	0/(25 + 75)
9c[e]	91/(9)	**11c**[g]	0/(25 + 75)

[a] In $CDCl_3$ at −60 °C. [b] In a 1:2 mixture of $CDCl_3$ and CD_2Cl_2 at −60 °C. [c] In a 1:2 mixture of $CDCl_3$ and CD_2Cl_2 at −80 °C. [d] In a 1:2 mixture of CS_2 and CD_2Cl_2 at −80 °C. [e] In a 1:2 mixture of CS_2 and CD_2Cl_2 at −100 °C. [f] In CD_2Cl_2 at −80 °C. [g] In a 1:2 mixture of CD_2Cl_2 and CS_2 at −80 °C.

reduction of the repulsive π–π interaction of the two facing rings by the fused 1,4-quinone moiety might be helpful in stabilizing the (T–C) conformation in compounds **8**, **9** and **10**. Reduction of the bridging carbonyl sp^2-carbon to a methylene (sp^3) makes the methanocyclodecadiene system more flexible, resulting in amplification of the previously mentioned reduced repulsion.

The absence of detectable amounts of conformer (T–C) in compounds **11** might be explained by the lack of any reduction in such a π–π repulsion.

In ester-substituted polycycles **8a**, **10**, and **11a**, the corresponding (B–C) conformer exists as a predominant conformer over (C–B). Upon removal of the ester groups, the fraction of conformer (C–B) increased, but was still smaller than that of (B–C). The reduction of the bridging carbonyl group of compound **11b** caused only a small change in the composition of product **11c**. On the other hand, the relative ratio is *ca.* 1:1 in compounds **9a** and **9b**. Thus, the electron-poor 1,4-naphthoquinone-annelated cycloheptene ring favours a boat conformation and the electron-rich aromatic-annelated system favours a chair in compounds **8**, **10** and **11**. This tendency was amplified by the presence of the electron-withdrawing ester groups on the bridgehead position in the cases of compounds **8a**, **10a** and **11a**.

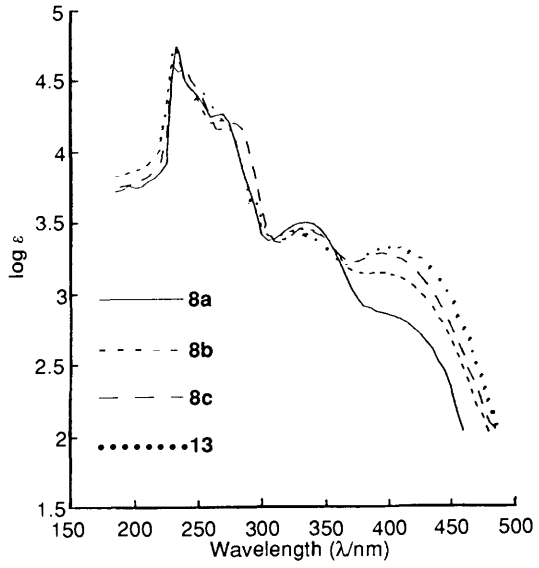


Fig. 3 Electronic spectra of compounds **8** in CH_2Cl_2 and compound **13** in $CHCl_3$

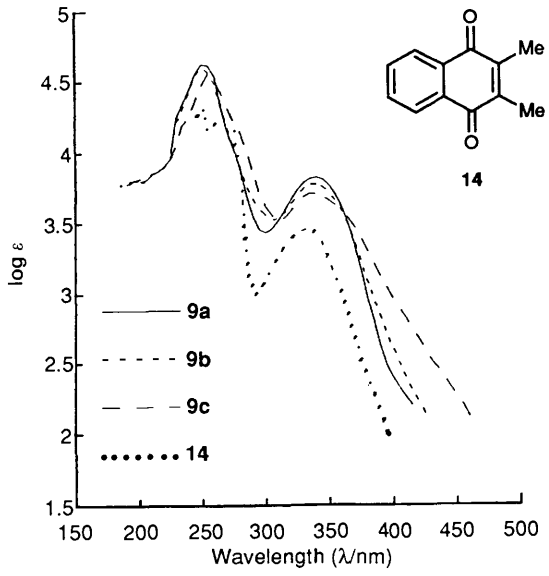


Fig. 5 Electronic spectra of compounds **9** in CH_2Cl_2 and compound **14** in $CHCl_3$

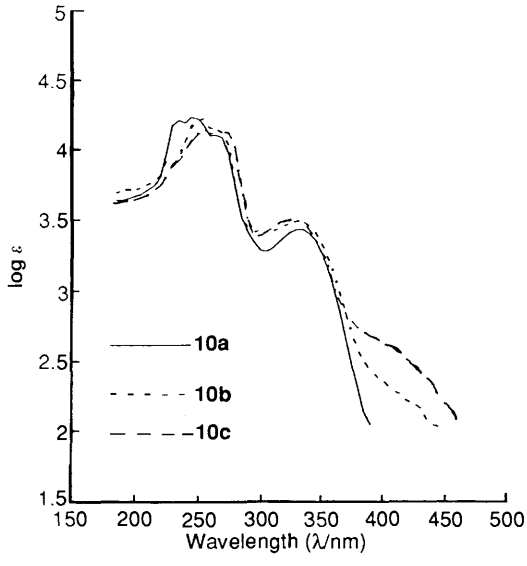
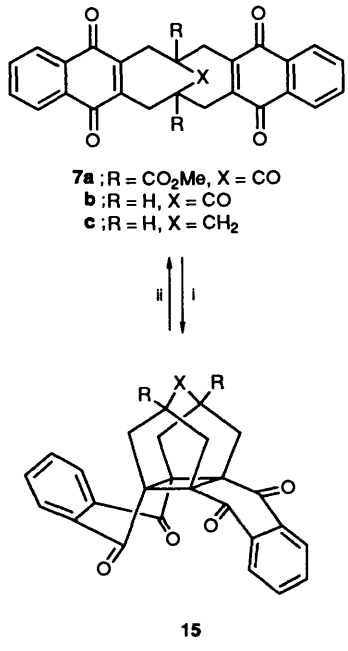


Fig. 4 Electronic spectra of compounds **10** in CH_2Cl_2



Scheme 4 *Conditions:* i, *hν*; ii, heat

Table 6 Content of (T–C) conformers of compound **8** determined by ^{1}H NMR and electronic spectroscopy

Compound	Content of (T–C) (%)	
	^{1}H NMR	Electronic spectra[a] (ε at 400 nm)
8b	54	65 (1350)
8c	82	89 (1850)

[a] The ε-value at 400 nm of compound **13** with layered structure is 2090.

Electronic Spectra.—Bisquinones **7a–c** showed electronic spectra similar to that of 2,3-dimethyl-1,4-naphthoquinone **14**. As expected, the spectra of compounds **8** and **13** (Fig. 3) clearly showed an absorption band due to a charge-transfer interaction between the naphthalene ring and the 1,4-naphthoquinone ring as a broad band at $\lambda \sim 400$ nm. Since the absorption coefficient of compound **8a** is independent of the concentration change in the range of 10^{-3}–10^{-5} mol dm^{-3}, the band at $\lambda \sim 400$ nm originates from an intramolecular interaction. Interestingly, the relative amounts of conformer (T–C) determined by ^{1}H NMR spectra and those calculated on the absorption coefficient of compounds **8b**, **8c** and **13** are in fairly good agreement (Table 6). A similar but weak C–T band was observed in compounds **10** (Fig. 4).

The spectra of compounds **9** broadened with increasing (T–C) fraction (Fig. 5), indicating through-space π–π interaction between two 1,4-naphthoquinone rings of the (T–C) confrontation.

Finally, in the (T–C) conformation of compounds **7**, although undetected, the two 1,4-naphthoquinone moieties may come into close proximity. Under irradiation by sunlight, compounds **7** gave the intramolecular [2 + 2] cycloadducts, **15** (Scheme 4). In sunlight, conversion of diester **7a** into compound **15a** took 9 h, while compounds **15b–c** was obtained quantitatively from substrate **7b–c** in 1 h. Thermal retro-addition of compound **15a** at 270 °C for 1 h gave compound **7a** in 60% yield.

Experimental

M.p.s were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on an IR A-102 spectrophotometer as KBr pellets. ^{1}H NMR (internal Me_4Si) spectra given in this section were taken in $CDCl_3$ at 25 °C on a JEOL GSX-270 NMR spectrometer unless stated otherwise. *J*-Values are given in Hz. Mass spectra were recorded on a JEOL JMS-01SG-2 mass spectrometer at 75 eV using a direct-inlet system. Column chromatography was carried out on silica gel (MERCK, Kiesel gel 60). Electronic spectra were recorded on a Hitachi 220A spectrophotometer.

6,7,8,15,16,17-*Hexahydro*-7,16-*methanodinaphtho*[2,3-a:2′,3-*f*]*cyclodecene* (**2c**).—After a mixture of $TiCl_3$ (11.5 g) and $LiAlH_4$ (0.81 g) in dry tetrahydrofuran (THF) (200 cm^3) had been refluxed under nitrogen for 1 h, a solution of ketone **2b** (2.50 g) in dry THF (120 cm^3) was added dropwise. The whole mixture was refluxed for 15.5 h and then cooled to room temperature. Aq. 20% K_2CO_3 (240 cm^3) was added and insoluble materials were filtered off. The filtrate was extracted with CH_2Cl_2, and the extract was washed with water, dried over $MgSO_4$, and evaporated under reduced pressure to leave a residue which, on chromatography with $CHCl_3$ as eluent, gave compound **2c** (1.63 g, 68%). Recrystallization from a 1:1 mixture of benzene and hexane gave the *title compound* **2c** as plates, m.p. 260.5–262 °C; ν/cm^{-1} 2922 and 749; δ_H [CD_2Cl_2–CS_2 (1:2)] 1.67 (2 H, s), 2.17–3.72 (10 H, m) and 7.06–8.00 (12 H, m); *m/z* 348 (M$^+$) (Found: C, 93.3; H, 7.0. $C_{27}H_{24}$ requires C, 93.06; H, 6.94%).

5,6,7,14,15,16-*Hexahydro*-6,15-*methanobenzo*[a]*naphtho*-[2,3-*f*]*cyclodecene* **3c**.—A mixture of $TiCl_3$ (3.61 g) and $LiAlH_4$ (0.45 g) in dry THF (150 cm^3) was refluxed for 1 h and to this mixture was added dropwise a solution of compound **3b** (1.38 g) in dry THF (20 cm^3). The reaction mixture was treated and worked up as described in the preparation of compound **2c**, and gave a residue which, on recrystallization from ethanol, afforded *title compound* **3c** as a crystalline powder (0.60 g, 46%), m.p. 134–137 °C; ν_{max}/cm^{-1} 2920 and 753; δ_H[CD_2Cl_2–CS_2 (1:2)] 1.64 (2 H, s), 1.95–4.03 (10 H, m) and 6.61–7.82 (10 H, m); *m/z* 298 (M$^+$) (Found: C, 92.9; H, 7.4. $C_{23}H_{22}$ requires C, 92.57; H, 7.43%).

Dimethyl 5,9,14,18,19-*Pentaoxo*-5,6,7,8,9,14,15,16,17,18-*decahydro*-7,16-*methanodinaphtho*[2,3-a:2′,3′-f]*cyclodecene*-7,16-*dicarboxylate* **7a**, *Dimethyl* 5,18,19-*Trioxo*-5,6,7,8,15,16,17,18-*octahydro*-7,16-*methanodinaphtho*[2,3-a:2′,3′-f]*cyclodecene*-7,16-*dicarboxylate* **8a**, *and Dimethyl* 1,4,9,14,19-*Pentaoxo*-1,4,6,7,8,9,14,15,16,17-*decahydro*-7,16-*methanodinaphtho*[2,3-a:2′3′-f]*cyclodecene*-7,16-*dicarboxylate* **9a**.—To a vigorously stirred mixture of compound **2a** (4.00 g) in $CHCl_3$ (38 cm^3) and $Na_2Cr_2O_7$ (24.4 g) in water (8 cm^3) was added dropwise conc. H_2SO_4 (19.2 cm^3) without external cooling at such a rate as to cause reflux of the reaction mixture. After the addition was complete, the mixture was stirred under reflux for 30 min. before being cooled to room temperature and poured into ice–water (200 cm^3). The organic layer was separated, washed with water, dried over Mg_2SO_4, and evaporated under reduced pressure to leave a residue which, on column chromatography with $CHCl_3$ as eluant, afforded compounds **7a** (0.30 g, 7%), **8a** (0.33 g, 8%), and **9a** (0.31 g, 7%). Recrystallization of compound **7a** from MeCN gave *yellow prisms*, m.p. 287–292 °C; ν_{max}/cm^{-1} 1745, 1696, 1665 and 1594; δ_H 3.05–4.00 (8 H, m), 3.67 (6 H, s), 7.72–7.90 (4 H, m) and 8.07–8.28 (4 H, m); *m/z* 538 (M$^+$) (Found: C, 69.3; H, 4.3. $C_{31}H_{22}O_9$ requires C, 69.14; H, 4.12%).

Compound **8a** was purified by recrystallization from MeCN, giving *yellow prisms*, m.p. 291–295 °C; ν_{max}/cm^{-1} 1745, 1696, 1659 and 1595; *m/z* 508 (M$^+$) (Found: C, 73.0; H, 4.9. $C_{31}H_{24}O_7$ requires C, 73.27; H, 4.72%).

Compound **9a** was obtained as a *yellow, crystalline powder*, m.p. 313–317 °C (from AcOH); ν_{max}/cm^{-1} 1745, 1696, 1671 and 1600; δ_H 2.39–4.08 (8 H, m), 3.75 (6 H, s), 6.88 (2 H, s), 7.48–7.77 (2 H, m), 7.91 (2 H, s) and 7.98–8.24 (2 H, m); *m/z* 538 (M$^+$) (Found: C, 68.7; H, 4.2. $C_{31}H_{22}O_9$ requires C, 69.14; H, 4.12%).

5,9,14,18,19-*Pentaoxo*-5,6,7,8,9,14,15,16,17,18-*decahydro*-7,16-*methanodinaphtho*[2,3-a:2′3′-f]*cyclodecene* **7b**, 5,18,19-*Trioxo*-5,6,7,8,15,16,17,18-*octahydro*-7,16-*methanodinaphtho*-[2,3-a:2′3′-f]*cyclodecene* **8b**, *and* 1,4,9,14,19-*Pentaoxo*-1,4,6,7,-8,9,14,15,16,17-*decahydro*-7,16-*methanodinaphtho*[2,3-a:2′,3′-f]*cyclodecene* **9b**.—Compound **2b** (1.50 g) in $CHCl_3$ (24 cm^3) was oxidized by a mixture of $Na_2Cr_2O_7$ (12.1 g) in water (3 cm^3) and conc. H_2SO_4 (6.3 cm^3), and worked up as described in the oxidation of compound **2a**, to give compounds **7b** (0.13 g, 7%), **8b** (0.07 g, 4%), and **9b** (0.13 g, 7%) together with recovered **2b** (0.03 g, 2%). Recrystallization of compound **7b** from MeCN gave *yellow plates*, m.p. 271–277 °C; ν_{max}/cm^{-1} 1691, 1664 and 1596; δ_H 2.83–3.04 (4 H, m), 3.11–3.35 (6 H, m), 7.60–7.78 (4 H, m) and 7.98–8.15 (4 H, m); *m/z* 422 (M$^+$) (Found: C, 76.6; H, 4.5. $C_{27}H_{18}O_5$ requires C, 76.77; H, 4.29%).

Compound **8b** was obtained as *yellow plates*, m.p. 291–295 °C (from MeCN); ν_{max}/cm^{-1} 1708, 1659 and 1595; δ_H [$CDCl_3$–CD_2Cl_2 (1:2)] 2.36–2.67 (2 H, m), 2.89–3.87 (8 H, m) and 6.93–8.22 (10 H, m); *m/z* 392 (M$^+$) (Found: C, 82.3; H, 5.3. $C_{27}H_{20}O_3$ requires C, 82.63; H, 5.14%).

Compound **9b** was obtained as a *yellow, crystalline* powder, m.p. 299–305 °C (from MeCN); ν_{max}/cm^{-1} 1701, 1667 and 1603; δ_H 2.54–2.75 (2 H, m), 3.08–3.92 (8 H, m), 6.68 (2 H, s), 7.54–7.74 (2 H, m), 7.64 (2 H, s) and 7.86–8.14 (2 H, s); *m/z* 422 (M$^+$) (Found: C, 76.5; H, 4.6. $C_{27}H_{18}O_5$ requires C, 76.77; H, 4.29%).

5,9,14,18-*Tetraoxo*-5,6,7,8,9,14,15,16,17,18-*decahydro*-7,16-*methanodinaphtho*[2,3-a:2′,3′-f]*cyclodecene* **7c**, 5,18-*Dioxo*-5,6,-7,8,15,16,17,18-*octahydro*-7,16-*methanodinaphtho*[2,3-a:2′,3′-f)-*cyclodecene* **8c**, *and* 1,4,9,14-*Tetraoxo*-1,4,6,7,8,9,14,15,16,17-*decahydro*-7,16-*methanodinaphtho*[2,3-a:2′,3′-f]*cyclodecene* **9c**.—Compound **2c** (1.50 g) in $CHCl_3$ (30 cm^3) was oxidized with a mixture of $Na_2Cr_2O_7$ (12.6 g) in water (5 cm^3) and conc. H_2SO_4 (9.9 cm^3), and worked up as described in the oxidation of compound **2a** to afford a residue which, on column chromatography with $CHCl_3$ as eluent, gave compounds **7c** (0.22 g, 13%), **8c** (0.11 g, 7%), and **9c** (0.11 g, 6%). Recrystallization of compound **7c** from benzene gave *yellow prisms*, m.p. 287–292 °C; ν_{max}/cm^{-1} 2892, 1659 and 1592; δ_H [CD_2Cl_2–CS_2 (2:1)] 2.04–2.16 (2 H, m), 2.33–2.49 (2 H, m), 2.78–2.89 (4 H, m), 3.10–3.27 (4 H, m), 7.49–7.66 (4 H, m) and 7.82–7.95 (4 H, m); *m/z* 408 (M$^+$) (Found: C, 79.1; H, 5.2. $C_{27}H_{20}O_4$ requires C, 79.40; H, 4.94%).

Compound **8c** was obtained as *yellow prisms* m.p. 264–265 °C [from benzene–hexane (1:1)]; ν_{max}/cm^{-1} 2892, 1652 and 1593; δ_H [CD_2Cl_2–CS_2 (2:1)] 2.09–2.68 (6 H, m), 2.74–4.02 (6 H, m) and 6.70–8.20 (10 H, m); *m/z* 378 (M$^+$) (Found: C, 85.4; H, 5.9. $C_{27}H_{22}O_2$ requires C, 85.69; H, 5.86%).

Compound **9c** was obtained as *yellow prisms*, m.p. 282–287 °C (from benzene); ν_{max}/cm^{-1} 2890, 1665 and 1593; δ_H [CD_2Cl_2–CS_2(2:1)] 2.23–2.66 (6 H, m), 2.95–3.14 (2 H, m), 3.18–3.35 (2 H, m), 3.52–3.75 (2 H, m), 6.45 (2 H, s), 7.32 (2 H, s), 7.39–7.52 (2 H, m) and 7.59–7.83 (2 H, m); *m/z* 408 (M$^+$) (Found: C, 79.4; H, 5.15. $C_{27}H_{20}O_4$ requires C, 79.40; H, 4.94%).

Dimethyl 8,13,17-*Trioxo*-5,6,7,8,13,14,15,16-*octahydro*-6,15-*methanobenzo*[a]*naphtho*[2,3-f]*cyclodecene*-6,15-*dicarboxylate* **10a** *and Dimethyl* 9,12,17-*Trioxo*-5,6,7,9,12,14,15,16-*octahydro*-6,15-*methanobenzo*[a]*naphtho*[2,3-f]*cyclodecene*-6,15-*dicarboxylate* **11a**.—Compound **3a** (1.29 g) in $CHCl_3$ (14 cm^3) was oxidized with a mixture of $Na_2Cr_2O_7$ (4.40 g) in water (2 cm^3) and conc. H_2SO_4 (3.4 cm^3), and worked up as described in the

oxidation of compound **2a**, to yield compounds **10a** (0.41 g, 30%) and **11a** (0.12 g, 9%), together with unchanged compound **3a** (0.22 g, 17% recovery). Recrystallization of compound **10a** from MeCN gave *yellow prisms*, m.p. 274–279 °C; ν_{max}/cm^{-1} 1748, 1702, 1667 and 1593; δ_H 2.36–3.96 (8 H, m), 3.68 (6 H, s), 7.24 (4 H, s), 7.64–7.83 (2 H, m) and 7.99–8.14 (2 H, m); *m/z* 458 (M^+) (Found: C, 70.94; H, 5.06. $C_{27}H_{22}O_7$ requires C, 70.74; H, 4.84%).

Compound **11a** was obtained as *yellow needles* on recrystallization from EtOH–benzene (3:1), m.p. 269–275 °C; ν_{max}/cm^{-1} 1743, 1699, 1670 and 1605; δ_H 2.91 (2 H, d, *J* 13.6), 3.03 (2 H, d, *J* 13.6), 3.19 (2 H, d, *J* 15.2), 3.62 (2 H, d, *J* 15.2), 3.75 (6 H, s), 6.91 (2 H, s), 7.17–7.44 (4 H, m) and 7.95 (2 H, s); *m/z* 458 (M^+) (Found: C, 70.5; H, 4.9%).

8,13,17-*Trioxo*-5,6,7,8,13,14,15,16-*octahydro*-6,15-*methanobenzo*[a]*naphtho*[2,3-f]*cyclodecene* **10b** *and* 9,12,17-*Trioxo*-5,6,7,9,12,14,15,16-*octahydro*-6,15-*methanobenzo*[a]*naphtho*[2,3-f]*cyclodecene* **11b**.—Compound **3b** (0.47 g) in $CHCl_3$ (7 cm^3) was oxidized with a mixture of $Na_2Cr_2O_7$ (2.20 g) in water (1 cm^3) and conc. H_2SO_4 (1.70 cm^3), and worked up as described in the oxidation of compound **2a**, to give compounds **10b** (0.15 g, 29%) and **11b** (0.03 g, 6%) together with unchanged substrate **3b** (0.07 g, 14%). Both compounds **10b** and **11b** were recrystallized from MeCN to give yellow prisms. *Compound* **10b** had m.p. 222–227 °C; ν_{max}/cm^{-1} 1700, 1664 and 1593; δ_H 2.65–3.31 (10 H, m), 6.81–6.96 (2H, m), 6.96–7.09 (2 H, m), 7.56–7.82 (2 H, m) and 7.91–8.06 (2 H, m); *m/z* 342 (M^+) (Found: C, 80.4; H, 5.3. $C_{23}H_{18}O_3$ requires C, 80.68; H, 5.30%).

Compound **11b** had m.p. 279–285 °C; ν_{max}/cm^{-1} 1696, 1668 and 1603; δ_H 2.65–3.03 (8 H, m), 3.03–3.29 (2 H, m), 6.92 (2 H, s), 7.24 (4 H, s), and 7.83 (2 H, s); *m/z* 342 (M^+) (Found: C, 80.6; H, 5.6%).

8,13-*Dioxo*-5,6,7,8,13,14,15,16-*octahydro*-6,15-*methanobenzo*[a]*naphtho*[2,3-f]*cyclodecene* **10c** *and* 9,12-*Dioxo*-5,6,7,9,12,14,15,16-*octahydro*-6,15-*methanobenzo*[a]*naphtho*[2,3-f]*cyclodecene* **11c**.—Compound **3c** (0.45 g) in $CHCl_3$ (17 cm^3) was oxidized with a mixture of $Na_2Cr_2O_7$ (2.20 g) in water (1 cm^3) and conc. H_2SO_4 (1.7 cm^3), and worked up as described in the oxidation of compound **2a**, to give compounds **10c** (0.11 g, 23%) and **11c** (0.03 g, 5%) together with unchanged substrate **3c** (0.03 g, 6%). Compound **10c** was recrystallized from ethanol to give *yellow prisms*, m.p. 155.5–158 °C; ν_{max}/cm^{-1} 2910, 1656 and 1592; δ_H[CD_2Cl_2–CS_2 (1:2)] 2.22 (2 H, s), 2.34–2.59 (4 H, m), 2.69–2.86 (2 H, m), 3.03–3.36 (4 H, m), 6.35–6.57 (2 H, m) 6.63–6.75 (2 H, m), 7.48–7.61 (2 H, m) and 7.75–7.90 (2 H, m); *m/z* 328 (M^+) (Found C, 84.4; H, 6.3. $C_{23}H_{20}O_2$ requires C, 84.11; H, 6.14%).

Compound **11c** was obtained as *yellow prisms*, m.p. 217–219 °C (from EtOH); ν_{max}/cm^{-1} 2886, 1667 and 1600; δ_H-[CD_2Cl_2–CS_2 (1:2)] 1.60–1.80 (2 H, m), 2.19–2.45 (2 H, m), 2.45–3.45 (8 H, m), 6.81 (2 H, s), 7.01 (4 H, s) and 7.65 (2 H, s); *m/z* 328 (M^+) (Found: C, 83.5; H, 6.2%).

19,19-*Ethylenedioxy*-5,18-*dioxo*-5,6,7,8,15,16,17,18-*octahydro*-7,16-*methanodinaphtho*[2,3-a:2′,3′-f]*cyclodecene* **13**.—To a vigorously stirred mixture of the acetal **12** (0.50 g) in AcOH (50 cm^3) was added dropwise a mixture of CrO_3 (0.75 g) in AcOH (5 cm^3)–water (5 cm^3) without external cooling at such a rate as to cause reflux of the reaction mixture. After the addition was complete, the reaction mixture was stirred under reflux for 15 min before being cooled to room temperature, poured into ice–water (300 cm^3), and kept overnight. The precipitated solid was collected and chromatographed with $CHCl_3$ as eluent, to give compounds **2b** (0.05 g, 10%), **13** (0.04 g, 8%), and **8b** (0.02 g, 4%). Compound **13** was recrystallized from benzene to give *yellow prisms*, m.p. 331–334 °C; ν_{max}/cm^{-1} 1653 and 1592; δ_H 2.40–2.55 (2 H, m), 2.66 (2 H, m), 2.84 (2 H, dd, *J* 5.9 and 15.0), 3.50–3.66 (4 H, m), 4.13 (4 H, s), 6.85–6.96 (2 H, m), 7.10 (2 H, s), 7.13–7.24 (4 H, m) and 7.47–7.55 (2 H, m); *m/z* 466 (M^+) (Found: C, 79.85; H, 5.5. $C_{29}H_{24}O_4$ requires C, 79.79; H, 5.54%).

Dimethyl 4,11,17,24,27-*Pentaoxooctacyclo*[12.12.1.0^{3,12}.0^{3,25}.0^{5,10}.0^{12,16}.0^{16,25}.0^{18,23}]*heptacosa*-5,7,9,18,20,22-*hexaene*-1,14-*dicarboxylate* **15a**.—A solution of compound **7a** (20 mg) in $CDCl_3$ (0.6 cm^3) was kept in daylight for 9 h, to afford the title compound **15a** quantitatively as a *crystalline powder*, m.p. 321–328 °C (decomp.) (from MeCN); ν_{max}/cm^{-1} 1744, 1685 and 1592; δ_H 2.68 (4 H, d, *J* 16), 3.23 (4 H, d, *J* 16), 3.83 (6 H, s), 7.24–7.51 (4 H, m) and 7.51–7.79 (4 H, m); *m/z* 538 (M^+) (Found: C, 69.2; H, 4.2. $C_{31}H_{22}O_9$ requires C, 69.14; H, 4.12%).

4,11,17,24,27-*Pentaoxooctacyclo*[12.12.1.0^{3,12}.0^{3,25}.0^{5,10}.0^{12,16}.0^{16,25}.0^{18,23}]*heptacosa*-5,7,9,18,20,22-*hexaene* **15b**.—A solution of compound **7b** (20 mg) in $CDCl_3$ (0.6 cm^3) was kept in sunlight for 1 h, to give compound **15b** quantitatively as *pale yellow prisms*, m.p. 325–327 °C (decomp.) (from EtOAc); ν_{max}/cm^{-1} 1700, 1687 and 1589; δ_H 2.34 (4 H, d, *J* 15.4), 2.94 (4 H, dd, *J* 7.0 and 15.0), 3.51 (2 H, t, *J* 6.6), 7.34–7.52 (4 H, m) and 7.60–7.81 (4 H, m); *m/z* 422 (M^+) (Found: C, 76.75; H, 4.4. $C_{27}H_{18}O_5$ requires C, 76.77; H, 4.29%).

4,11,17,24-*Tetraoxooctacyclo*[12.12.1.0^{3,12}.0^{3,25}.0^{5,10}.0^{12,16}.0^{16,25}.0^{18,23}]*heptacosa*-5,7,9,18,20,22-*hexaene* **15c**.—A solution of compound **7c** (5 mg) in a 1:1 mixture of CD_2Cl_2 and CS_2 (0.6 cm^3) was kept in sunlight for 1 h, to give *compound* **15c** quantitatively as pale yellow prisms, m.p. 298.5 °C (decomp.) (from benzene); ν_{max}/cm^{-1} 2918, 1690 and 1592; δ_H[CD_2Cl_2–CS_2 (2:1)] 1.89 (2 H, t, *J* 3.7), 2.00 (4 H, d, *J* 14.7), 2.27 (4 H, dd, *J* 7.7 and 14.6), 3.05 (2 H, m), 7.30–7.44 (4 H, m) and 7.55–7.80 (4 H, m); *m/z* 408 (M^+) (Found: C, 79.1; H, 5.2. $C_{27}H_{20}O_4$ requires C, 79.40; H, 4.94%).

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