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THE SYNTHESIS OF RIGID NORBORNYLOGS FOR THE PURPOSE OF STUDYING ORBITAL INTERACTIONS THROUGH BONDS

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Abstract—The synthesis of members of the series of rigid bichromophoric norbornylogs **4–8** is described. Dienes **4a** and **b** were synthesized according to Scheme 1. Reductive dechlorination of **26–28** (Scheme 2) gave dienes **5b–d**, respectively. Benzene annelation of the appropriate ene substrate, using tetrachlorodimethoxycyclopentadiene, as outlined in Scheme 3, gave the dibenzo compounds **6a–c**. The dibromoquinodimethane intermediate **49** was trapped by the appropriate diene to give the bisnaphtho compounds **7a–c**. The extended norbornylogs **8a** and **b** were synthesized using a combination of metal catalyzed (2+2) cycloaddition of DMAD and (2+2+2) cycloaddition of quadricyclane to ene substrates (Scheme 5). The photoelectron spectra of some of the dienes are discussed in terms of through bond orbital interactions.

Our interest in the synthesis of "non-natural products" stems from the need for a variety of rigid model bichromophoric systems, having well-defined molecular configurations, in order to explore systematically long-range electron transfer processes, and the role played therein by through bond effects. Such a study is timely considering the relevance of electron transfer processes to the mechanism of biological electron transport phenomena.

Hoffmann's seminal papers on the conceptual dissection of orbital interactions into the through-space (OITS) and through-bond (OITB) varieties[1,2] formed the inspiration for our work. Since OITB is central to our studies, a brief description of it is given. OITB is a form of hyperconjugation[2–6] but in which two, and not one, π-orbitals, located in separate regions of the molecule, mutually mix with the connecting σ framework. This is shown schematically in Fig. 1 for the cases of a pair of degenerate filled π-type orbitals interacting through four σ-bonds (OIT-4-B). The levels of both symmetry adapted pairs of π-orbitals are raised through their mixing with the σ-orbital of appropriate symmetry *but by different amounts*. This arises because in general the hybrid atomic orbital AO_3, which is principally responsible for the σ–π mixing, is associated with different coefficients in σ-HOMO and σ-SHOMO.[4,7] The splitting, Δ_s, of the two π levels is taken to be a measure of the magnitude of OITB and is usually equated with ΔI_p, the observed difference in the π ionization potentials measured for example by photoelectron spectroscopy (pes).[8] Δ_s corresponds to the larger of the two level shifts brought about by hyperconjugation and is an important quantity for it provides information about the degree of σ–π mixing in the symmetry adapted MO more affected and hence the extent of delocalization of that MO over the whole molecular framework. Although OITB has been exemplified using filled π MOs it is a simple matter to extend the treatment to cover interactions involving π^*MOs.[9]

Model calculations[1,2] predict that Δ_s for OIT-*n*-B is only weakly attenuated with increasing number, *n*, of relaying σ-bonds and should even be observable ($\Delta_s = 0.2$ eV[1]) for OIT-8-B, corresponding to an interorbital separation of *ca* 10 Å. This contrasts sharply with OITS which becomes negligible for interorbital separations greater than 4 Å. It was also predicted that, for a given value of *n*, Δ_s should depend on the conformation of the σ relay and is maximized for an all-*trans* arrangement of σ-bonds. For example, this

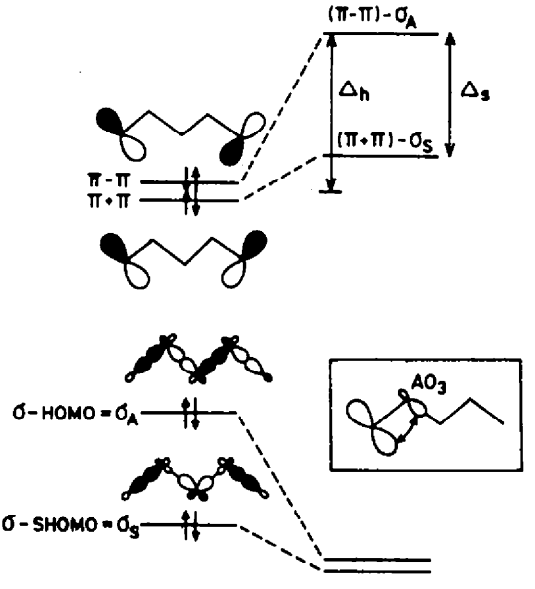


Fig. 1. Interaction diagram for a pair of degenerate π-orbitals mixing with a relay of four σ-bonds.

"*trans*" effect predicts that OIT-4-B should diminish along the series $1 > 2 > 3$. Perhaps even more intriguing than these predictions is the realization[10] that although simple C-approximation calculations[11] indicate that Δ_s becomes negligible for $n > 8$ σ-bonds, this is by no means the case for Δ_h, which is predicted to be significant even for $n = 20$, corresponding to an interorbital separation of *ca* 25 Å. This arises because, although the coefficients of AO_3 in the σ-HOMO and σ-SHOMO converge for $n = 8$, thereby making Δ_s very small, the magnitudes of these coefficients diminish quite slowly with increasing n. Thus Δ_h, and the degree of σ–π mixing, likewise should display a sluggish dependence on n. This prediction has exciting implications for the mechanisms of long-range charge transfer processes since it provides a very efficient mechanism for the intramolecular transfer of electrons or positive holes between two chromophores over extremely large distances via the σ framework.

Notwithstanding the potential importance of the above predictions little systematic experimental work bearing on their validity had been carried out prior to this study. To be sure OIT-3-B has been thoroughly studied, particularly by pes,[3,6,8] but little was known about orbital interactions through four,[12] five,[13] or more bonds. Also, although some very beautiful investigations on long-range electron transfer processes have been carried out[14–17] they suffered from at least one disadvantage such as the lack of any molecular symmetry in the substrates, the chromophores were connected by σ relays of unequal lengths, or the chromophores were not rigidly attached to the molecular framework and were allowed to rotate with respect to one another.

Our goal was to synthesize a series of substrates subject to the following requirements.

(1) The framework should be rigid and readily amenable to homologation.

(2) The chromophores must be rigidly attached to the molecular backbone in order to preclude any conformational "floppiness".

(3) The molecular framework should be such as to allow straightforward attachment of a wide variety of chromophores to the system.

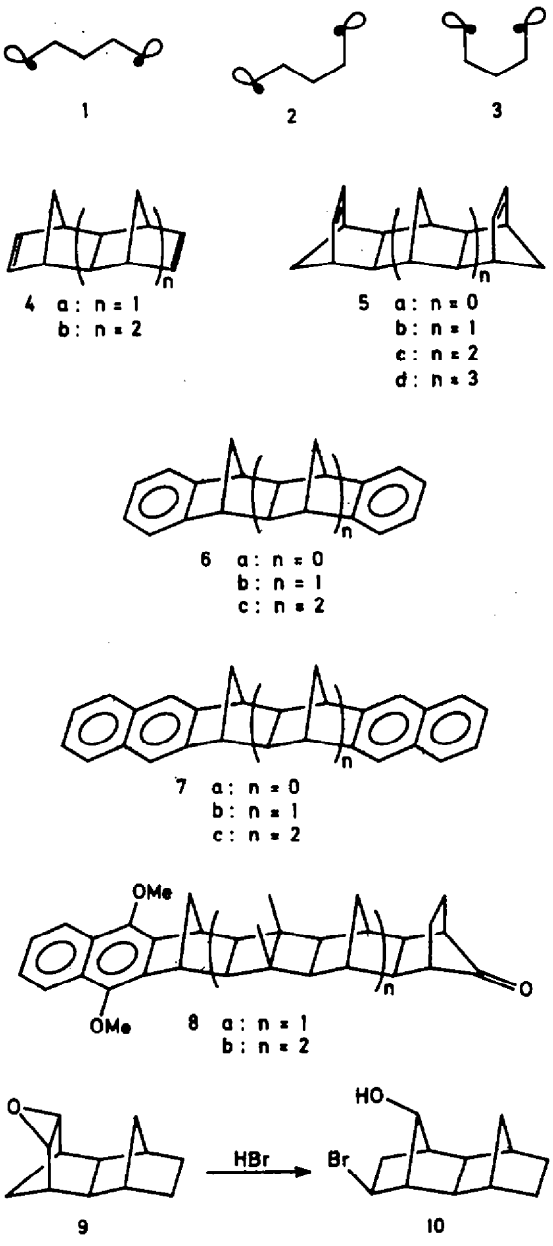
(4) The complete substrate should have at least C_s point group symmetry since this would greatly simplify analysis of the data.

The largely unknown series of dienes **4**–**8**, consisting of linearly concatenated norbonyl rings, nicely fulfils these requirements. Thus each diene is expected to be conformationally rigid and to exhibit C_s point group symmetry. Homologation should be straightforward since each diene of the series is related to its immediate predecessor through formal Diels–Alder attachment of cyclopentadiene. Naturally stereochemical control of the cycloaddition is required. Attachment of other chromophores to the norbornylogs, such as benzo **6**, naphthaleno **7**, and carbonyl **8** should be achievable through annelation reactions.

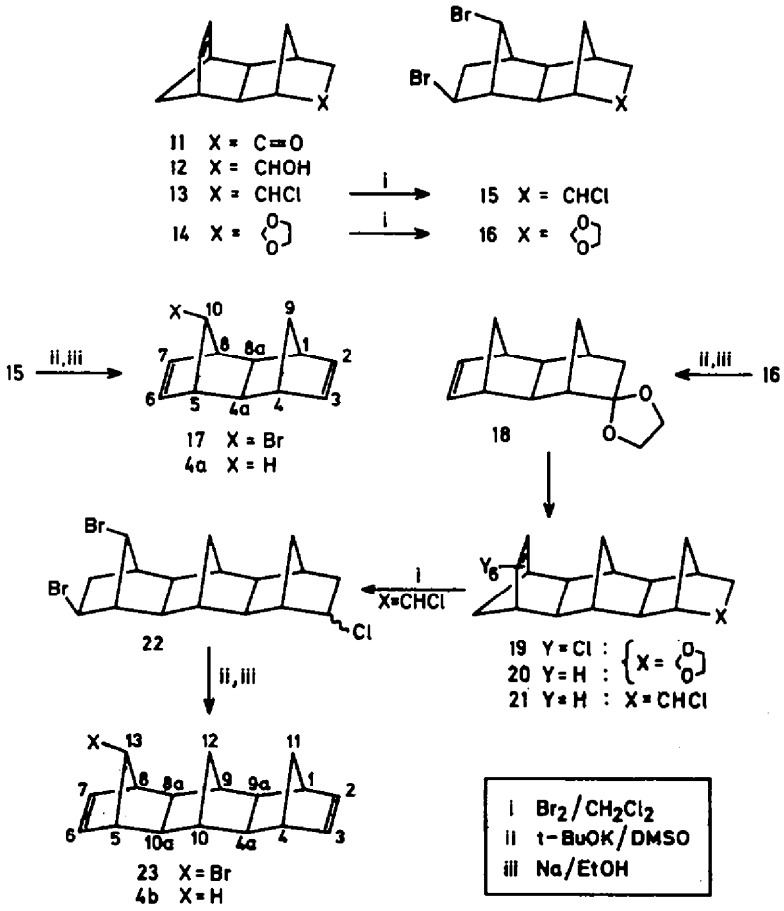
Synthesis of the dienes **4** *and* **5**

The diene **5b** has been prepared in low yield from the double Diels–Alder cycloaddition of cyclopentadiene to norbornadiene.[18,19] The stereochemistry of this cycloaddition reaction is representative of the vast majority of such reactions involving norbornadiene. Therefore indirect methods, involving molecular rearrangements are required for the synthesis of the all-*trans* dienes **4a** and **b**.

A few derivatives of **4a** have been reported.[20] The key step in their synthesis involves the acid catalyzed skeletal rearrangement of the epoxide **9** to **10**. We chose



a similar, but shorter pathway to **4a** but which could also be used in the synthesis of the next higher norbornylog **4b**. The synthesis of both dienes is outlined in Scheme 1. Cycloaddition of cyclopentadiene to norborn-5-ene-2-one at 180° gave the enone **11** in good yield.[21] Reduction of this compound with sodium borohydride, followed by treatment of the resulting *endo* alcohol **12** with thionyl chloride in HMPA gave a mixture of *endo*- and *exo*-chlorides **13**. This mixture was not purified but was treated directly with bromine in CH_2Cl_2. Precedent from brominations of related compounds[22,23] would suggest that skeletal rearrange-



Scheme 1.

ment should accompany bromination of **13** to give the diastereoisomeric mixture **15**. Owing to the suspected high toxicity of 2,7-dibromonorbornyl compounds[24] the mixture of diastereomers **15** was not isolated but was immediately bisdehydrohalogenated to give **17**. Reductive debromination of **17** (Na/EtOH[25]) gave the diene **4a** in 22% overall yield from **11**.[26]

The ketal **18** provided access to **4b**. Unfortunately cycloaddition of cyclopentadiene to **18** gave only a paltry yield of **20**, accompanied by large quantities of polymeric material. This problem was circumvented through reaction of **18** with hexachlorocyclopentadiene, HCCPD, and subsequent reduction of the resulting adduct **19** (Na/EtOH)[25] to give **20**. Conversion of **20** to the chloro compound **21** using standard methods, followed by bromination delivered the rearranged material **22**. Bisdehydrohalogenation of **22** and reductive debromination of the resulting product **23** gave the diene **4b** in 15% overall yield from **18**. The ^{1}H-NMR spectrum of **4b** revealed C_{2v} symmetry, thereby fully confirming its structure (see Experimental).

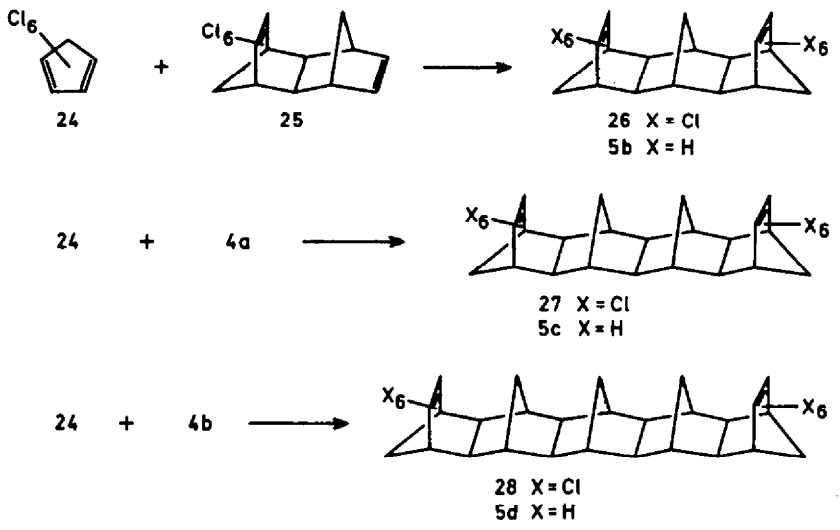
As mentioned earlier, **5b** has been prepared from norbornadiene and cyclopentadiene but in low yield.[18,19] We have improved the synthesis of this diene through Diels–Alder cycloaddition of HCCPD **24** to aldrin **25**, followed by reductive dechlorination of the adduct **26**, to give **5b** in 43% overall yield (Scheme 2). The adduct **26** could also be prepared directly from norbornadiene by heating it with at least two equivalents of **24**. In a similar fashion, the higher norbornylogs **5c** and **d** were prepared from double addition of **24** to the dienes **4a** and **b**, followed by reductive dechlorination of the resulting bisadducts. The ^{1}H-NMR spectra of these dienes reveal that they possess C_{2v} symmetry (see Experimental). This, together with the strong precedent that Diels–Alder reactions between HCCPD and norbornenes give exclusively *endo, exo* adducts,[27] e.g. **18** → **19**, clearly establishes the configurations of the dienes.

We now turn to the problem of attaching aromatic chromophores to the dienes **4**.

Benzene annelation

The most efficient route for the benzene annelation of alkenes utilizes tetrachlorothiophen-1,1-dioxide **30a**[28] as shown in Scheme 3 for the projected synthesis of dibenzonorbornadiene from benzonorbornadiene **29**. Spontaneous loss of SO_2 from the initially formed adduct **31a**, between **29** and **30a**, will produce **32**. Aromatization of **32** (KOH)[29] and reductive dehalogenation should give **6a**. Indeed **6a** was synthesized from **29** in 26% yield using this procedure and represents a considerable improvement over the previously reported synthesis involving the double Diels–Alder cycloaddition of butadiene to norbornadiene.[30]

However, because large quantities of dibenzo compounds **6** were required an alternative (but



Scheme 2.

somewhat lengthier) annelation method was devised in which the more readily available and cheaper tetrachlorodimethoxycyclopentadiene **30b** was used in place of the thiophene-1,1-dioxide[31] (Scheme 3). In this scheme the adduct **31b** is deacetalized to the ketone **31c** which is thermally decarbonylated to **32**. The overall yield of **6a** from **29** using this method is 13%.

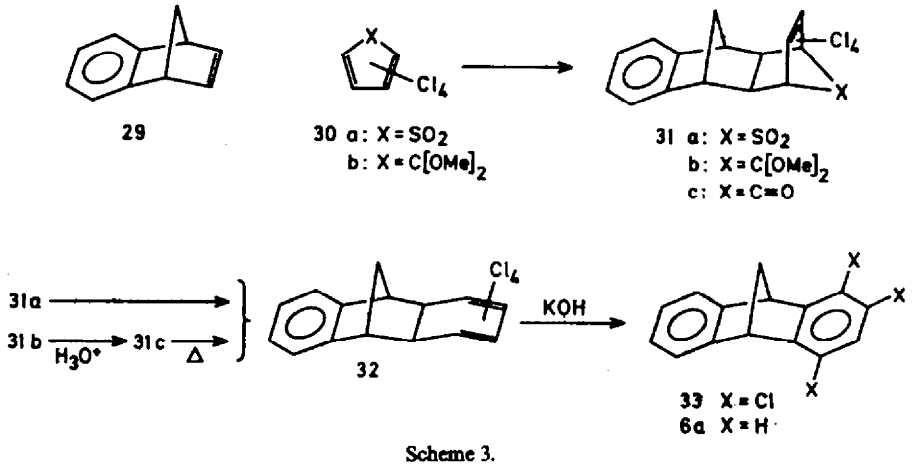
The dibenzo compounds **6b** and **c** were synthesized in a similar fashion (Scheme 4). Bromination of **34a**, the cycloadduct of cyclopentadiene and benzonorbornadiene,[32] gave the rearranged dibromo compound **35a** which was readily converted into **36a** using techniques shown in Scheme 1. Benzene annelation of **36a** gave **6b**. Reaction of **36a** with cyclopentadiene gave **34b**, which was then easily converted into **6c** via **35b** and **36b**.

Introduction of the naphthalene chromophore

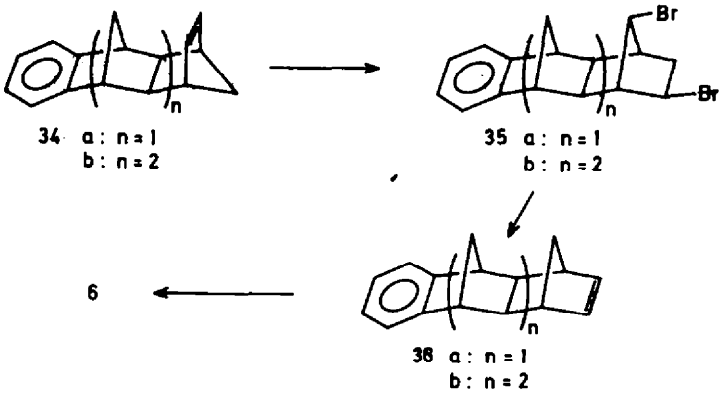
The standard synthetic entry into naphthalene containing norbornyl compounds is via the adduct **37** of 1,4-naphthoquinone and cyclopentadiene, from which both **38a**[33] and **38b**[34] are readily obtained. We have exploited this technique to synthesize **8a** and **45** in which the naphthalene and carbonyl chromophores are separated by eight and ten σ-bonds, respectively (Scheme 5).

Ruthenium catalysed (2+2) cycloaddition[35] of dimethylacetylene dicarboxylate (DMAD) to **38a** cleanly gave the adduct **40a**, which then underwent the expected[36] (2+2+2) thermal cycloaddition with quadricyclane. The resulting adduct **41a** was converted to the dimethyl analog **41d** through the diol **41b**, and $LiAlH_4$ reduction of the bismesylate derivative **41c**. Cycloaddition of the cyclopentadiene **30b** to **41d** gave **43a** which, upon treatment with Na/EtOH, gave not only the desired **43b**, but also products resulting from the partial reduction of the naphthalene ring. However, rearomatization of these compounds was easily achieved through treatment of the mixture with DDQ. Conversion of **43b** to **8a**, and thence to **46**, was straightforward. The ketone **45** was obtained from **39** using the same procedures as were just described. The compound **39** was prepared from **47** using the rearrangement methodology described in Scheme 1.

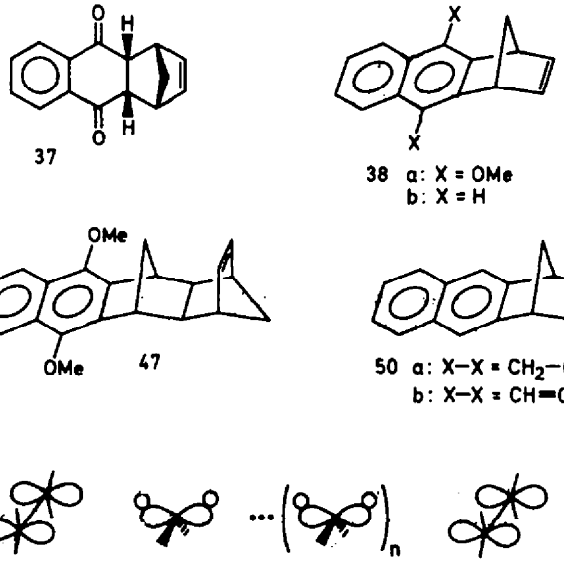
A veritable host of rigid systems in which the naphthalene and carbonyl chromophores are separated by virtually any desired number of σ-bonds should be accessible using the reactions outlined in Scheme 5.



Scheme 3.



Scheme 4.



53 n = 0, 1, ...

Thus the synthesis of **8b**, in which the chromophores are separated by twelve σ-bonds, has been almost completed in our laboratory. We also sought an alternative strategy for introducing the naphthalene moiety into our systems through annelation of double bonds since this would provide access to the series **7** from the dienes **4**.

It is well known[37,38] that treatment of **48** with NaI in DMF produces the evanescent dibromoquinodimethane **49** which can be trapped with electron-deficient dienophiles, such as maleic anhydride, to give naphthalene annelated products through spontaneous loss of HBr (Scheme 6). Although the ability of unactivated alkenes to trap **49** seems not to have been previously investigated we were pleased to discover that double bonds of norbornenyl systems do indeed trap **49** quite effectively. Thus norbornene reacts with **49** to give the adduct **50a** in 78% yield. Norbornadiene gives the monoadduct **50b** using a diene : **48** molar ratio of 10 : 1. The bisadduct **7a** is produced when the diene : **48** ratio is 1 : 6. In a similar manner bisadducts **7b** and **c** were prepared from **4a** and **b**, respectively.

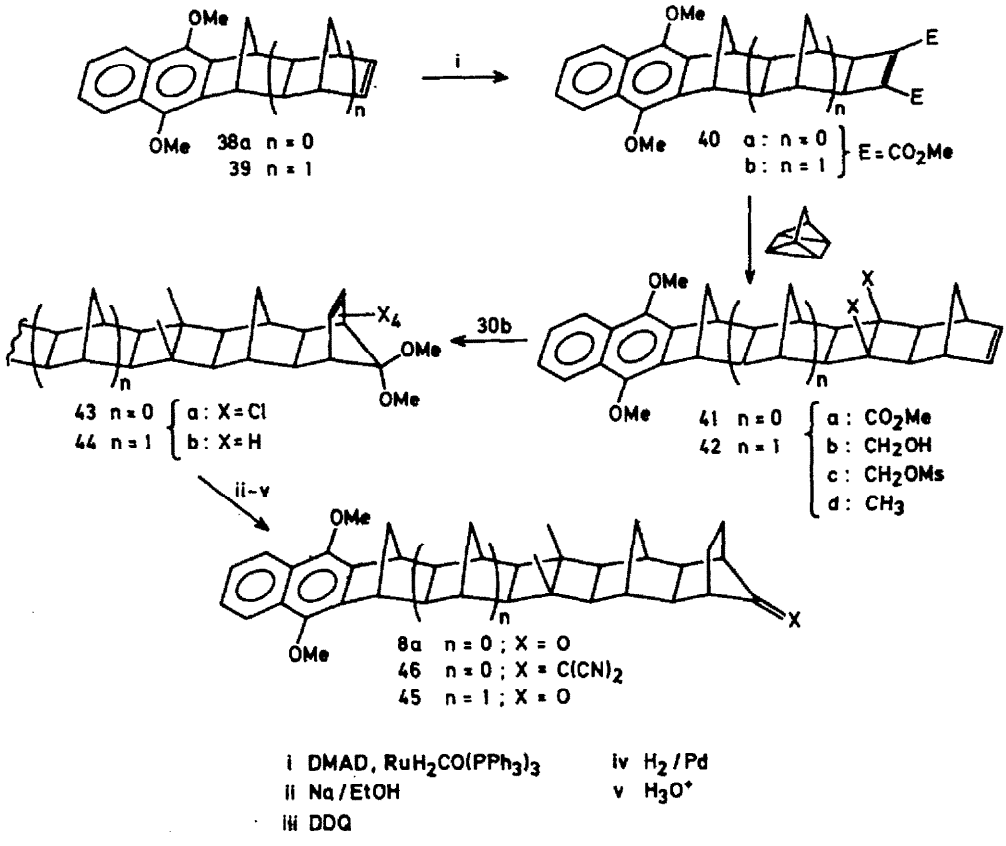
Investigations of OITB

One of the most useful ways of studying OITS and OITB is through pes and electron transmission spectroscopy[39] since they provide direct estimates (through Koopmans' theorem) of the energies of filled and virtual MOs, respectively. Application of these techniques to the series of dienes **4** and **5** and benzo compounds **6** has produced much valuable data on OITB[4,7,9,10,40–44] of which only a few of the highlights will be mentioned here. Figure 2 summarizes the π-orbital energies, determined by pes, and the corresponding Δ_s values of some dienes. The Δ_s values for **4a** and **b** are impressively large and must be the consequence of OIT-4-B and OIT-6-B, respectively.[7,41] The latter result provided the first unequivocal experimental evidence that OIT-*n*-B can operate over such large distances (7.5 Å). The form of the decay of Δ_s with n can be determined from the series of all-*trans* dienes **51**,[44] **4a**, **52**,[43] and **4b**, along which n increases from 3 to 6. As predicted,[1] an exponential decay was found:

$$\ln \Delta_s = -0.46n + 1.56.$$

From this equation it can be seen that the magnitude of Δ_s is significant (3 meV) even for n as large as 16 or, equivalently, for an inter-π-orbital separation of 21 Å!

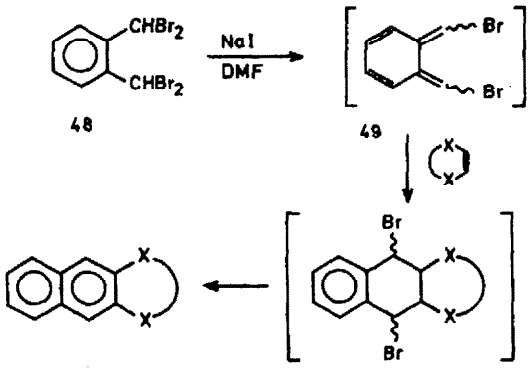
Interestingly, for large values of n (>16), when Δ_s becomes negligible, both π levels converge to a limiting value of *ca* -8.8 eV, which lies 0.55 eV above the $\pi+\pi$



Scheme 5.

level (−9.35 eV) for **4a**. This value, which is a measure of Δ_h, the degree of σ–π hyperconjugative mixing in the π MOs, is substantial, even when the π MOs are separated by such a large number of σ-bonds that OITB (as measured by Δ_e) is negligible. Because Δ_h is larger than was hitherto thought,[15] hyperconjugative interactions could very well play an important role in long-range intramolecular electron transfer processes.

The pes data for the dienes **5** are particularly interesting in that their analysis has revealed a new type of hyperconjugative interaction. The Δ_e values for these dienes (Fig. 2) are much too large to be accounted for in terms of OIT-*n*-B involving the connecting σ-bonds. For example it is expected that Δ_e for **4b** should be greater than that for **5b** since the connecting six σ-bonds have the optimum all-*trans* conformation in the former compound. In fact Δ_e for **5b** is almost double that for **4b**! For diene **5c**, in which the MOs are connected by eight σ-bonds, Δ_e is comparable to that for **4b**. The anomalous Δ_e values for **5b** and **c** are attributed to a type of hyperconjugation, called laticyclic hyperconjugation,[10] in which the π MOs mix with the pseudo-π MOs of the intervening CH_2 groups as in **53**. Laticyclic hyperconjugation, like OITB, appears to operate over large distances (the double bonds in **5c** are *ca* 9.5 Å apart).



Scheme 6.

Electron transfer studies

Although these studies have only just commenced the preliminary results are extremely encouraging. For example the rate of photoinduced intramolecular electron transfer in **8a** was found to be 1.47×10^{10} s^{-1}.[45] This rate is extraordinarily rapid considering the large separation of 13.5 Å between the chromophores. It is almost certain that OITB is playing an important role in this process.

CONCLUDING REMARKS

The synthesis of the rigid norbornylogs **4–8** is providing unique opportunities for studying long-range processes, such as intramolecular electron transfer, between two chromophores as a function of their relative orientation and separation. These studies are of particular relevance to the mechanism of biological electron transport phenomena, including

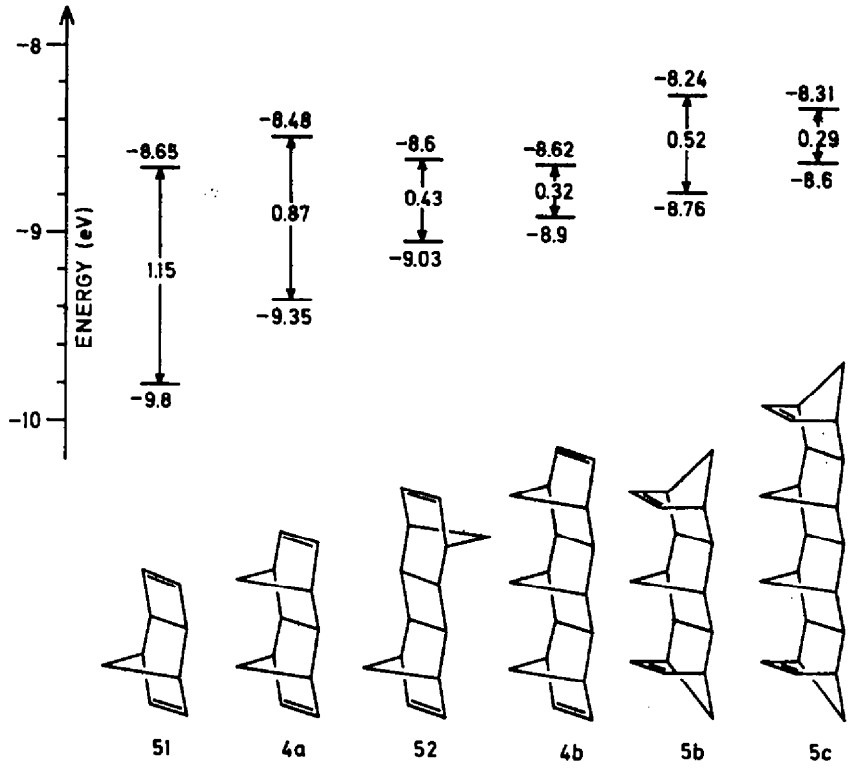


Fig. 2. π MO energies (eV) for some dienes.

those occurring within the photochemical unit. But this is only the first step in what promises to be an exciting but complex journey: attachment of chromophores, such as porphyrins, to the norbornylogs and the synthesis of rigid systems containing more than two chromophores that constitute a gradient of redox centres arranged within a spatially well-defined array are goals for the near future!

EXPERIMENTAL

General methods. M.ps are uncorrected and were recorded on an electrothermal m.p. apparatus. ^{1}H-NMR spectra were run at 60 MHz on a JEOL model PMX-60 spectrometer; $CDCl_3$ was used as a solvent with TMS employed as internal standard. IR spectra were run on a Perkin–Elmer model 621 spectrometer. Mass spectra were measured on an A.E.I. MS902-Pye 105 GLC–MS system.

(1α, 4α, 4aβ, 5β, 8α, 8aα)-1, 2, 3, 4, 4a, 5, 8, 8a-*Octahydro*-1, 4 : 5, 8-*dimethanonaphthalen*-2-*one ethylene acetal*, **18**

The ketone **11**[21] (34.8 g, 0.2 mol) was converted into the acetal **14** (44 g, 94%) using standard methodology (ethane-1,2-diol, 13 g; benzene, 350 ml; *p*-toluenesulfonic acid, 100 mg; Dean–Stark trap). ^{1}H-NMR δ 0.95–3.0 (m, 12H), 3.83 (br s, 4H), 5.95 (t, 2H). The solid acetal was not characterized further. Br_2 (33 g, 0.2 mol) in CH_2Cl_2 (25 ml) was added dropwise to a soln of **14** (43.6 g, 0.2 mol) in CH_2Cl_2 (250 ml) at 25°. Standard workup procedure for this reaction[26] gave rearranged dibromide, **16** (70 g), which was not characterized owing to its suspected toxicity.[24] A soln of **16** (70.2 g), DMSO (400 ml) and t-BuOK (40 g, 0.36 mol) was stirred for 48 hr at 25°. Workup[26] gave crude **24** (44 g) as a thick oil which was immediately reductively debrominated using Na (23 g, 1 mol) in refluxing EtOH (325 ml), to give, after standard workup,[25] **18** as a low melting solid (62% from **11**); ^{1}H-NMR δ 0.9–2.3 (m, 10H), 2.86 (m, 2H), 3.83 (br s, 4H), 6.16 (t, 2H).

(1α, 4α, 4aβ, 5β, 8β, 8aβ)-1, 2, 3, 4, 4a, 5, 8, 8a-*Octahydro*-1, 4 : 5, 8-*dimethanonaphthalen*-2-*one ethylene acetal*, **20**

Addition of HCCPD (47 g, 0.17 mol) to **18** (28.3 g, 0.13 mol) at 140° and 26 hr, gave adduct **19**, m.p. 178–179° (acetone) (54 g, 85%); ^{1}H-NMR δ 1.05–2.4 (m, 10H), 2.38 (s, 2H), 2.67 (s, 2H), 3.87 (br s, 4H). Dechlorination of this material (24.5 g, 0.05 mol) with Na (46 g, 2 mol) in refluxing EtOH, followed by the usual workup procedure,[25] gave **20** (9.5 g, 67%), m.p. 92–94° (acetone/MeOH); ^{1}H-NMR δ 0.98–2.25 (m, 16H), 2.8 (m, 2H), 3.83 (br s, 4H), 5.88 (t, 2H). (Found: $M^{+\cdot}$, 284.1780. $C_{19}H_{24}O_2$ Requires: M, 284.1776.)

(1α, 4α, 4aβ, 5α, 8α, 8aβ, 9α, 9aβ, 10α, 10aβ)-1, 4, 4a, 5, 8, 8a, 9, 9a, 10, 10a-*Decahydro*-1, 4 : 9, 10 : 5, 8-*trimethanoanthracene*, **4b**

Deacetalization of **20** (2.16 g, 7.6 mmol; THF, 25 ml; 1 M H_2SO_4, 25 ml, 25°, 18 hr) gave **20** (X = CO) in quantitative yield. Treatment of **20** (X = CO) (1.8 g) with $LiAlH_4$ (0.58 g) in refluxing THF (20 ml) for 1.5 hr, followed by standard workup procedure, gave the alcohol **20** (X = CHOH) (1.75 g, 96%). This material was immediately converted into **21** using the $SOCl_2$/HMPA procedure as described elsewhere.[26] The crude **21** (1.2 g) in CH_2Cl_2 (10 ml) was treated with Br_2 (0.8 g, 5 mmol) in CH_2Cl_2 (3 ml) and worked up[26] to give crude rearranged dibromo material which was immediately dehydrobrominated using t-BuOK (3 g) in DMSO (30 ml) (25°, 18 hr) to give **23**. Debromination of **23** (1.08 g) with Na (4.0 g, 0.17 mol) in refluxing EtOH gave, after normal workup,[25] **4b** (0.44 g, 26% from **20**), m.p. 123–125° (acetone/MeOH); ^{1}H-NMR δ 1.0 (d, J = 10 Hz, 2H), 1.28 (s, 4H), 1.7–2.2 (m, 6H), 2.63 (m, 4H),

6.11 (t, 4H). (Found: $M^{+\cdot}$, 224.1568. $C_{17}H_{20}$ Requires: M, 224.1565.)

(1α,4α,4aα,5α,8α,8aα,9β,9aα,10β,10aα)-1,4,4a,5,8,8a,9,9a,10,10a-*Decahydroanthracene*, **5b**

A mixture of aldrin **25** (36.5 g, 0.1 mol) and HCCPD **24** (54.6 g, 0.2 mol) was heated at 150° for 36 hr. The product mixture was triturated with MeOH and the resulting solid, presumably **26** (58 g, 90%), was immediately subjected to reductive dechlorination[25] using Na (143 g) in a refluxing mixture of i-PrOH (540 ml) and THF (900 ml). Normal workup procedure[25] gave **5b** (7.2 g, 48%) whose spectral properties were identical with those reported.[18,19]

(1α,4α,4aα,5β,5aα,6β,6aα,7α,10α,10aα,11β,11aα,12β,12aα)-1,4,4a,5,5a,6,6a,7,10,10a,11,11a,12,12a-*Tetradecahydro*-1,4:5,12:6,11:7,10-*tetramethanonephthacene*, **5c**

A mixture of **4a** (1.1 g, 7 mmol) and HCCPD, **24** (10.9 g, 40 mmol) was heated in a sealed tube at 130° for 48 hr. Recrystallization of the product from EtOAc gave **27** (4.3 g, 88%); ^{1}H-NMR ($CDCl_3$) δ 1.2 (d, J = 15 Hz, 2H), 1.83 (d, J = 15 Hz, 2H), 2.5 (s, 2H), 2.62 (br s, 4H), 2.85 (s, 4H). The adduct **27** (3.1 g, 4.3 mmol) was dechlorinated using Na (8.0 g, 0.35 mol), i-PrOH (25 ml) and THF (50 ml). Normal workup procedure gave **5c** (0.6 g, 48%), m.p. 195–198° (CH_2Cl_2/MeOH); ^{1}H-NMR ($CDCl_3$) δ 1.09–1.96 (m, 18H), 2.78 (m, 4H), 5.87 (m, 4H). (Found: C, 90.38; H, 8.94. $C_{22}H_{26}$ Requires C, 90.98, H, 9.02%.)

(1α,4α,4aα,5β,5aα,6β,6aα,7β,7aα,8α,11α,11aα,12β,12aα,13β,13aα,14β,14aα)-1,4,4a,5,5a,6,6a,7,7a,8,11,11a,12,12a,13,13a,14,14a-*Octadecahydro*-1,4:5,14:6,13:7,12:8,11-*pentamethanopentacene*, **5d**

A mixture of **4b** (0.2 g, 0.89 mmol), HCCPD **24** (2 g, 7.3 mmol) and $NaHCO_3$ (50 mg) was heated at 110° for 20 hr. Addition of acetone to the product mixture gave adduct **28** (0.5 g, 74%) which was immediately dechlorinated using Na (3 g) in a refluxing mixture of i-PrOH (10 ml) and THF (20 ml). Normal workup procedure[25] gave **5d** (0.11 g, 47%), m.p. 224–226° (CH_2Cl_2/MeOH); ^{1}H-NMR δ 0.88–2.1 (m, 24H), 2.78 (br s, 4H), 5.89 (t, 4H). (Found: C, 90.29; H, 9.25. $C_{27}H_{32}$ Requires: C, 90.95; H, 9.05%.)

9,10-*Dihydro*-9,10-*methanoanthracene*, **6a**

(a) *From tetrachlorodimethoxycyclopentadiene*, **30b**. A mixture of **29** (2.82 g, 20 mmol) and **30b** (7.9 g, 30 mmol) was heated at 120° for 6 hr. Addition of MeOH gave the adduct **31b** (6.2 g, 76.4%) which was used without further purification. The adduct **31b** was deacetalized by stirring in a mixture of CH_2Cl_2 (60 ml) and conc H_2SO_4 (10 ml) at room temp. Usual workup gave **31c** (3.1 g, 62.4%) which was decarbonylated in boiling xylene (20 ml) (5 hr) to give **32** in quantitative yield. Treatment of **32** with ethanolic KOH (6 g in 50 ml) and normal workup gave **33** (1.5 g, 60%). ^{1}H-NMR ($CDCl_3$) 2.50 (m, 2H), 4.53 (m, 2H), 6.83–7.50 (m, 5H).

Compound **33** (0.95 g, 3.2 mmol) was dechlorinated by treatment with Na (1.9 g, 80 mmol) in a boiling mixture of THF (10 ml) and i-PrOH (5 ml) as described earlier. The crude product was purified by chromatography (neutral alumina, petroleum spirit eluant), followed by recrystallization to give pure **6a** (0.44 g, 71%), m.p. 155° (reported[30] 154°). ^{1}H-NMR ($CDCl_3$) δ 2.48 (t, 2H), 4.23 (t, 2H), 6.73–7.31 (sym m, 8H). The overall yield of **6a** from **2a** was 21%.

(b) *From tetrachlorothiophene-1,1-dioxide*, **30a**. An equimolar mixture of **29** (1.42 g, 10 mmol) and **30a** was heated at 130° for 15 hr. Dilution with MeOH gave a ppt of **32** (3.15 g, 95%) whose spectroscopic properties were identical to that prepared by method (a). The overall yield of **6a** from **2a** by this method was 41%.

(5α,5aβ,6α,11α,11aβ,12α)-5,5a,6,11,11a,12-*Hexahydro*-5,12:6,11-*dimethanonaphthacene*, **6b**

To a soln of alkene **34a** (6.2g, 30 mmol) in CH_2 (50 ml) was added dropwise Br_2 (5.1 g, 32 mmol) in CH_2Cl_2 (10 ml) at room temp. Normal workup gave crude **35a** which was dehydrohalogenated with t-BuOK (7.0 g, 62 mmol) in DMSO (50 ml) as discussed above. The crude product was recrystallized from acetone to give 4.2 g (49%) of bromomonoene, m.p. 144–145°. ^{1}H-NMR ($CDCl_3$) δ 1.47–1.87 (m, 4H), 2.30 (dt, 1H), 3.10 (m, 2H), 3.20 (m, 2H), 5.15 (br s, 1H), 6.16 (m, 2H), 7.03 (m, 4H). The debromination of bromo-monoene was carried out by treatment with Na (5.0 g, 0.22 mol) in refluxing EtOH (50 ml) to give **36a** (1.4 g, 84%), m.p. 61–62° (acetone/MeOH). ^{1}H-NMR ($CDCl_3$) δ 1.47 (sym m, 2H), 1.63 (m, 2H), 2.33 (sym m, 2H), 2.73 (m, 2H), 3.10 (m, 2H), 6.15 (m, 2H), 7.00 (m, 4H). (Found: C, 92.34; H, 7.74. $C_{16}H_{16}$ Requires: C, 92.26; H, 7.74%.)

A mixture of **36a** (1.6 g, 7.7 mmol) and **30a** (2.7 g, 10 mmol) was heated at 130° for 15 hr. Workup gave crude tetrachloro adduct (3.0 g) which was immediately dehydrohalogenated using ethanolic KOH (15 g in 150 ml) and then dehalogenated using Na/EtOH as described above for **6a**. Pure **6b** was obtained by chromatography (neutral Al_2O_3, petroleum spirit), followed by recrystallization, m.p. 142–144° (hexane–EtOH) in an overall yield of 43.8% (0.87 g). ^{1}H-NMR ($CDCl_3$) δ 1.47–1.77 (m, 4H), 2.47 (dt, 2H), 3.27 (m, 4H), 6.93 (m, 8H). (Found: C, 93.14; H, 7.19. $C_{20}H_{18}$ Requires: C, 92.98; H, 7.02%.)

(1α,4α,4aβ,5α,5aβ,6α,11α,11aβ,12α,12aβ)-1,4,4a,5,5a,6,11,11a,12,12a-*Decahydro*-1,4:5,12:6,11-*trimethanonaphthacene*, **36b**

A mixture of **36a** (3.12 g, 15 mmol) and cyclopentadiene (4.0 g, 60 mmol) was heated at 185–190° for 24 hr. The crude product was purified by chromatography (neutral Al_2O_3, petroleum spirit), followed by recrystallization, m.p. 206–208° (acetone–MeOH) to give **34b** (2.1 g, 50%). ^{1}H-NMR ($CDCl_3$) δ 1.00–2.43 (m, 12H), 2.77 (m, 2H), 3.15 (br s, 2H), 5.90 (t, 2H), 7.0 (br s, 4H). (Found: $M^{+\cdot}$, 274.1723. $C_{21}H_{22}$ Requires: M, 274.1722.)

Rearrangement of **34b** to **36b** as shown in Scheme 4 was carried out as described above for **36a** from **34a** in 35.4% yield, m.p. 132–134° (acetone–MeOH); ^{1}H-NMR ($CDCl_3$) δ 0.83–2.33 (m, 12H), 2.63 (m, 2H), 3.17 (br s, 2H), 6.00 (m, 2H), 6.97 (m, 4H). (Found $M^{+\cdot}$, 274.1722. $C_{21}H_{22}$ Requires: M, 274.1722.)

(5α,5aβ,6α,6aβ,7α,12α,12aβ,13α,13aβ,14α)-5,5a,6,6a,7,12,12a,13,13a,14-*Decahydro*-5,14:6,13:7,12-*trimethanopentacene*, **6c**

This was prepared from **36b** (247 mg, 0.9 mmol) and **30a** (304 mg, 1.2 mmol) as described above for **6b** from **36a** in 38.4% yield, m.p. 176–177° (acetone). ^{1}H-NMR ($CDCl_3$) δ 1.20–2.50 (m, 12H), 3.20 (br s, 4H), 6.95 (m, 8H). (Found: C, 91.93; H, 7.63. $C_{25}H_{24}$ Requires: C, 92.54; H, 7.46%.)

Compounds **7a**, **7b**, **7c**, **50a**, **50b**

The syntheses of these compounds have been described elsewhere.[46]

Dimethyl-(2aα,3β,10α,10aα)-2a,3,10,10a-*tetrahydro*-3,10-*methano*-4,9-*dimethoxycyclobuta*(b)*anthracene*-1,2-*dicarboxylate*, **40a**

A soln of **38a** (10 g, 40 mmol), DMAD (5 g, 60 mmol) and $RuH_2CO(PPh_3)_3$[35] (0.92 g, 0.8 mmol) in benzene (40 ml) was heated in a sealed tube at 80° for 12 hr. The mixture was worked up in the usual way[35] to give **40a** (12.5 g, 80%), m.p. 99–100° (from EtOH); IR (nujol) 1735 cm^{-1}; ^{1}H-NMR δ 1.83 (br s, 2H11), 2.93 (s, 2H, H2a and H10a), 3.70 (br s, 2H, H3 and H10), 3.83 (s, 6H, 2 × OCH_3), 4.02 (s, 6H, 2 × OCH_3), 7.3–7.5 (m, 2H, aromatic), 8.0–8.2 (m, 2H, aromatic). (Found: $M^{+\cdot}$, 394.1421. $C_{23}H_{22}O_6$ Requires: M, 394.1415.)

The (1α,4α,4aβ,4bα,4cβ,5α,12α,12aβ,12bα,12cβ)-1,4,4a,4c,5,12,12a,12c-*octahydro*-1,4:5,12-*dimethano*-6,11-*dimethoxybenzo*(3′,4′)*cyclobuta*(1′,2′:3,4)*cyclobut*(1,2-b)*anthracene system*

(*a*) *Dimethyl*-4b,12b-*dicarboxylate*, **41a**. A mixture of **40a** (0.98 g, 2.5 mmol) and quadricyclane (4.6 g, 50 mmol) was heated in a sealed tube at 180° for 17 hr. The mixture was evaporated, passed through a column of alumina (EtOAc) and

recrystallized from EtOH to give **41a** (0.76 g, 63%), m.p. 200–201°; ^{1}H-NMR δ 1.16 (d, J = 9 Hz, 1H), 1.67 (d, J = 11 Hz, 1H), 1.96 (d, J = 11 Hz, 1H), 2.12 (s, 2H), 2.5 (s, 2H), 2.55 (d, J = 9 Hz, 1H), 2.9 (br s, 2H), 3.73 (br s, 2H), 3.81 (s, 6H, 2 × OCH_3), 3.98 (s, 6H, 2 × OCH_3), 6.02 (t, 2H, vinylic), 7.2–7.5 (m, 2H, aromatic), 7.9–8.2 (m, 2H, aromatic). (Found: C, 74.20; H, 6.31. $C_{30}H_{36}O_6$ Requires: C, 74.06; H, 6.21%.)

(b) 4b,12b-*Dimethyl compound*, **41d**. A mixture of **41a** (8.1 g, 16.7 mmol) and $LiAlH_4$ (0.95 g, 25 mmol) in THF (110 ml) was refluxed for 15 hr. Standard workup procedure and subsequent recrystallization from EtOH gave diol **41b** (6.2 g); IR (CCl_4) 3630 (OH) cm^{-1}, which was not characterized further. A mixture of **41b** (3.0 g, 6.6 mmol) and methanesulfonyl chloride (2.12 g, 16.3 mmol) in pyridine (75 ml) was left at −5° for 18 hr. The mixture was poured onto crushed ice and extracted with ether. The ether extract was freed from pyridine with aq HCl and evaporated to give crude dimesylate **41c** (5.0 g) which was not purified further but immediately treated with $LiAlH_4$ (1.0 g) in refluxing THF (100 ml) for 48 hr. Standard workup procedure gave **41d** (1.6 g, 58% overall yield from **41b**), m.p. 158–159° (from petroleum); ^{1}H-NMR δ 0.92 (s, 6H, 2 × CH_3), 1.3–2.1 (m, 8H), 2.73 (br s, 2H, H1, H4), 3.67 (br s, 2H, H5, H12), 3.94 (s, 6H, 2 × OCH_3), 5.91 (br s, 2H), 7.2–7.5 (m, 2H), 7.9–8.2 (m, 2H). (Found: C, 84.41; H, 7.50. $C_{28}H_{30}O_2$ Requires: C, 84.38; H, 7.59%.)

(1α, 4α, 4aα, 5β, 5aα, 5bβ, 5cα, 6β, 13β, 13aα, 13bβ, 13cα, 14β, 14aα)-1, 2, 3, 4, 4a, 5, 5a, 5c, 6, 13, 13a, 13c, 14, 14a-*Tetradecahydro*-1, 4:5, 14:6, 13-*trimethano*-7, 12-*dimethoxy*-5b, 13b-*dimethylnaphtho*(2, 3:3′, 4′)*cyclobuta*(1′, 2′:3, 4)*cyclobut*(1, 2-b)*anthracen*-15-*one*, **8a**, *and the dicyanomethylene derivative*, **46**

A mixture of **41d** (11.5 g, 29 mmol) and **30b** (7.4 g, 28 mmol) was heated at 120° for 48 hr. The resulting solid was recrystallized from acetone–EtOH to give **43a** (16.5 g, 86%), m.p. 231–232°; ^{1}H-NMR δ 0.91 (s, 6H, 2 × CH_3), 1.4–2.5 (m, 12H), 3.47 (d, 6H, 2 × OCH_3), 3.61 (br s, 2H), 3.92 (s, 6H, 2 × OCH_3), 7.2–7.5 (m, 2H), 7.9–8.2 (m, 2H).

Compound **43a** (16.0 g, 24.2 mmol) was dechlorinated using Na (31.7 g, 1.38 mol) and EtOH (170 ml) as described elsewhere[23] (reflux time, 18 hr). The resulting solid after workup[25] (12.1 g) was found by ^{1}H-NMR spectroscopy to be a mixture of **43b** and products resulting from reduction of the naphthalene ring. Treatment of this mixture with DDQ (10.2 g, 45 mmol) in benzene (90 ml) for 17 hr at 25° gave, after column chromatography (EtOAc), the acetal **43b** (12.0 g) which was not purified further but was hydrogenated (10% Pd/C, 200 mg; EtOAc, 100 ml, 1 atm, 25°) until ^{1}H-NMR spectroscopy revealed total absence of double bond. A soln of the product after hydrogenation (11.0 g) in THF (100 ml) and 40% H_2SO_4 (100 ml) was stirred for 48 hr at 25°. Standard workup procedure gave ketone **8a** (6.7 g; 48% overall yield from **41d**), m.p. 237–239° ($CHCl_3$–petroleum); IR (nujol) 1780 (C=O) cm^{-1}; ^{1}H-NMR δ 0.98 (s, 6H, 2 × CH_3), 1.7–2.3 (m, 18H), 3.67 (br s, 2H), 3.97 (s, 6H, 2 × OCH_3), 7.2–7.5 (m, 2H), 7.9–8.2 (m, 2H). (Found: C, 81.93; H, 7.41. $C_{33}H_{36}O_3$ Requires: C, 82.46; H, 7.55%.)

A soln of **8a** (1.0 g, 2.1 mmol), malononitrile (152 mg, 2.3 mmol), AcOH (0.37 ml), and NH_4OAc (161 mg) in toluene (5 ml) was refluxed for 2 hr, the water being removed through a Dean–Stark apparatus. CH_2Cl_2 (20 ml) was added to the mixture and the soln was washed successively with $NaHCO_3$ aq and H_2O. Evaporation of the organic layer gave **46** (0.71 g, 66%), m.p. 193–195° (EtOH); IR (nujol) 2250 (C≡N) cm^{-1}; ^{1}H-NMR δ 1.0 (s, 6H, 2 × CH_3), 1.2–2.3 (m, 18H), 2.97 (br s, 2H), 3.65 (s, 2H), 3.98 (s, 6H, 2 × OCH_3), 7.2–7.5 (m, 2H), 7.9–8.2 (m, 2H).

(1α,4α,4aα,5β,12β,12aα) - 1,4,4a,5,12,12a - *Hexahydro* - 1,4:5,12 - *dimethano* - 6,11 - *dimethoxynaphthacene*, **47**

A mixture of **38a**[33] (100 g, 0.4 mol) and cyclopentadiene (38.4 g, 0.58 mol) was heated with stirring in a Parr pressure reactor at 185° for 18 hr. The mixture was passed through an alumina column (50:50 mixture of CH_2Cl_2 and petroleum spirit 40–60° fraction), and recrystallized from EtOH to give **47** (66 g, 49%), m.p. 137–138°; ^{1}H-NMR δ 1.30–1.67 (m, 3H, 2H13, H14), 2.37 (br s, 2H, H4a, H12a), 2.87 (d, J = 10 Hz, H14), 2.95 (br s, 2H, H1, H4), 3.53 (br s, 2H, H5, H12), 4.01 (s, 6H, 2 × OCH_3), 6.13 (t, 2H, H2, H3), 7.33–7.53 (m, 2H, aromatic), 7.93–8.13 (m, 2H, aromatic). (Found: C, 83.01; H, 7.04. $C_{22}H_{22}O_2$ Requires: C, 82.99; H, 6.96%.)

(1α,4α,4aβ 5α,12α,12aβ)-1,4,4a 5,12,12a - *Hexahydro* - 1,4:5,12-*dimethano*-6, 11-*dimethoxynaphthacene*, **39**

To a soln of **47** (50 g, 0.16 mol) in CH_2Cl_2 (100 ml) was added dropwise pyridinium hydrobromide perbromide (55 g, 0.17 mol) in CH_2Cl_2 (2 l). The resulting soln was washed successively with 10% NaOH and H_2O and then evaporated to give crude rearranged dibromo adduct (76.0 g). This material was successively dehydrobrominated and debrominated, using the same procedures described above for the preparation of **4b**. The resulting solid was recrystallized from EtOH to give **39** (26 g, 52% overall yield from **47**), m.p. 106–107°; ^{1}H-NMR δ 1.25 (d, J = 9 Hz, 1H), 1.63 (d, J = 11 Hz, 1H), 1.78 (s, 2H), 2.47 (d, J = 9 Hz, 1H), 2.81 (br s, 2H), 3.53 (br s, 2H), 3.92 (s, 6H, 2 × OCH_3), 6.11 (t, 2H), 7.2–7.5 (m, 2H), 7.9–8.2 (m, 2H). (Found: C, 83.06; H, 6.91. $C_{22}H_{22}O_2$ Requires: C, 82.99; H, 6.96%.)

The (1α, 4α, 4aβ, 4bα, 4cβ, 5α, 5aβ, 6α, 13α, 13aβ, 14α, 14aβ, 14bα, 14cβ)-1, 4, 4a, 4c, 5, 5a, 6, 13, 13a, 14, 14a, 14c-*dodecahydro*-1, 4:5, 14:6, 13-*trimethano*-7, 12-*dimethoxybenzo*(3′, 4′)*cyclobuta*(1′, 2′:3, 4)*cyclobuta*(1, 2-b)*naphthacene system*

(a) *Dimethyl*-4b,14b-*dicarboxylate*, **42a**. A mixture of **39** (31.8 g, 0.1 mol), DMAD (15.6 g, 0.11 mol), $RuH_2CO(PPh_3)_3$ (2.4 g, 2 mmol) in benzene (400 ml) was refluxed for 24 hr. Standard workup procedure[35] gave **40b** (28 g, 61%) as a semisolid which was not purified further but was heated with quadricyclane (40 g) at reflux for 64 hr. Evaporation and recrystallization of the resulting solid from EtOH gave **42a** (22 g, 53% overall yield from **39**), m.p. 127–129°; ^{1}H-NMR δ 1.03 (d, J = 10 Hz, 1H), 1.40 (d, J = 12 Hz, 1H), 1.6–2.4 (m, 12H), 2.77 (br s, 2H), 3.63 (br s, 2H), 3.71 (s, 6H, 2 × OCH_3), 3.97 (s, 6H, 2 × OCH_3), 5.93 (m, 2H), 7.2–7.5 (m, 2H), 7.9–8.2 (m, 2H). (Found: C, 76.12; H, 6.63. $C_{35}H_{36}O_6$ Requires: C, 76.06; H, 6.57%.)

(b) 4b,14b-*Dimethyl compound*, **42d**. The conversion of **42a** into **42d** followed the same procedure that was used to convert **41a** into **41d**. Yield of **42d**, 63% (from **42a**), m.p. 118° (petroleum); ^{1}H-NMR 0.77 (s, 3H, 2 × CH_3), 1.1–2.7 (m, 16H), 3.67 (br s, 2H, H6, H13), 3.98 (s, 6H, 2 × OCH_3), 5.97 (m, 2H, H2, H3), 7.2–7.5 (m, 2H), 7.9–8.2 (m, 2H). (Found: C, 85.37; H, 7.89. $C_{33}H_{36}O_2$ Requires: C, 85.30; H, 7.81%.)

(1α, 4α, 4aα, 5β, 5aα, 5bβ, 5cα, 6β, 6aα, 7β, 14β, 14aα, 15β, 15aα, 15bβ, 15cα, 16β, 16aα)-1, 2, 3, 4, 4a, 5a, 5b, 6, 6a, 7, 14, 14a, 15, 15a, 15c, 16, 16a-*Octadecahydro*-1, 4:5, 16:6, 15:7, 14 - *tetramethano* - 8,13 - *dimethoxy* - 5b,15b - *dimethylnaphtho*-(2,3:3′,4′)*cyclobuta*(1′,2′:3,4)*cyclobuta*(1,2-b)*naphthacene* - 17 - *one*, **45**.

The conversion of **42d** into **45** via **44a** and **44b** followed the same procedure as was described above for the conversion of **41d** into **8a**. Overall yield of **45**, 55% (from **42d**), m.p. 285–287° (CH_2Cl_2–pentane); IR (nujol) 1776 (C=O) cm^{-1}; ^{1}H-NMR δ 0.78 (s, 6H, 2 × CH_3), 1.5–2.3 (m, 24H), 3.63 (br s, 2H, H7, H14), 3.97 (s, 6H, 2 × OCH_3), 7.2–7.5 (m, 2H), 7.9–8.2 (m, 2H). (Found: C, 82.95; H, 7.56. $C_{38}H_{42}O_3$ Requires: C, 83.48; H, 7.74%.)

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