The Synthesis of Two Rigid Bichromophoric Systems in which the Chromophores are separated by Relays of Nine and Thirteen σ-Bonds: Two Useful Models for further exploring the Distance Dependence of Long-range Intramolecular Electron Transfer

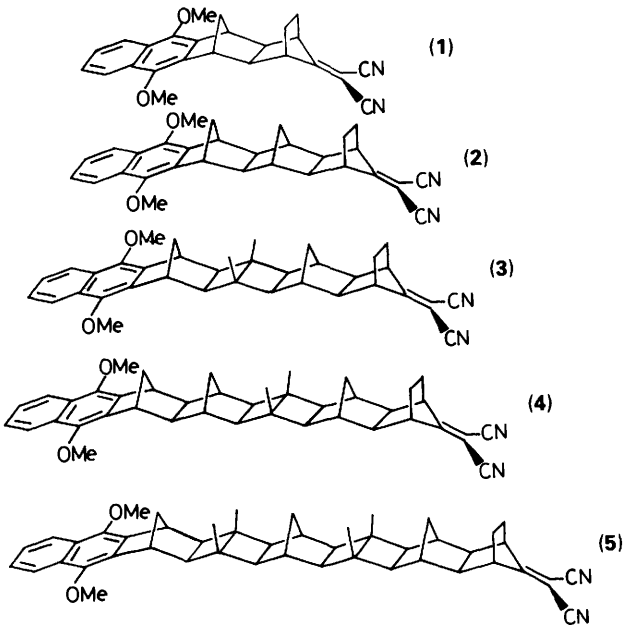
Anna M. Oliver and Michael N. Paddon-Row*
Department of Organic Chemistry, University of New South Wales, P.O. Box 1, Kensington, New South Wales, Australia 2033

This paper describes the synthesis of two novel rigid bichromophoric systems, (**6**) and (**7**), in which the dimethoxynapthalene donor and the dicyanoethylene acceptor groups are separated, by relays of nine and thirteen σ-bonds. Treatment of 1,4-naphthoquinone (**8**) with quadricyclane (**9**) gave the [2 + 2 + 2] adduct (**10**) which, upon treatment with sodium hydride and methyl iodide, gave the methanobenzo[*b*]biphenylene compound (**11**). Thermal reaction of (**11**) with dimethyl acetylenedicarboxylate and $RuH_2CO(PPh_3)_3$ gave the adduct (**12**) which readily underwent [2 + 2 + 2] cycloaddition with quadricyclane to give (**13a**), and finally (**13d**), after a series of simple transformations. Treatment of (**13d**) with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene gave the adduct (**16**) which was easily converted into the ketone (**6a**), and finally into the dicyanomethylene derivative (**6b**) by a Knoevenagel condensation. Subjecting (**13d**) to the same series of reactions that were applied to (**11**) led to the formation of the ketone (**7a**) and the dicyanomethylene derivative (**7b**), *via* (**15a**)–(**15d**) and (**17**).

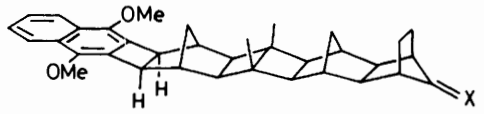
Single-electron transfer constitutes one of the most fundamental chemical reactions[1] and plays a crucial role in a variety of synthetic and biological processes, occurring under either thermal[1–7] or photochemical processes.[8–25] It is therefore hardly surprising that considerable effort from many groups continues to be spent on probing the mechanistic features of electron transfer.[1–26] During the past few years, measurements of intramolecular electron-transfer dynamics have provided deeper insight into the effect of distance, energy, and orientation on electron-transfer rates.[4–7,11–25] Although the distance dependence of electron-transfer rates is of paramount importance in the theoretical treatments of electron transfer,[1] an unambiguous experimental determination of this dependence has been very difficult to obtain, largely through the problems associated with synthesizing a suitable series of molecules that maintain the donor and acceptor groups in well defined, completely rigid, geometries.

Recently, however, we successfully synthesized the series of molecules (**1**)–(**5**), in which the dimethoxynaphthalene donor and the dicyanoethylene acceptor groups are held by a polynorbornyl type 'spacer' in a fixed relative orientation with respect to each other, and at a rigidly defined separation, the edge-to-edge donor–acceptor separation ranging from 4.6 Å in (**1**), in which the chromophores (*i.e.*, the donor–acceptor pairs) are connected by relays consisting of four σ-bonds, to 13.5 Å in (**5**), in which the chromophores are connected by twelve σ-bonds.[14–18,27,28] The rates of photoinduced intramolecular electron transfer in this series of molecules were found to be extremely fast, which are presumably the result of mediating through-bond coupling between the orbitals of the chromophores with those of the hydrocarbon 'spacer.'[28,29]

Unfortunately, the rates of electron transfer in the 4-σ- and 6-σ-bonded systems, (**1**) and (**2**), respectively, were too fast to be measured accurately. Consequently, the distance dependence obtained for the electron-transfer rate, based on only three interchromophore separations, corresponding to the systems (**3**)–(**5**), is necessarily only approximate.[18] Clearly, it would be desirable to obtain more rate–distance data so that the empirically derived distance dependence can be placed on a surer footing. In principle this can be achieved through the synthesis of bichromophoric systems similar to (**3**)–(**5**), but in which the chromophores are separated by hydrocarbon 'spacers' possessing an odd number of σ-bonds.



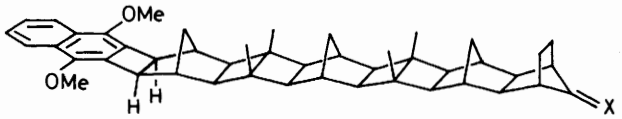
We have addressed this problem by synthesizing the novel pair of systems (**6**) and (**7**), in which the chromophores are separated by relays consisting of nine and thirteen σ-bonds, respectively. Thus, the interchromophore separation in (**6**) lies roughly midway between that in (**3**) and (**4**), whereas the separation in (**7**) is even greater than that in (**5**), making it the longest system prepared by us to date. We report herein the synthesis of these systems.



(6)

a: X = O

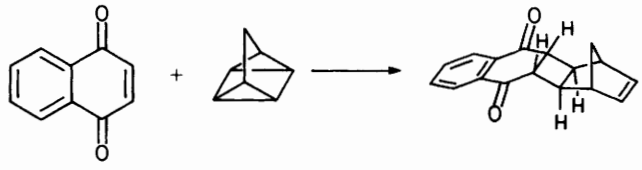
b: X = $C(CN)_2$



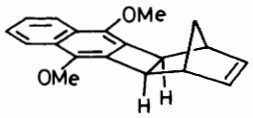
(7)

a: X = O

b: X = $C(CN)_2$



(8) (9) (10)



(11)

The key compound to the overall synthetic scheme is the 1,4-methanobenzo[*b*]biphenylene compound (**11**). This should be readily available through thermal [2 + 2 + 2] cycloaddition of 1,4-naphthoquinone (**8**) with quadricyclane (**9**), a reaction that has ample literature precedent.[30] Indeed, overnight refluxing of a solution of (**8**) and (**9**) in dioxane led to near-quantitative formation of the adduct (**10**). Treatment of (**10**) with sodium hydride and methyl iodide gave the desired tetrahydro-1,4-methanobenzo[*b*]biphenylene compound (**11**), in 84% overall yield from naphthoquinone. The *exo*-disposition of the naphthocyclobutane group in (**11**), relative to the norbornyl ring, follows from the observation that the vinyl protons, 2-H and 3-H, in (**11**) are *deshielded* (δ 6.26) with respect to the same protons in norbornene (δ 5.95[31]). In contrast, an *endo*-disposition of the cyclobutane ring would place the double bond protons within the shielding zone of the naphthalene ring, and this should result in a *shielding* of these protons of about 0.5 ppm. This has, indeed, found to be the case for the corresponding *exo*- and *endo*-isomers of 1,4,4a,8b-tetrahydro-1,4-methanobiphenylene [this system is generated from (**11**) by replacing the dimethoxynaphthalene ring with a benzene ring]; the vinyl protons in the *endo*-isomer (δ 5.57) are shielded by 0.54 ppm, relative to those in the *exo*-isomer (δ 6.11).[32]

The strategy employed to convert (**11**) into (**6**) and (**7**) is shown in the Scheme, and is identical to that employed for the synthesis of the bichromophoric systems (**3**) and (**5**).[18,27] The key to the synthesis lies in the homologation cycle which can extend a norbornenyl ring by any number of tricyclo-[4.3.0.$0^{2,5}$]nonanyl units.[18,27,33] Applied to the present situation, this cycle enables (**13d**) and (**15d**) to be synthesized from (**11**).

Thus, thermal $RuH_2CO(PPh_3)_3$-catalysed[34] [2 + 2] cycloaddition of dimethyl acetylenedicarboxylate (DMAD) to (**11**) gave the adduct (**12**) in 81% yield. This compound readily underwent the expected[18,27,30a,35] [2 + 2 + 2] thermal cycloaddition with quadricyclane to give (**13a**). Transformation of this compound into the dimethyl analogue (**13d**) was easily achieved through $LiAlH_4$ reduction to the diol (**13b**), and subsequent $LiAlH_4$ reduction of the bismesylate derivative (**13c**) formed therefrom. The overall yield of (**13d**) from (**11**) is 41%. Using the same sequence of reactions that were employed to convert (**11**) into (**13d**), we obtained (**15d**) from (**13d**) in an overall yield of 67%.

Diels–Alder reaction between 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and (**13d**) gave the adduct (**16**; X = Cl) in high yield (96%). The stereochemistry of this cycloaddition is well known from X-ray crystallographic studies on (**3**), whose synthesis utilized the same cycloaddition reaction.[28] Reductive dehalogenation of (**16**; X = Cl), using sodium and propan-2-ol,[36] gave (**16**, X = H) in 80% yield. Catalytic hydrogenation of this material, followed by deketalization (using formic acid), gave (**6a**) in 54% overall yield from (**13d**). Knoevenagel condensation of this ketone with malononitrile gave (**6b**) in 91% yield. In a similar fashion, the higher homologous ketone (**7a**), and the dicyanomethylene derivative (**7b**) were obtained from (**15d**) in 50 and 41% yields, respectively.

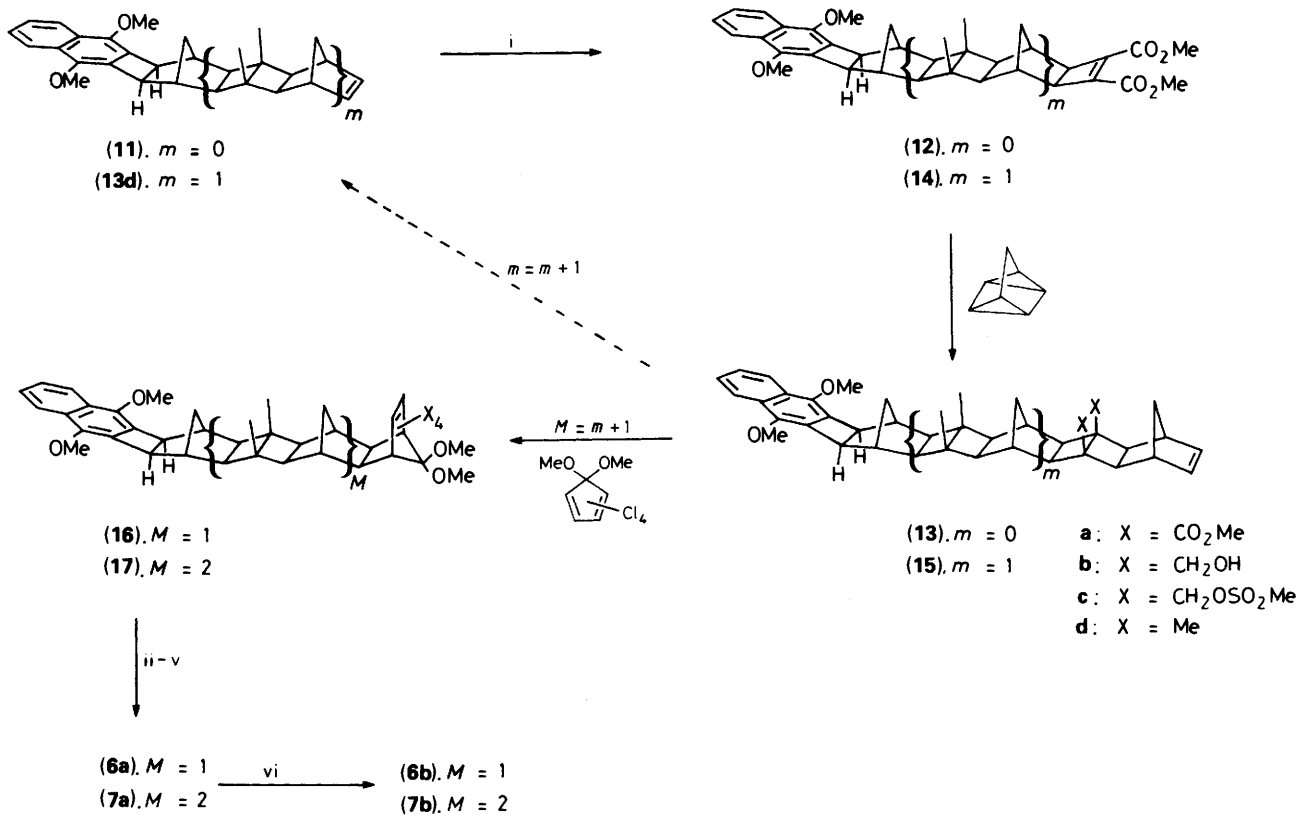
The dynamics of photoinduced intramolecular electron transfer in (**6b**) and (**7b**) will be the subject of a forthcoming paper.

Experimental

General.—M.p.s were taken on a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra were recorded either at 60 MHz, using a Varian 360L machine, or at 500 MHz, using a Bruker AM-500 spectrometer. All NMR spectra were measured using $CDCl_3$ as solvent.

(1α,4α,4aβ,4bα,10aα,10bβ)-1,4,4a,4b,10a,10b-*Hexahydro*-1,4-*methanobenzo*[b]*biphenylene*-5,10-*dione* (**10**).—A solution of 1,4-naphthoquinone (23.7 g, 150 mmol) and quadricyclane (20.7 g, 225 mmol) in dioxane (25 ml) was refluxed for 17 h. Evaporation of the solvent left a solid that was recrystallized from acetone to give the *diketone* (**10**) (35 g, 93%); m.p. 127–128 °C; (500 MHz; $CDCl_3$) 1.53 (1 H, d, *J* 9.8 Hz, 11-H), 1.67 (1 H, d, *J* 9.8 Hz, 11-H), 2.12 (2 H, d, *J* 2.4 Hz, 4a-H, 10b-H), 3.01–3.04 (4 H, br m, 1-H, 4-H, 4b-H, 10a-H), 5.98 (2 H, t, *J* 1.8 Hz, 2-H, 3-H), 7.76 (2 H, m, ArH), and 8.12 (2 H, m, ArH) (Found: C, 81.6; H, 5.5. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%).

(1α,4α,4aβ,10bβ)-5,10-*Dimethoxy*-1,4,4a,10b-*tetrahydro*-1,4-*methanobenzo*[b]*biphenylene* (**11**).—To a stirred slurry of sodium hydride (11.3 g, 470 mmol) in anhydrous tetrahydrofuran (THF) (150 ml) was added dropwise a solution of diketone (**10**) (35 g, 140 mmol) in anhydrous THF (60 ml). After the addition was complete, the mixture was chilled in an ice bath and methyl iodide (64.5 g, 450 mmol) was cautiously added dropwise. The mixture was then allowed to reach room temperature and stirred for a further 16 h, after which it was treated with ice–water and extracted with ether (3 × 200 ml). The combined extracts was washed with brine, dried (Na_2SO_4) and evaporated to give the *dimethoxy compound* (**11**) (35 g, 90%), which was recrystallized from ethanol; m.p. 105–106 °C; δ_H(500 MHz; $CDCl_3$) 1.36 (1 H, d, *J* 11.2 Hz, 11-H), 1.38 (1 H, d,



Scheme. *Reagents:* i, DMAD, $RuH_2CO(PPh_3)_3$; ii, Na, Pr^iOH; iii, DDQ; iv, H_2, Pd; v, HCO_2H; vi, $CH_2(CN)_2$.

J 11.2 Hz, 11-H), 2.96 (2 H, t, *J* 1.8 Hz, 1-H, 4-H), 3.42 (2 H, s, 4a-H, 10b-H), 4.13 (6 H, s, 2 × OCH_3), 6.26 (2 H, t, *J* 1.8 Hz, 2-H, 3-H), 7.41 (2 H, m, ArH), and 8.10 (2 H, m, ArH) (Found: C, 81.7; H, 6.3. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%).

Dimethyl(2aα,3β,3aα,9bα,10β,10aα)-4,9-*Dimethoxy*-2a,3,3a,-9b,10,10a-*hexahydro*-3,10-*methanocyclobuta*[1″,2″:4′,5′]-*benzo*[1′,2′:3,4]*cyclobuta*[1,2-b]*naphthalene*-1,2-*dicarboxylate* (**12**).—A magnetically stirred solution of (**11**) (35 g, 126 mmol), DMAD (17.9 g, 126 mmol), and $RuH_2CO(PPh_3)_3$[37] (1.5 g, 1.3 mmol) in benzene (120 ml) was refluxed in a nitrogen atmosphere for 18 h. Ethanol (250 ml) was added to the cooled reaction mixture, and the precipitated material was collected and recrystallized from ethanol to give the *diester* (**12**) (42.5 g, 81%); m.p. 195–196 °C; δ_H(500 MHz; $CDCl_3$) 1.32 (1 H, d, *J* 11.7 Hz, 11-H), 1.39 (1 H, d, *J* 11.7 Hz, 11-H), 2.54 (2 H, br s, 3-H, 10-H), 2.88 (2 H, s, 2a-H, 10a-H), 3.53 (2 H, s, 3a-H, 9b-H), 3.81 (6 H, s, 2 × CO_2CH_3), 4.09 (6 H, s, 2 × OCH_3), 7.40 (2 H, m, ArH), and 8.09 (2 H, m, ArH) (Found: C, 71.3; H, 5.6. $C_{25}H_{24}O_6$ requires C, 71.4; H, 5.7%).

Dimethyl(1α,4α,4aβ,4bα,4cβ,5α,5aβ,11bβ,12α,12aβ,12bα,-12cβ)-6,11-*Dimethoxy*-1,4,4a,4b,4c,5,5a,11b,12,12a,12b,12c-*dodehydro*-1,4:5,12-*dimethanobenzo*[1‴,2‴:3‴,4‴]-*cyclobuta*[1,2-b]*naphthalene*-4b,12b-*dicarboxylate* (**13a**).—A solution of (**12**) (42 g, 100 mmol) in quadricyclane (35.2 g, 383 mmol) was refluxed in nitrogen atmosphere for two days. Acetone (150 ml) was added to the cooled solution and the resulting precipitate was collected and recrystallized from acetone to give (**13a**) (40.2 g, 78.5%); m.p. 273–274 °C; δ_H (500 MHz; $CDCl_3$) 1.12 (1 H, d, *J* 9.9 Hz, 13-H), 1.27 (1 H, d, *J* 11.8 Hz, 14-H), 1.82 (1 H, d, *J* 9.9 Hz, 13-H), 2.00 (1 H, d, *J* 11.8 Hz, 14-H), 2.20 (2 H, br s), 2.40 (2 H, s), 2.46 (2 H, s), 2.86 (2 H, t, *J* 1.8 Hz, 1-H, 4-H), 3.42 (2 H, br s, 5a-H, 11b-H), 3.72 (6 H, s, 2 × CO_2CH_3), 4.05 (6 H, s, 2 × OCH_3), 6.09 (2 H, t, *J* 1.8 Hz, 2-H, 3-H), 7.39 (2 H, m, ArH), and 8.08 (2 H, m, ArH) (Found: C, 74.8; H, 6.1. $C_{32}H_{32}O_6$ requires C, 75.0; H, 6.25%).

(1α,4α,4aβ,4bα,4cβ,5α,5aβ,11bβ,12α,12aβ,12bα,12cβ)-6,11-*Dimethoxy*-4b,12b-*dimethyl*-1,4,4a,4b,4c,5,5a,11b,12,12a,12b,12c-*dodecahydro*-1,4:5,12-*dimethanobenzo*[1‴,2‴:3‴,4‴]*cyclobuta*[1‴,2‴:3‴,4‴]*cyclobuta*[1″,2″:4′,5′]*benzo*[1′,2′:3,4]*cyclobuta*[1,2-b]*naphthalene* (**13d**).—To a solution of (**13a**) (19 g, 37 mmol) in dry THF (200 ml), under nitrogen, was added $LiAlH_4$ (2.82 g, 73 mmol) in small portions. The mixture was refluxed for 18 h. To the cooled mixture was added successively water (3 ml) (**CAUTION**!), 15% aq. NaOH (3 ml), and water (9 ml). The mixture was then filtered and the filtrate dried and evaporated under reduced pressure to give the diol (**13b**) (16.6 g, 98%) which was not purified further; ν_{max}(Nujol) 3 250 cm^{-1}.

To a cooled solution (−5 °C) of the diol (**13b**) (16.6 g, 36 mmol) in dry pyridine (250 ml) was added slowly methanesulphonyl chloride (10.0 g, 87 mmol). The resulting solution was kept at −5 °C for 72 h, after which it was poured onto crushed ice and then extracted with CH_2Cl_2 (3 × 200 ml). The organic extract was washed successively with 1M HCl (100 ml) and saturated aqueous $NaHCO_3$, and then dried, and evaporated to give the dimesylate (**13c**) (16.6 g, 75%) which was not purified.

A magnetically stirred mixture of the dimesylate (**13c**) (16.6 g, 27 mmol) and $LiAlH_4$ (2.05 g, 54 mmol) in dry THF (300 ml) was refluxed for 18 h in a nitrogen atmosphere. Use of a work-up procedure that was identical with that described above for the synthesis of the diol (**13b**) gave the *heptacycle* (**13d**) (10 g, 87%); m.p. 287 °C (from acetone); δ_H(500 MHz; $CDCl_3$) 0.81 (6 H, s, 2 × CH_3), 1.16 (1 H, d, *J* 8.8 Hz, 13-H), 1.35 (2 H, br d, *J* 9 Hz, 13-H, 14-H), 1.45 (1 H, d, *J* 10.9 Hz, 14-H), 1.81 (2 H, s), 2.06 (2 H, s), 2.37 (2 H, s), 2.75 (2 H, t, *J* 1.8 Hz, 1-H, 4-H), 3.40 (2 H, br s, 5a-H, 11b-H), 4.08 (6 H, s, 2 × OCH_3), 6.04 (2 H, t, *J* 1.8 Hz, 2-H, 3-H), 7.39 (2 H, m, ArH), and 8.08 (2 H, m, ArH) (Found: C, 85.2; H, 7.6. $C_{30}H_{32}O_2$ requires C, 84.9; H, 7.6%).

(1α,4α,4aα,5β,5aα,5bβ,5cα,6β,6aα,12bα,13β,13aα,13bβ,13cα,-14β,14aα)-7,12-*Dimethoxy*-5b,13b-*dimethyl*-1,2,3,4,4a,5,5a,5b,-5c,6,6a,12b,13,13a,13b,13c,14,14a-*octadecahydro*-1,4:5,14:6,13-*trimethanonaphtho*[2‴,3‴:3‴,4‴]*cyclobuta*[1‴,2‴:3″,4″]*cyclobuta*[1″,2″:4′,5′]*benzo*[′,2′:3,4]*cyclobuta*[1,2-b]*naphthalene*-15-*one* (**6a**), *and the Dicyanomethylene Derivative* (**6b**).—A solution of (**13d**) (3 g, 7 mmol) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (3 g, 11.4 mmol) in xylene (b.p. 138–141 °C) (20 ml) was refluxed for 3 days. Azeotropic removal of the xylene, through addition of ethanol (50 ml), gave a solid residue which was assumed to be (**16**) (4.7 g, 96%) since its 60 MHz ^{1}H NMR spectrum revealed the complete absence of the peak at δ 6.04 due to the double bond protons of (**13d**).

Sodium (20.0 g, 0.87 mol) was added piecewise to a refluxing solution of (**16**) (4.7 g, 6.8 mmol) in THF (30 ml) and propan-2-ol (100 ml). The resulting mixture was refluxed for 17 h. Ethanol (20 ml) was added to the cooled reaction mixture followed by crushed ice (100 g). Extraction with dichloromethane (3 × 150 ml) and evaporation of the organic extracts (after washing with water and drying) gave a solid whose ^{1}H NMR spectrum revealed the presence of (**16**, X = H), together with compounds resulting from partial reduction of the naphthalene ring.[27] Rearomatization was achieved by treating this material with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (3 g) in benzene (150 ml) at room temperature for 18 h. The cooled reaction mixture was filtered, and the filtrate washed with aqueous NaOH (100 ml). Evaporation of the dried filtrate gave a brownish solid which was subjected to column chromatography (alumina; EtOAc–hexane, 30:70, as eluant). Although the eluted solid (3.0 g) was not further purified, its identity as (**16**, X = H) was secured from its partial 60 MHz ^{1}H NMR spectrum which revealed the presence of the doubled bond protons (δ 6.1) and three OCH_3 signals at δ 3.0, 3.1, and 4.0, with relative areas of 1:1:2, respectively. These data are in accord with the ^{1}H NMR spectra of related compounds.[18,27]

Compound (**16**, X = H) (2.5 g, 4.5 mmol) in ethyl acetate (150 ml) was hydrogenated at 1 atm and 25 °C by using 10% Pd/C (200 mg) until uptake of H_2 had ceased. Standard work-up procedures gave the *dimethoxy ketal* derivative of (**6a**) (2.3 g, 92%); m.p. 288–289 °C; δ_H(500 MHz; $CDCl_3$) 0.80 (6 H, s, 2 × CH_3), 1.30 (1 H, d, *J* 10.1 Hz), 1.42 (2 H, br d, *J* 10.9 Hz), 1.61 (4 H, br s), 1.82 (2 H, br s), 1.89 (1 H, d, *J* 11.8 Hz), 2.03 (2 H, s), 2.05 (4 H, br s), 2.11 (2 H, s), 2.31 (2 H, s), 3.25 (3 H, s, OCH_3), 3.26 (3 H, s, OCH_3), 3.39 (2 H, s), 4.07 (6 H, s, 2 × OCH_3), 7.38 (2 H, m, ArH), and 8.09 (2 H, m, ArH) (Found: C, 80.1; H, 7.9. $C_{37}H_{44}O_4$ requires C, 80.4; H, 8.0%).

A solution of the ketal of (**6a**) (2.0 g, 3.6 mmol) in formic acid (50 ml) and THF (20 ml) was stirred for 18 h at room temperature (*ca.* 21 °C). The formic acid was removed under reduced pressure to give (**6a**) (1.4 g, 77%). Recrystallization from methanol gave the pure *ketone* (**6a**) (0.9 g); m.p. 284 °C (decomp.); δ_H(500 MHz; $CDCl_3$) 0.83 (6 H, s, 2 × CH_3), 1.32 (1 H, d, *J* 11.0 Hz), 1.42 (1 H, d, *J* 11.0 Hz), 1.63 (1 H, d, *J* 12.3 Hz), 1.75 (2 H, m), 1.89 (2 H, t, *J* 2.3 Hz), 1.96–1.99 (5 H, m), 2.07 (2 H, s), 2.13 (2 H, s), 2.26 (2 H, s), 2.31 (2 H, s), 2.40 (2 H, s), 4.07 (6 H, 2 × OCH_3), 7.39 (2 H, m, ArH), and 8.08 (2 H, m, ArH); ν_{max}(Nujol) 1 779 cm^{-1} (C=O) (Found: C, 83.1; H, 7.8. $C_{35}H_{38}O_3$ requires C, 83.0; H, 7.6%).

A solution of the ketone (**6a**) (0.4 g, 0.8 mmol) and malononitrile (0.2 g, 3 mmol), acetic acid (0.5 ml), and ammonium acetate (0.2 g) in toluene (10 ml) was refluxed in a Dean–Stark apparatus for 24 h. The cooled reaction mixture was successively washed with saturated aqueous $NaHCO_3$ (50 ml) and water (50 ml). The dried solution was evaporated under reduced pressure to give the *dicarbonitrile* (**6b**) (0.4 g, 91%); m.p. 297–298 °C (decomp.) (from methanol); δ_H(500 MHz; $CDCl_3$) 0.82 (6 H, s, 2 × CH_3), 1.32 (1 H, d, *J* 11.0 Hz), 1.40 (1 H, d, *J* 11.0 Hz), 1.61–1.68 (3 H, br m), 1.81 (2 H, t, *J* 2.2 Hz), 1.90 (1 H, d, *J* 12.0 Hz), 2.01 (2 H, s), 2.04–2.09 (2 H, m), 2.11 (2 H, s), 2.29 (2 H, s), 2.32 (2 H, s), 3.02 (2 H, t, *J* 2.2 Hz), 3.41 (2 H, s), 4.07 (6 H, 2 × OCH_3), 7.37 (2 H, m, ArH), and 8.09 (2 H, m, ArH); ν_{max}(Nujol) 2 241 cm^{-1} (CN) (Found: C, 82.1; H, 6.7; N, 4.95. $C_{38}H_{38}N_2O_2$ requires C, 82.3; H, 6.9; N, 5.05%).

Dimethyl(2aα,3β,3aα,3bβ,3cα,4β,4aα,10bα,11β,11aα,11bβ,-11cα,12β,12aα)-5,10-*Dimethoxy*-3b,11b-*dimethyl*-2a,3,3a,3b,3c,-4,4a,10b,11,11a,11b,11c,12,12a-*tetradecahydro*-3,12:4,11-*dimethanocyclobuta*[1⁗,2⁗:4⁗,5⁗]*benzo*[1‴,2‴:3‴,4⁗]*cyclobuta*[1‴,2‴:3″,4″]*cyclobuta*[1″,2″:4′,5′]*benzo*[1′,2′:3,4]-*cyclobuta*[1,2-b]*naphthalene*-1,2-*dicarboxylate* (**14**).—A magnetically stirred solution of (**13d**) (5 g, 11.8 mmol), DMAD (1.68 g, 11.8 mmol), and $RuH_2CO(PPh_3)_3$[37] (1.4 g, 1.2 mmol) in benzene (50 ml) was refluxed in a nitrogen atmosphere for 20 h. Use of a similar work-up procedure to that used in the synthesis of (**11**) gave the *octacycle* (**14**) (6.2 g, 92%); m.p. 262 °C (from ethanol); δ_H(500 MHz; $CDCl_3$) 0.81 (6 H, s, 2 × CH_3), 1.31 (1 H, d, *J* 11.5 Hz), 1.33 (1 H, d, *J* 11.0 Hz), 1.41 (1 H, d, *J* 11.5 Hz), 1.43 (1 H, d, *J* 11.0 Hz), 2.04 (2 H, s), 2.13 (2 H, s), 2.21 (2 H, s), 2.33 (2 H, s), 2.63 (2 H, s), 3.41 (2 H, s), 3.79 (6 H, 2 × CO_2CH_3), 4.08 (6 H, 2 × OCH_3), 7.39 (2 H, m, ArH), and 8.09 (2 H, m, ArH) (Found: C, 76.0; H, 6.6. $C_{36}H_{38}O_6$ requires C, 76.3; H, 6.8%).

Dimethyl(1α,4α,4aβ,4bα,4cβ,5α,5aβ,5bα,5cβ,6α,6aβ,12bβ,13α,-13aβ,13bα,13cβ,14α,14aβ,14bα,14cβ)-7,12-*Dimethoxy*-5b,13b-*dimethyl*-1,4,4a,4b,4c,5,5a,5b,5c,6,6a,12b,13,13a,13b,13c,14,-14a,14b,14c-*icosahydro*-1,4:5,14:6,13-*trimethanobenzo*[1⁗⁗,-2⁗⁗:3⁗⁗,4⁗⁗]*cyclobuta*[1⁗⁗,2⁗⁗:3⁗⁗,4⁗⁗]*cyclobuta*[1‴,2‴:-4‴,5⁗]*benzo*[1‴,2‴:3‴,4⁗]*cyclobuta*[1‴,2‴:3″,4″]*cyclobuta*-[1″,2″:4′,5′]*benzo*[1′,2′:3,4]*cyclobuta*[1,2-b]*naphthalene*-4b,14b-*dicarboxylate* (**15a**).—A solution of (**14**) (6.2 g, 11 mmol) in quadricyclane (10 g, 109 mmol) was refluxed in a nitrogen atmosphere for 5 days. Use of an identical work-up procedure to that used in the synthesise of (**13a**) gave (**15a**) (7.02 g, 97%); m.p. > 315 °C (from acetone); δ_H(500 MHz; $CDCl_3$) 0.77 (6 H, s, 2 × CH_3), 1.09 (1 H, d, *J* 9.8 Hz), 1.29 (1 H, d, *J* 11.0 Hz), 1.40 (1 H, d, *J* 11.0 Hz), 1.54 (1 H, d, signal partially masked by water peak), 1.81 (1 H, d, *J* 9.8 Hz), 2.00 (2 H, s), 2.09 (4 H, br s), 2.13 (2 H, s), 2.17 (1 H, d, *J* 11.2 Hz), 2.29 (4 H, br s), 2.81 (2 H, t, *J* 1.5 Hz), 3.38 (2 H, s), 3.74 (6 H, s, 2 × CO_2CH_3), 4.06 (6 H, s, 2 × OCH_3), 6.05 (2 H, d, *J* 1.7 Hz), 7.38 (2 H, m, ArH), and 8.08 (2 H, m, ArH) (Found: C, 78.6; H, 6.8. $C_{43}H_{46}O_6$ requires C, 78.4; H, 7.0%).

(1α,4α,4aβ,4bα,4cβ,5α,5aβ,5bα,5cβ,6α,6aβ,12bβ,13α,13aβ,13bα,13cβ,14α,14aβ,14bα,14cβ)-7,12-*Dimethoxy*-4b,5b,13b,14b-*tetramethyl*-1,4,4a,4b,4c,5,5a,5b,5c,6,6a,12b,13,13a,13b,13c,14,-14a,14b,14c-*icosahydro*-1,4:5,14:6,13-*trimethanobenzo*[1⁗⁗,-2⁗⁗:3⁗⁗,4⁗⁗]*cyclobuta*[1⁗⁗,2⁗⁗:3⁗⁗,4⁗⁗]*cyclobuta*[1⁗⁗,2⁗⁗:-4⁗⁗,5⁗⁗]*benzo*[1⁗⁗,2⁗⁗:3⁗⁗,4⁗⁗]*cyclobuta*[1‴,2‴:3″,4″]*cyclobuta*-[1″,2″:4′,5′]*benzo*[1′,2′:3,4]*cyclobuta*[1,2-b]*naphthalene* (**15d**).—To a solution of (**15a**) (10 g, 15 mmol) in dry THF (150 ml), under nitrogen, was added $LiAlH_4$ (1.50 g, 39 mmol) in small portions. The mixture was refluxed for 20 h. Use of the same work-up procedure that was employed for the synthesis of (**13b**) gave the diol (**15b**) (8.9 g, 97%) which was not purified further; ν_{max}(Nujol) 3 251 cm^{-1}.

To a cooled solution (−5 °C) of the diol (**15b**) (8.9 g, 15 mmol) in dry pyridine (100 ml) was added slowly methanesulphonyl chloride (5.0 g, 44 mmol). The resulting solution was kept at −5 °C for 3 days, after which it was worked up, using the same procedure that was employed for the synthesis of (**13c**), to give the dimesylate (**15c**) (9.0 g, 80%) which was not further purified.

A magnetically stirred mixture of the dimesylate (**15c**) (9.0 g, 12 mmol) and $LiAlH_4$ (1.5 g, 39 mmol) in dry THF (150 ml) was refluxed for 19 h. Use of the same work-up procedure that was described for the synthesis (**13d**) the *tetramethyl compound* (**15d**)

(6.0 g, 87%); m.p. 287 °C (from methanol); δ_H(500 MHz; $CDCl_3$) 0.79 (6 H, s, 2 × CH_3), 0.81 (6 H, s, 2 × CH_3), 1.12 (1 H, d, *J* 8.7 Hz), 1.25–1.35 (2 H, m), 1.43 (1 H, d, *J* 11.0 Hz), 1.60 (2 H, br s), 1.74 (2 H, s), 1.86 (2 H, s), 1.97 (2 H, s), 2.04 (2 H, s), 2.11 (2 H, s), 2.30 (2 H, s), 2.71 (2 H, br s), 3.40 (2 H, s), 4.07 (6 H, 2 × OCH_3), 6.00 (2 H, t, *J* 1.7 Hz), 7.38 (2 H, m, ArH), and 8.08 (2 H, m, ArH) (Found: C, 86.2; H, 8.1. $C_{41}H_{46}O_2$ requires C, 86.3; H, 8.1%).

(1α,4α,4aα,5β,5aα,5bβ,5cα,6β,6aα,6bβ,6cα,7β,7aα,13bα,14β,-14aα14bβ,14cα,15b,15aα,15bβ,15cα,16b,16aα)-8,13-*Dimethoxy*-5b,6b,14b,15b-*tetramethyl*-1,2,3,4,4a,5,5a,5b,5c,6,6a,6b,6c,7,7a,-13b,14,14a,14b,14c,15,15a,15b,15c,16,16a-*hexacosahydro*-1,4:-5,16:6,15:7,14-*tetramethanonaphtho*[2‴″,3‴″:3‴″,4‴″]*cyclo*-*buta*[1‴″,2‴″:3‴″,4‴″]*cyclobuta*[1‴″,2‴″:4‴″,5‴″]*benzo*[1‴″,-2‴″:3‴″,4‴″]*cyclobuta*[1‴″,2‴″:3″,4″]*cyclobuta*[1″,2″:4′,5′]*benzo* [1′,2′:3,4]*cyclobuta*[1,2-b]*naphthalene* (**7a**), *and the Dicyanomethylene Derivative* (**7b**).—A solution of (**15d**) (5 g, 8.8 mmol) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (3 g, 11.4 mmol) in xylene (b.p. 138–141 °C) (25 ml) was refluxed for 3 days. Use of the same work-up procedure that was employed for the synthesis of (**16**) gave (**17**) (7.1 g, 97%) which was not purified further; partial ^1H NMR, δ_H(500 MHz; $CDCl_3$) 0.75 (6 H, s, 2 × CH_3), 0.79 (6 H, s, 2 × CH_3), 3.51 (3 H, s, OCH_3), 3.57 (3 H, s, OCH_3), and 4.07 (6 H, s, 2 × OCH_3); complete absence of double bond proton signals.

Sodium (20.0 g, 0.87 mol) was added piecewise to a refluxing solution of (**17**) (7.0 g, 8.4 mmol) in THF (50 ml) and propan-2-ol (150 ml). The resulting mixture was refluxed for 17 h. Use of the same work-up procedure that was employed for the synthesis of (**16**, X = H), including the DDQ treatment, gave (**17**, X = H) (4.5 g, 77%) which was not purified further, δ_H(500 MHz; $CDCl_3$) 6.03 (2 H, t, *J* 2.3 Hz). This material (4.5 g) was immediately hydrogenated, using conditions identical to those employed for the hydrogenation of (**16**, X = H), to give the crude dimethoxy ketal derivative of (**7a**) (4.2 g, 92%); m.p. 308–309 °C; δ_H(60 MHz; $CDCl_3$) 0.75 (6 H, s, 2 × CH_3), 0.78 (6 H, s, 2 × CH_3), 3.25 (6 H, br s, 2 × OCH_3), and 4.1 (6 H, s, 2 × OCH_3).

A solution of the ketal of (**7a**) (2.0 g, 2.9 mmol) in formic acid (50 ml) and THF (25 ml) was stirred for 18 h at room temperature (*ca.* 21 °C). The formic acid was removed under reduced pressure to give the *undecacycle* (**7a**) (1.35 g, 72%); m.p. 304 °C (decomp.) (from methanol); δ_H(500 MHz; $CDCl_3$) 0.80 (6 H, s, 2 × CH_3), 0.81 (6 H, s, 2 × CH_3), 1.29 (1 H, d, *J* 10.9 Hz), 1.42 (1 H, d, *J* 11.0 Hz), 1.58 (2 H, br s), 1.61 (1 H, d, *J* 11.5 Hz), 1.73 (2 H, near superposition of two doublets, *J ca.* 10 Hz), 1.86 (2 H, br s), 1.93–2.00 (12 H, complex set of peaks), 2.03 (1 H, d, *J* 11.5 Hz), 2.11 (2 H, s), 2.21 (2 H, s), 2.30 (2 H, s), 3.40 (2 H, s), 4.07 (6 H, 2 × OCH_3), 7.38 (2 H, m, ArH), and 8.09 (2 H, m, ArH); ν_{max}(Nujol) 1 778 cm^{-1} (C=O) (Found: C, 84.3; H, 7.9. $C_{46}H_{52}O_3$ requires C, 84.6; H, 8.0%).

A solution of the ketone (**7a**) (0.5 g, 0.77 mmol) and malonitrile (0.25 g, 3.8 mmol), acetic acid (0.6 ml), and ammonium acetate (0.25 g) in toluene (10 ml) was refluxed in a Dean–Stark apparatus for 24 h. The cooled reaction mixture was then successively washed with saturated aqueous $NaHCO_3$ (50 ml) and water (50 ml). The dried solution was evaporated under reduced pressure to give the *dicarbonitrile* (**7b**) (0.45 g, 83%); m.p. > 320 °C (from ethyl acetate); δ_H(500 MHz; $CDCl_3$) 0.79 (6 H, s, 2 × CH_3), 0.80 (6 H, s, 2 × CH_3), 1.30 (1 H, d, *J* 11.1 Hz), 1.42 (1 H, d, *J* 10.8 Hz), 1.54–1.60 (3 H, m), 1.66 (2 H, near superposition of two doublets, *J ca.* 10 Hz), 1.78 (2 H, br s), 1.87 (1 H, d, *J* 13.3 Hz), 1.93 (2 H, s), 1.94 (2 H, s), 1.98 (2 H, s), 1.99 (2 H, s), 2.05 (2 H, m), 2.11 (2 H, s), 2.24 (2 H, s), 2.30 (2 H, s), 2.99 (2 H, t, *J* 2.2 Hz), 3.40 (2 H, s), 4.07 (6 H, 2 × OCH_3), 7.38 (2 H, m, ArH), and 8.08 (2 H, m, ArH); ν_{max}(Nujol) 2 241 cm^{-1} (CN) (Found: C, 84.2; H, 7.3; N, 3.9. $C_{49}H_{52}N_2O_2$ requires C, 84.0; H, 7.5; N, 4.0%).

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