

Synthesis and Crystal Structures of Three Rigidly Linked Donor–Acceptor Systems Designed to Test the Effect of Bridge Configuration on the Dynamics of Long-Range Intramolecular Electron Transfer Processes

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The synthesis and single crystal X-ray structures of three rigid bichromophoric systems are described, namely the dicyanovinyl derivatives of 7,12-dimethoxydodecahydro-1,4:6,13-dimethanopentacen-15-one, **3**, 8,13-dimethoxyhexadecahydro-1,4:5,16:6,17:7, 14-tetramethanohexacen-17-one, **4** and 6,11-dimethoxy-4b,12b-dimethylododecahydro-4,13;5,12-dimethano-2*H*-indeno-[5',6':3',4']cyclobuta[1',2':3,4]cyclobuta[1,2-*b*]anthracen-2-one **5**. Compounds **3** and **4** were synthesized from dimethanonaphthacene **8** *via* Diels–Alder reaction with tetrachlorodimethoxycyclopentadiene **9** (in the case of **3**) and *via* successive Diels–Alder reactions, firstly with hexachlorocyclopentadiene, **14**, and then with **9**, in the case of **4**. The synthesis of **5** was achieved through ring expansion of the dichloroketene [2 + 2] cycloadduct formed from **21**. Differences in the rates of photoinduced intramolecular electron transfer in **3–5**, compared with those for **1** and **2**, are rationalized in terms of the differing configurations of the hydrocarbon bridges in these systems, as revealed by X-ray crystallography.

Over the past several years a wealth of experimental evidence has been accumulated demonstrating that both thermal and photoinduced electron transfer between a donor and acceptor pair can occur over distances that are considerably greater than the sum of the donor and acceptor van der Waals radii. These studies are providing a detailed mechanistic picture of how the dynamics of long-range electron transfer depend on such factors as the driving force, reorganization energies, donor–acceptor distance, and the relative orientation between the donor and acceptor groups.¹ Long-range intramolecular electron transfer processes continue to play a fundamental role in these mechanistic studies because the attachment of the donor and acceptor groups to a fairly rigid bridge (or spacer) allows the dependence of electron transfer dynamics on donor–acceptor distance and orientation to be determined unambiguously.^{1–18} A variety of hydrocarbon bridges, covalently linked to the donor and acceptor groups have been used in such studies, including polynorbornyl (norbornylogous) bridges,^{2–10} cyclohexane, decalin and steroid systems,^{11–15} bicyclo[2.2.2]octane,¹⁶ triptycene¹⁷ and polyspirocyclobutanes.¹⁸

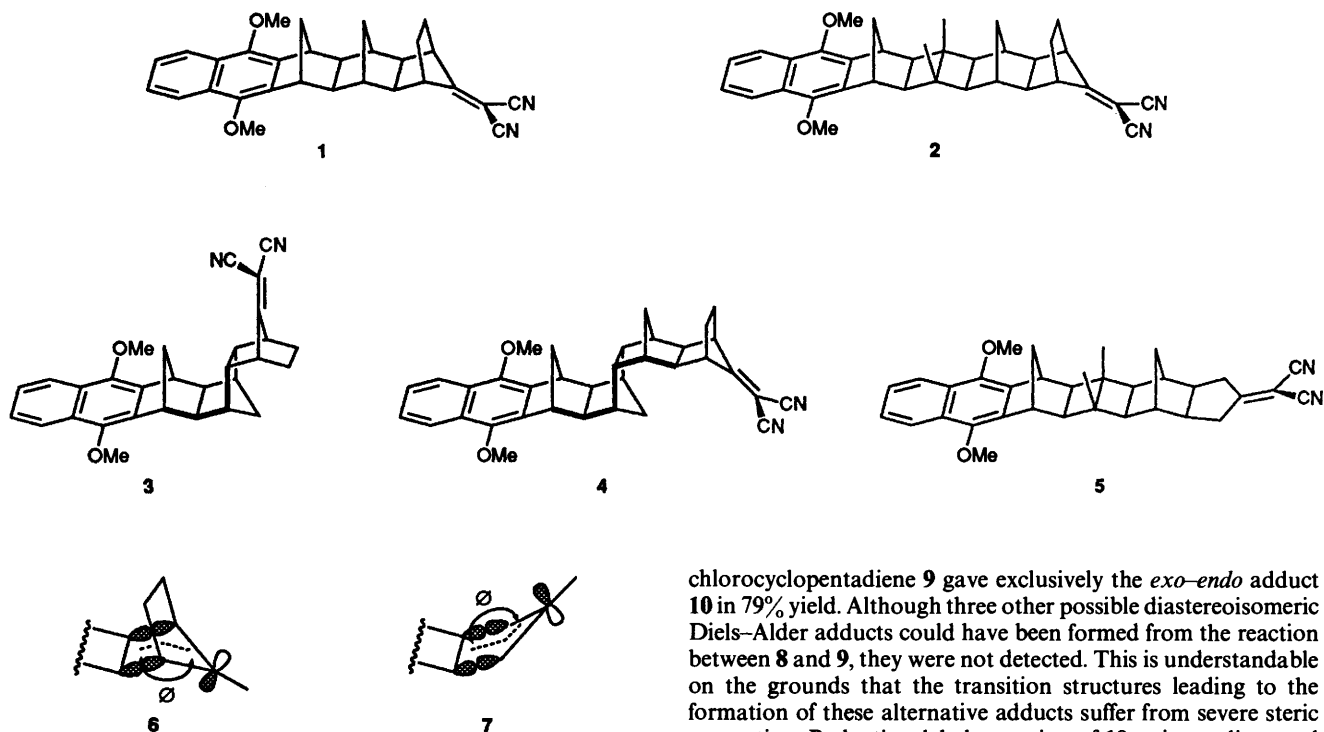
Photoinduced and pulse radiolysis electron transfer studies on the norbornylogous compounds, such as **1** and **2**,^{2–10} in which the donor and acceptor are separated by relays of six and eight σ bonds, respectively, and other systems, notably steroid analogues,^{11–15} have revealed that intramolecular electron transfer can take place extremely rapidly over large distances. For example, the rate constant for photoinduced electron transfer in **2**, from the locally electronically excited state of the dimethoxynaphthalene donor to the dicyanovinyl acceptor, is $2 \times 10^{10} \text{ s}^{-1}$,⁵ notwithstanding the edge-to-edge separation of 9.4 \AA ¹⁹ between the donor–acceptor pair. Indeed, photoinduced electron transfer is rapid ($1.6 \times 10^8 \text{ s}^{-1}$) even for an analogue of **2** in which the chromophores are separated by relays of 12 σ bonds, corresponding to an estimated edge-to-edge donor acceptor distance of 13.5 \AA .⁵

These results strongly suggest that the observed rapid rates

of electron transfer in these systems are due largely to through-bond (TB) interactions between the orbitals of the donor and acceptor groups with those of the intervening sigma bonded relays.^{20,21} The argument that TB interactions mediate long-range electron transfer processes in molecules such as **1** and **2** was further strengthened from studies on the dependence of electron transfer dynamics on the configuration of the bridge connecting the donor and acceptor groups. Thus, application of the all-*trans* rule of TB interactions²⁰ leads to the prediction that TB interactions should be stronger in **1** and **2**, in which the bridge relays consist exclusively of all-*trans* (or antiperiplanar) alignments of σ bonds, than in the respective molecules, **3** and **4**, in which one (in the case of **3**) and two (in the case of **4**) sets of σ bonds have *cis* or *gauche* conformations (these are highlighted in the structures). It was found^{7,8} that the rates of photoinduced electron transfer in **3** and **4** were, indeed, about an order of magnitude slower than those of **1** and **2**, respectively.

An additional way to verify that TB coupling can mediate electron transfer in the norbornylogous systems is to modify the hydrocarbon bridge so as to reduce the overlap between the π and π^* orbitals of the donor and/or acceptor groups with those of the bridge. A straightforward method of achieving this is to remove the ethano bridge associated with the norbornyl group containing the dicyanovinyl chromophore in **2**, thereby forming **5**. This removal should cause a flattening of the cyclopentyl ring, and a corresponding increase in the flap angle, ϕ , upon going from **2** to **5**, as shown schematically by **6** and **7**, respectively. Indeed, it was found that electron transfer was significantly slower in **5**, compared to **2**.¹⁰

In this paper, we describe the synthesis and the X-ray crystal structures of the compounds **3–5** (those for **1** and **2** have been reported previously¹⁹). The crystal structure data are important for two reasons. Firstly, they provide precise measurements of donor–acceptor distances and orientational effects in the series **1–5**, thereby allowing one to assess more



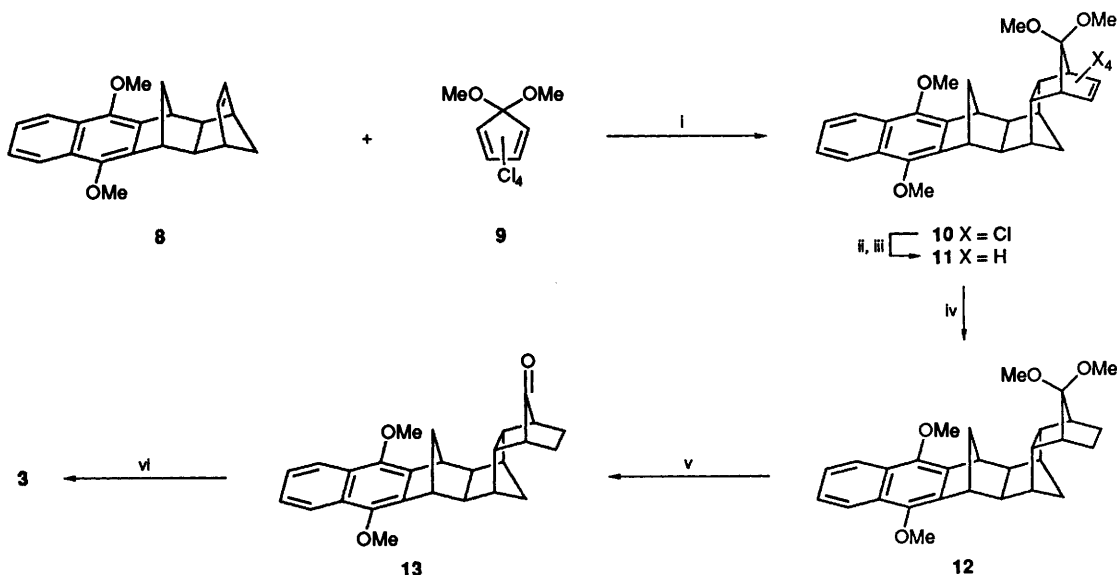
accurately how these factors govern electron transfer dynamics. Secondly, there is much interest in calculating the interaction matrix elements for electron transfer.²²⁻²⁴ These are important quantities because they form a central part of the Marcus electron transfer rate theory.^{1c} In order to calculate these quantities, accurate molecular geometries are required. The ketones **13** (Scheme 1), **20** (Scheme 2), and **24** (Scheme 3) are also of interest because of their use as probes for investigating the role of TB coupling in long-range singlet-singlet energy transfer processes.²⁵

Results and Discussion

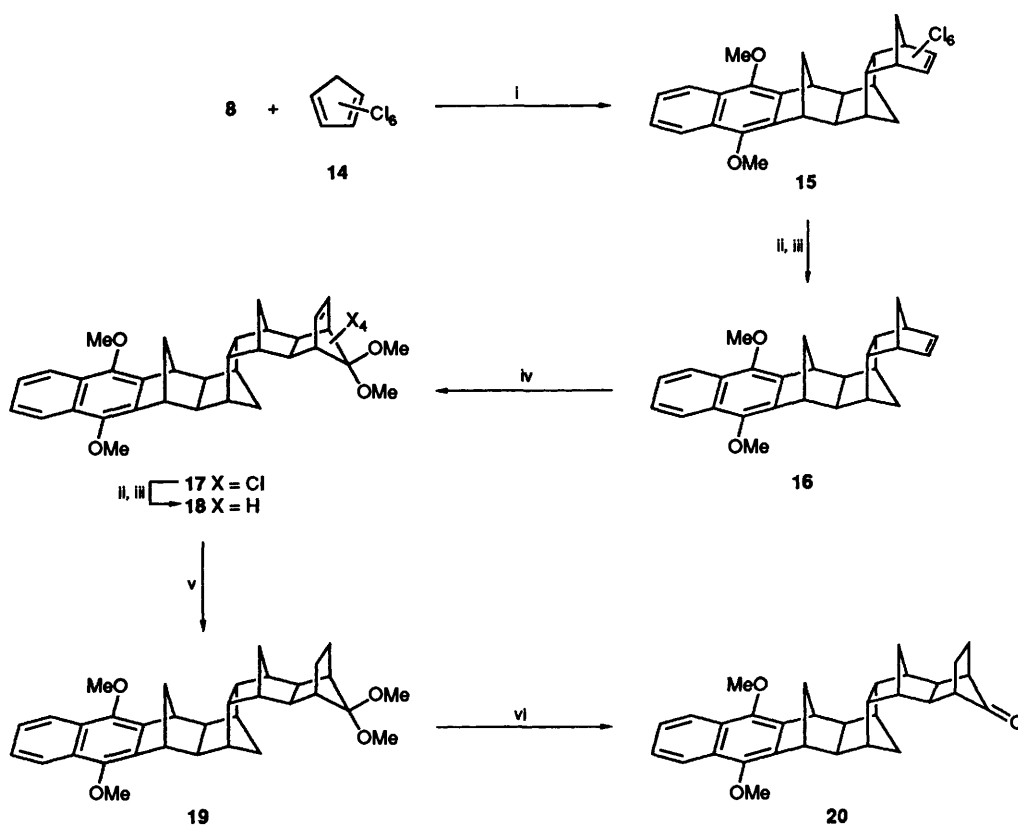
Syntheses.—The syntheses of **3**, **4** and **5** are outlined in Schemes 1, 2 and 3, respectively. Diels-Alder reaction between the known dimethanonaphthalene **8**²¹ and dimethoxytetra-

chlorocyclopentadiene **9** gave exclusively the *exo-endo* adduct **10** in 79% yield. Although three other possible diastereoisomeric Diels-Alder adducts could have been formed from the reaction between **8** and **9**, they were not detected. This is understandable on the grounds that the transition structures leading to the formation of these alternative adducts suffer from severe steric congestion. Reductive dehalogenation of **10**, using sodium and propan-2-ol gave a mixture consisting of **11** and products arising from reduction of the naphthalene ring of **11**.²¹ Treatment of this mixture with DDQ led to smooth aromatization to produce **11** in 66% yield. Catalytic hydrogenation of **11** gave **12** and deketalization of this material with formic acid gave the ketone **13** which, upon application of the Knoevenagel condensation reaction with malononitrile, produced the dicyanovinyl system **3**, in 45% overall yield from **8**.

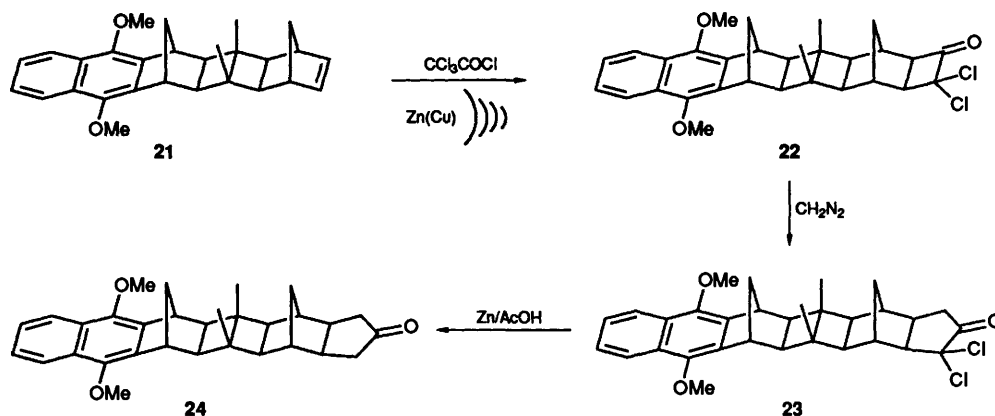
The synthesis of the ketone **20** (Scheme 2) was readily achieved through the application of two Diels-Alder reactions, the first between **8** and hexachlorocyclopentadiene **14**, to give the adduct **15**, and the second between **9** and **16**, the latter being obtained from reductive dechlorination of the adduct **15**. The remaining steps in the synthesis of **20** are identical with those employed in the synthesis of **13** from **10** (Scheme 1).



Scheme 1 Reagents and conditions: i, Heat; ii, Na/Pr^tOH; iii, DDQ, iv, H₂, Pd/C; v, HCO₂H; vi, CH₂(CN)₂



Scheme 2 Reagents and conditions: i, Heat; ii, Na/PrⁱOH; iii, DDQ; iv, **9**; v, H₂, Pd/C; vi, HCO₂H



Scheme 3

The synthesis of the ketone **24** (Scheme 3) began with the [2 + 2] cycloaddition between dichloroketene and the known alkene **21**²¹ to give the adduct **22** in 71% yield. The ketene was generated *in situ* from trichloroacetyl chloride and zinc-copper couple²⁶ and was promoted by ultrasound.²⁷ Ring expansion of **22** with diazomethane occurred smoothly to give a near quantitative yield of a single regioisomer **23**, formed from formal insertion of methylene into the CH-CO bond rather than into the C(Cl)₂-CO bond. The preferred mode of insertion was deduced from precedent²⁸ and from the ¹³C NMR spectrum of the ketone **24**, obtained by reductive dechlorination of **21** with zinc and acetic acid, which is only consistent with **24** possessing C_s point group symmetry (the alternative insertion product would have led to the formation of a dechlorinated ketone having C₁ symmetry). Knoevenagel condensation between the ketone **24** and malonitrile gave the dicyanovinyl product **5**.

Structural Commentary.—X-Ray crystal structures of **3–5** were determined (see Experimental section for details). Fractional coordinates for the non-hydrogen atoms for **3–5** are given in Tables 1–3. Interplanar angles (Tables 4–6) and selected torsional angles (Table 7) are also presented. ORTEP drawings of **3, 4** and **5** are given in Figures 1–3, respectively. In these Figures, the hydrogen atoms have been omitted for clarity. Tables of final fractional coordinates, thermal parameters, bond lengths and angles for all atoms (including hydrogen) have been deposited at the Cambridge Crystallographic Data Centre.

The results of the three X-ray crystal structure determinations are consistent with the expected stoichiometries and connectivities. The rigid frameworks of all three molecules have nearly C_s point group symmetry, although the two methoxy groups adopt conformations that destroy this symmetry. The bond lengths, and bond angles of the norbornyl units in **3–5**, and the

Table 1 Non-hydrogen atomic parameters for compound **3**. Esd's in parentheses.

	x	y	z
O(1)	0.334 2(3)	0.360 8(4)	0.211 1(1)
O(2)	0.246 2(3)	0.056 8(2)	0.361 8(1)
N(1)	1.017 0(4)	0.576 5(4)	0.565 1(1)
N(2)	1.141 4(4)	0.853 2(4)	0.464 5(1)
C(1)	0.642 1(3)	0.698 7(3)	0.481 7(1)
C(2)	0.561 1(3)	0.844 7(4)	0.481 7(1)
C(3)	0.597 0(3)	0.932 1(3)	0.442 0(1)
C(4)	0.697 1(3)	0.828 2(3)	0.423 5(1)
C(5)	0.609 2(3)	0.693 3(3)	0.397 4(1)
C(6)	0.450 9(3)	0.707 3(3)	0.360 0(1)
C(7)	0.397 5(3)	0.557 9(3)	0.336 8(1)
C(8)	0.499 0(3)	0.453 7(3)	0.318 7(1)
C(9)	0.389 8(3)	0.332 0(4)	0.295 6(1)
C(10)	0.318 6(4)	0.293 6(4)	0.250 3(1)
C(11)	0.224 2(3)	0.165 6(4)	0.240 7(1)
C(12)	0.152 7(4)	0.118 3(4)	0.194 3(1)
C(13)	0.068 7(4)	-0.005 8(4)	0.185 8(1)
C(14)	0.049 2(4)	-0.085 8(4)	0.222 7(2)
C(15)	0.113 6(4)	-0.043 3(4)	0.268 4(1)
C(16)	0.202 3(3)	0.084 6(3)	0.278 2(1)
C(17)	0.270 9(3)	0.134 5(3)	0.325 3(1)
C(18)	0.362 6(3)	0.252 9(3)	0.333 0(1)
C(19)	0.451 8(3)	0.327 4(3)	0.377 9(1)
C(20)	0.362 4(3)	0.470 5(3)	0.377 3(1)
C(21)	0.397 7(3)	0.580 2(3)	0.418 1(1)
C(22)	0.571 9(3)	0.605 5(3)	0.437 7(1)
C(23)	0.779 1(3)	0.753 1(3)	0.468 8(1)
C(24)	0.338 8(3)	0.717 1(3)	0.389 3(1)
C(25)	0.592 1(3)	0.372 5(4)	0.363 0(1)
C(26)	0.928 0(3)	0.735 2(3)	0.491 3(1)
C(27)	0.977 9(4)	0.649 0(4)	0.532 9(1)
C(28)	1.045 6(4)	0.800 4(4)	0.475 4(1)
C(29)	0.344 9(7)	0.504 2(6)	0.208 6(2)
C(30)	0.125 9(5)	0.108 8(5)	0.377 1(2)

bicyclo[2.2.0]hexyl group in **5**, resemble those found in **1** and **2**,¹⁹ and in simpler systems, such as aldrin and analogues.^{29,30}

The average angle between two planes intersecting along the line of fusion of two adjacent norbornyl or bicyclo[2.2.0] units [*e.g.*, the angle between the planes defined by C(9)–C(10)–C(21)–C(22) and C(8)–C(9)–C(22)–C(23) of **4**, Fig. 2] is substantially larger, by 7–10°, for **3** and **4**, than for **5** (Tables 4–6). This, no doubt, reflects the greater degree of steric congestion that obtains between the bridge methano (CH₂) groups and the ethano bridges within the aldrin-type subunits in the former pair of molecules.³⁰

The torsional angles for the C–C bonds in the relays of **3–4** clearly reveal the degree of deviation from the optimal all-*trans* (antiperiplanar) alignments required to maximise through-bond interactions (Table 7). Thus, the absolute values of the torsional angles for *trans* arrangements of bonds in **3** and **4**, such as C(9)–C(8)–C(7)–C(6) in **3**, are greater than 173° and are therefore close to the idealized antiperiplanar value of 180°. This was also found in the crystal structures for **1** and **2**.¹⁹ However, the torsional angles for *cis*-type alignments, such as C(8)–C(7)–C(6)–C(5) in **3**, are *ca.* 46° and are therefore gauche-like. Importantly, such gauche-type alignments substantially weaken through-bond interaction energies, compared to those systems, such as **1** and **2**, in which only antiperiplanar alignments of C–C bonds are present.

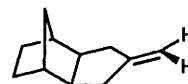
The flap angle, ϕ , for the cyclopentyl ring of **5**, measured by the angle between the planes C(1)–C(3)–C(4)–C(25) and C(1)–C(2)–C(3), is *ca.* 156°. This is considerably larger than the value of *ca.* 120° for the flap angle ϕ of the cyclopentyl subunit for **3** and **4** (see **6** for the definition of ϕ in this context). Orbital overlap of the type indicated by **6** and **7** should therefore be

Table 2 Non-hydrogen atomic parameters for compound **4**. Esd's in parentheses.

	x	y	z
O(1)	0.340 7(3)	0.028 5(1)	0.059 9(2)
O(2)	0.542 8(3)	0.266 6(1)	-0.007 5(2)
N(1)	1.753 1(4)	0.080 9(2)	0.594 7(3)
N(2)	1.584 0(4)	-0.099 4(2)	0.649 2(3)
C(1)	1.405 3(4)	0.138 2(2)	0.581 0(3)
C(2)	1.414 5(4)	0.154 3(2)	0.669 5(3)
C(3)	1.352 4(4)	0.088 5(2)	0.685 8(2)
C(4)	1.316 3(4)	0.041 6(2)	0.605 9(2)
C(5)	1.186 1(3)	0.066 5(2)	0.511 8(2)
C(6)	1.043 8(4)	0.091 3(2)	0.498 2(2)
C(7)	0.925 4(4)	0.105 6(2)	0.396 0(2)
C(8)	0.894 6(3)	0.058 3(2)	0.318 1(2)
C(9)	0.758 4(3)	0.083 3(2)	0.226 5(2)
C(10)	0.612 8(4)	0.106 5(2)	0.212 7(2)
C(11)	0.512 8(4)	0.120 2(2)	0.111 6(3)
C(12)	0.394 0(4)	0.086 8(2)	0.043 4(3)
C(13)	0.315 0(4)	0.114 7(2)	-0.046 8(3)
C(14)	0.186 0(5)	0.083 3(2)	-0.118 8(3)
C(15)	0.112 4(5)	0.112 8(3)	-0.203 1(4)
C(16)	0.160 0(6)	0.174 1(3)	-0.219 2(3)
C(17)	0.285 6(5)	0.205 5(2)	-0.151 3(3)
C(18)	0.366 4(4)	0.175 4(2)	-0.063 7(3)
C(19)	0.495 6(4)	0.206 7(2)	0.009 3(3)
C(20)	0.564 8(4)	0.180 8(2)	0.094 6(3)
C(21)	0.696 7(4)	0.203 1(2)	0.185 9(2)
C(22)	0.816 9(3)	0.149 8(2)	0.207 5(2)
C(23)	0.978 5(3)	0.153 9(2)	0.290 5(2)
C(24)	0.984 7(4)	0.171 9(2)	0.377 2(2)
C(25)	1.130 3(4)	0.186 0(2)	0.471 2(2)
C(26)	1.247 0(4)	0.132 6(2)	0.494 0(2)
C(27)	1.439 9(4)	0.063 5(2)	0.597 4(2)
C(28)	1.075 6(4)	0.166 2(2)	0.530 6(2)
C(29)	1.010 1(4)	0.076 9(2)	0.299 0(2)
C(30)	0.641 3(4)	0.181 6(2)	0.245 3(2)
C(31)	1.551 4(4)	0.028 1(2)	0.608 5(2)
C(32)	1.662 9(5)	0.058 3(2)	0.600 6(3)
C(33)	1.568 4(4)	-0.043 4(2)	0.630 5(3)
C(34)	0.403 4(4)	-0.032 9(2)	0.054 4(3)
C(35)	0.655 4(5)	0.260 3(2)	-0.022 6(4)
EC(14)	1.176 8(8)	0.151 2(3)	1.129 9(5)
EC(23)	1.031 9(11)	0.144 5(5)	1.054 1(9)
EO(1)	0.977 2(13)	0.091 9(4)	0.994 7(9)
EC(32)	0.872 5(10)	0.114 2(7)	0.903 0(8)
EC(41)	0.836 3(8)	0.052 9(5)	0.857 3(5)
EO(2)	0.819 0(13)	0.158 2(6)	0.887 2(11)
EO(1)'	1.019 5(13)	0.130 3(10)	0.979 4(8)
EO(2)'	0.925 0(13)	0.127 9(7)	1.053 6(7)

weaker in **5**, compared to **2**. Interestingly, and in contrast to **2**, the direction of puckering of the cyclopentyl ring in **5** occurs in an 'upward' direction, towards the CH₂ bridge of the adjacent norbornyl ring (Fig. 3).

That the observed magnitude and direction of cyclopentyl ring puckering in **5** are not due to crystal packing effects was verified by carrying out a full-geometry optimization (C_s symmetry constraint) on the model system, **25**, using the Hartree-Fock theoretical model and the STO-3G basis set (HF/STO-3G).³¹ The HF/STO-3G model is known to give reliable geometries for norbornyl molecules.³² The GAUSSIAN 82 suite of programs³³ was used to achieve the geometry optimization. Two stable optimized structures for **25** were

**25**

located at the HF/STO-3G level, and they differed mainly in the direction of puckering of the cyclopentyl ring. The structure in which the puckering occurs in an upward direction, as defined above, was found to be slightly more stable (by 0.3 kcal mol⁻¹ using the 3-21G basis set³⁴ on the STO-3G optimized

Table 3 Non-hydrogen atomic parameters for compound **5**. Esd's in parentheses

	x	y	z
O(1)	0.278 7(1)	0.639 4(1)	0.669 2(1)
O(2)	0.206 3(1)	0.385 7(1)	0.844 1(1)
N(1)	0.003 3(2)	0.037 7(3)	0.128 2(3)
N(2)	0.102 0(3)	0.220 2(3)	0.010 4(2)
C(1)	0.133 4(1)	0.129 0(2)	0.296 0(2)
C(2)	0.130 4(1)	0.169 3(2)	0.215 3(2)
C(3)	0.178 5(1)	0.237 7(2)	0.229 4(2)
C(4)	0.189 1(1)	0.263 5(2)	0.320 5(2)
C(5)	0.147 5(1)	0.336 8(1)	0.332 8(1)
C(6)	0.172 5(1)	0.359 8(1)	0.423 3(1)
C(7)	0.134 1(1)	0.422 8(1)	0.460 8(1)
C(8)	0.178 9(1)	0.452 6(1)	0.544 1(2)
C(9)	0.159 9(1)	0.529 4(1)	0.585 5(2)
C(10)	0.204 8(1)	0.529 3(1)	0.671 9(2)
C(11)	0.257 6(1)	0.575 9(1)	0.708 8(2)
C(12)	0.291 4(1)	0.562 2(2)	0.792 3(2)
C(13)	0.344 9(1)	0.612 0(2)	0.835 1(2)
C(14)	0.376 2(2)	0.597 2(2)	0.915 2(2)
C(15)	0.357 1(2)	0.532 6(2)	0.957 7(2)
C(16)	0.306 5(2)	0.484 7(2)	0.918 5(2)
C(17)	0.271 7(1)	0.497 6(2)	0.835 7(2)
C(18)	0.217 4(1)	0.447 0(2)	0.794 4(2)
C(19)	0.183 7(1)	0.463 6(1)	0.715 4(2)
C(20)	0.125 1(1)	0.426 6(1)	0.651 9(2)
C(21)	0.155 0(1)	0.381 6(1)	0.590 5(1)
C(22)	0.109 0(1)	0.349 8(1)	0.508 1(2)
C(23)	0.147 5(1)	0.289 1(1)	0.468 5(1)
C(24)	0.110 1(1)	0.235 3(1)	0.397 2(2)
C(25)	0.162 1(1)	0.192 4(1)	0.363 7(2)
C(26)	0.081 6(1)	0.296 3(2)	0.328 0(2)
C(27)	0.093 2(1)	0.485 7(2)	0.403 5(2)
C(28)	0.039 2(1)	0.328 2(2)	0.505 9(2)
C(29)	0.096 0(1)	0.503 2(2)	0.603 1(2)
C(30)	0.092 5(2)	0.148 7(2)	0.142 3(2)
C(31)	0.043 5(2)	0.086 0(3)	0.133 2(2)
C(32)	0.097 8(2)	0.189 1(3)	0.068 1(2)
C(33)	0.307 6(4)	0.619 8(3)	0.608 5(4)
C(34)	0.152 5(2)	0.333 2(2)	0.818 2(2)

structures) than the structure in which the direction of puckering occurs in a downward direction, away from the CH₂ bridge of the adjacent norbornyl ring. In addition, the flap angle, ϕ , for the more stable structure was calculated to be 157.2°, which is in good agreement with that found experimentally for **5** (ϕ for the less stable structure is 154°). Notwithstanding the small calculated energy difference between the conformers, which may very well be due to basis set deficiencies, our results indicate that the conformation of the dicyanomethylenecyclopentyl ring in **5** will be the same in solution (in which state the electron transfer kinetic measurements are carried out) as it is in the solid state.

Electron Transfer Rates and Bridge Configuration.—An important molecular metric property of relevance to electron transfer dynamics is the edge-to-edge (R_e) distance between the two chromophores. This quantity refers to the smallest distance between the two chromophores, that is, between C(23) and the midpoint of the C(9)–C(18) bond vector of **3**. The R_e values for **1–5** are given in Table 8, those for **1** and **2** being extrapolated values derived from the ketone precursors.¹⁹ Also given in the Table are the centre-to-centre (R_c) values, defined as the distance between the approximate 'centres of gravity' of the two chromophores, that is, between C(26) and the midpoint of the C(11)–C(16) bond vector of **3**. Table 8 also lists the relative rate constants for photoinduced intramolecular electron transfer for **1–5** in acetonitrile solvent. Although the rate data have been discussed in more detail elsewhere,^{5,7,8,10} the following important points are worth mentioning.

Photoinduced electron transfer from the first electronically excited singlet state dimethoxynaphthalene donor to the dicyanovinyl acceptor occurs in the six-bond systems, **1** and **3**, and takes place *ca.* seven times more rapidly in the former all-*trans* compound than in the latter system. This is so in spite of the fact that the edge-to-edge donor–acceptor separation, R_e , is 0.3 Å smaller in **3**, compared to **1**. A similar result obtains for the eight-bond systems, **2** and **4**, electron transfer occurring 13.6 times more rapidly in the former system, even though R_e is 0.4 Å smaller in **4**, compared to **2**. These results are only consistent with a through-bond mediated electron transfer mechanism, since electron transfer occurring *via* a direct through-space mechanism would occur more rapidly in **3** and **4**, compared to the respective systems, **1** and **2** (the R_e values are smaller in the former pair, compared to the latter pair of compounds). That the **2**:**4** rate ratio is larger than the **1**:**3** rate ratio is also entirely consistent with a through-bond mechanism since the hydro-

Table 4 Interplanar angles (°) of compound **3***†

Plane	a	b	c	d	e	f	g	h	i	j
b	177.4									
c	175.9	178.6								
d	119.8	121.9	122.5							
e	111.2	109.5	108.9	128.6						
f	160.3	158.6	158.1	100.6	130.8					
g	98.5	96.5	95.9	141.5	167.0	117.8				
h	133.9	136.0	136.6	165.9	114.5	114.8	127.4			
i	172.1	171.0	170.7	113.3	118.0	167.3	105.1	127.5		
j	125.2	127.3	127.9	174.6	123.3	106.0	136.2	171.2	118.7	
k	112.9	111.0	110.4	127.0	177.9	132.3	165.5	112.9	119.6	121.7

* Defining atoms: a, C(11, 12, 13, 14, 15, 16); b, C(9, 10, 11, 16, 17, 18); c, C(8, 9, 18, 19); d, C(8, 19, 25); e, C(7, 8, 19, 20); f, C(6, 7, 20, 21); g, C(6, 21, 24); h, C(5, 6, 21, 22); i, C(1, 4, 5, 22); j, C(1, 4, 23); k, C(1, 2, 3, 4).

† Typical esd's in this and in Tables 5 and 6 are of the order of 0.5°

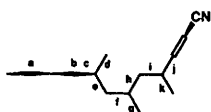
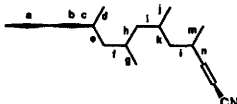
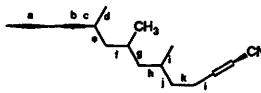


Table 5 Interplanar angles ($^{\circ}$) of compound 4*


Plane	a	b	c	d	e	f	g	h	i	j	k	l	m
b	176.8												
c	174.9	178.0											
d	116.9	119.9	121.9										
e	114.2	111.3	109.3	128.8									
f	163.6	160.7	158.7	100.6	130.5								
g	99.7	96.7	94.7	143.4	165.4	116.0							
h	131.0	134.0	136.0	165.9	114.7	114.7	129.3						
i	177.1	175.3	173.4	115.3	115.8	165.3	103.7	129.4					
j	117.4	120.4	122.4	179.2	128.3	101.1	142.9	166.4	115.9				
k	114.5	111.5	109.5	128.6	179.8	130.8	165.2	114.5	116.0	128.1			
l	166.9	164.1	162.1	104.0	127.2	176.6	112.6	118.1	168.6	104.5	127.4		
m	132.7	135.7	137.7	164.1	113.0	116.4	127.6	178.0	131.2	164.7	112.8	119.8	
n	107.7	104.7	102.7	135.4	173.3	123.9	172.0	121.3	109.2	134.9	173.1	120.6	119.6

* Defining atoms: a, C(13, 14, 15, 16, 17, 18); b, C(11, 12, 13, 18, 19, 20); c, C(10, 11, 20, 21); d, C(10, 21, 30); e, C(9, 10, 21, 22); f, C(8, 9, 22, 23); g, C(8, 23, 29); h, C(7, 8, 23, 24); i, C(6, 7, 24, 25); j, C(6, 25, 28); k, C(5, 6, 25, 26); l, C(1, 4, 5, 26); m, C(1, 2, 3, 4); n, C(1, 4, 27).

Table 6 Interplanar angles ($^{\circ}$) of compound 5*


Plane	a	b	c	d	e	f	g	h	i	j	k
b	178.4										
c	178.5	179.2									
d	124.2	125.7	125.2								
e	110.7	109.2	109.8	125.0							
f	170.1	168.7	169.2	114.4	120.5						
g	98.9	97.4	98.0	136.8	168.2	108.8					
h	158.3	156.9	157.4	102.7	132.3	168.2	120.5				
i	148.3	149.8	149.3	155.9	100.9	138.5	112.7	126.8			
j	91.5	92.9	92.4	147.2	157.8	98.4	169.6	110.2	123.1		
k	148.2	146.8	147.4	92.7	142.2	158.1	130.4	169.8	116.8	120.1	
l	171.2	170.0	170.6	116.4	118.5	176.7	106.8	166.2	140.4	96.5	156.3

* Defining atoms: a, C(12, 13, 14, 15, 16, 17); b, C(10, 11, 12, 17, 18, 19); c, C(9, 10, 19, 20); d, C(9, 20, 29); e, C(8, 9, 20, 21); f, C(7, 8, 21, 22); g, C(6, 7, 22, 23); h, C(5, 6, 23, 24); i, C(5, 24, 26); j, C(4, 5, 24, 25); k, C(1, 3, 4, 25); l, C(1, 2, 3).

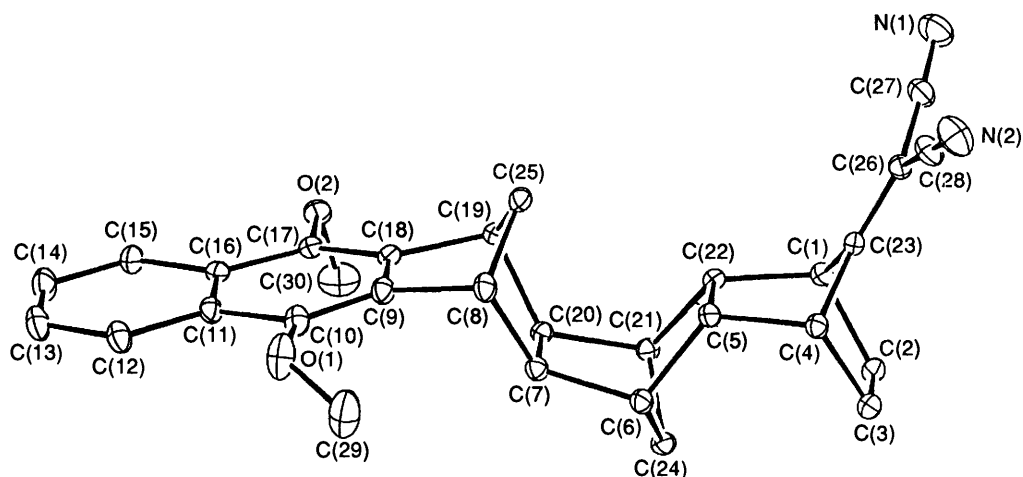
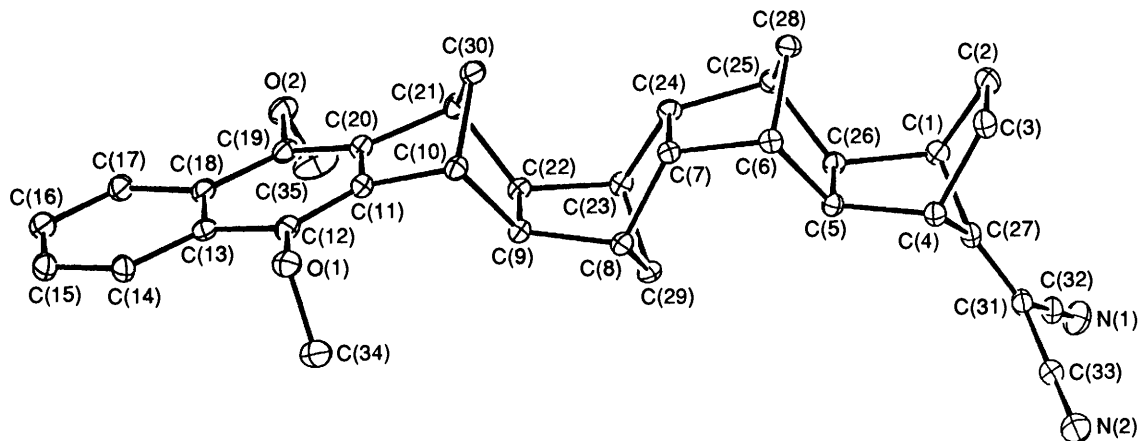
**Fig 1** ORTEP projection of compound 3, as determined by single crystal X-ray diffraction. Hydrogen atoms are omitted for clarity.

Table 7 Selected torsional angles ($^{\circ}$). Esd's in parentheses.

Compound 3			
C(9)–C(8)–C(7)–C(6)	–175.0(3)	C(18)–C(19)–C(20)–C(21)	173.8(3)
C(8)–C(7)–C(6)–C(5)	–46.9(3)	C(19)–C(20)–C(21)–C(22)	44.6(3)
C(7)–C(6)–C(5)–C(4)	174.9(2)	C(20)–C(21)–C(22)–C(1)	–174.1(2)
C(6)–C(5)–C(4)–C(23)	149.6(2)	C(21)–C(22)–C(1)–C(23)	–149.9(2)
C(6)–C(5)–C(4)–C(3)	46.8(3)	C(21)–C(22)–C(1)–C(2)	–47.2(3)
Compound 4			
C(11)–C(10)–C(9)–C(8)	–175.6(3)	C(20)–C(21)–C(22)–C(23)	174.3(3)
C(10)–C(9)–C(8)–C(7)	–45.1(4)	C(21)–C(22)–C(23)–C(24)	45.3(4)
C(9)–C(8)–C(7)–C(6)	173.3(3)	C(22)–C(23)–C(24)–C(25)	–174.8(3)
C(8)–C(7)–C(6)–C(5)	43.8(4)	C(23)–C(24)–C(25)–C(26)	–46.1(4)
C(7)–C(6)–C(5)–C(4)	–173.7(3)	C(24)–C(25)–C(26)–C(1)	175.7(3)
C(6)–C(5)–C(4)–C(27)	–148.3(3)	C(25)–C(26)–C(1)–C(27)	150.1(3)
C(6)–C(5)–C(4)–C(3)	–45.8(4)	C(25)–C(26)–C(1)–C(2)	47.4(4)
Compound 5			
C(10)–C(9)–C(8)–C(7)	167.7(2)	C(19)–C(20)–C(21)–C(22)	–168.7(2)
C(9)–C(8)–C(7)–C(6)	165.8(2)	C(20)–C(21)–C(22)–C(23)	–165.8(2)
C(8)–C(7)–C(6)–C(5)	–164.4(2)	C(21)–C(22)–C(23)–C(24)	166.8(2)
C(7)–C(6)–C(5)–C(4)	–170.2(2)	C(22)–C(23)–C(24)–C(25)	171.7(2)
C(6)–C(5)–C(4)–C(3)	–171.7(2)	C(23)–C(24)–C(25)–C(1)	174.6(2)
C(5)–C(4)–C(3)–C(2)	–96.9(2)	C(24)–C(25)–C(1)–C(2)	100.4(2)

**Fig. 2** ORTEP projection of compound 4, as determined by single crystal X-ray diffraction. Hydrogen atoms are omitted for clarity.

carbon bridge in 4 has two *cis* or *gauche* conformations in each relay, compared to only one such conformation in 3 (through-bond coupling is diminished with increasing numbers of *cis* conformations in the σ bond relay²⁰).

Finally, electron transfer takes place five times more slowly in 5 compared to 2, notwithstanding that the R_e values for these systems are identical. However, the smaller measured value for the flap angle, ϕ , of 120° for 2 (see 6), compared to 156° for 5 (see 7), results in stronger overlap between the hydrocarbon bridge orbitals and the dicyanovinyl π^* orbitals in 2, compared to 5 (*cf.* 6 and 7). Consequently, through-bond coupling is stronger in 2 than in 5, and this is manifested in a faster rate of photoinduced electron transfer in the former system.

Experimental

General.—M.p.s were taken on a Koffler hot-stage and are uncorrected. ^1H NMR spectra and ^{13}C NMR spectra were recorded using a Bruker AM-500 spectrometer operating at 500 and 122.725 MHz, respectively. All NMR spectra were measured using CDCl_3 as solvent. J Values are recorded in Hz. IR spectra were recorded on a Perkin-Elmer 580-B spectrometer. Elemental analyses were performed by Dr. H. P.

Pham of the School of Chemistry, University of New South Wales.

(1 α ,4 α ,4 $\alpha\alpha$,5 β ,5 $\alpha\beta$,6 α ,13 α ,13 $\alpha\beta$,14 β ,14 $\alpha\alpha$)-1,2,3,4-Tetrachloro-7,12,15,15-tetramethoxy-1,4,4 α ,5,5 α ,6,13,13 α ,14,14 α -decahydro-1,4:6,13-dimethanopentacene 10.—A solution of 8²¹ (2.0 g, 6.28 mmol) and tetrachlorodimethoxycyclopentadiene 9 (2.0 g, 7.58 mmol) in xylene (20 ml) was refluxed for 2 days, after which time, the solvent was removed under reduced pressure. The residue was recrystallized from methanol to give 10 (2.9 g, 79%), m.p. 296–298 $^{\circ}\text{C}$; δ_{H} (500 MHz; CDCl_3) 1.09 (1 H, d, J 11.9), 1.63 (1 H, d, J 11.9), 1.75 (1 H, d, J 10.9), 2.10 (2 H, br s), 2.34 (1 H, d, J 10.9), 2.57 (2 H, s), 2.91 (2 H, s), 3.57 (3 H, s, 15-OCH₃), 3.66 (3 H, s, 15-OCH₃), 3.68 (2 H, s, 6-H, 13-H), 3.98 (6 H, s, 2 \times OCH₃), 7.44 (2 H, m, aromatic) and 8.04 (2 H, m, aromatic) (Found: C, 59.6; H, 4.9. $\text{C}_{29}\text{H}_{28}\text{Cl}_4\text{O}_4$ requires C, 59.8; H, 4.85%).

(1 α ,4 α ,4 $\alpha\alpha$,5 β ,5 $\alpha\beta$,6 α ,13 α ,13 $\alpha\beta$,14 β ,14 $\alpha\alpha$)-7,12,15,15-Tetramethoxy-1,4,4 α ,5,5 α ,6,13,13 α ,14,14 α -decahydro-1,4:6,13-dimethanopentacene 11.—Sodium pieces (5.0 g, 0.22 mol) were added to a refluxing solution of 10 (2.5 g, 4.3 mmol) in THF (50 ml) and propan-2-ol (150 ml). After the addition was completed, the mixture was refluxed for 18 h. The cooled

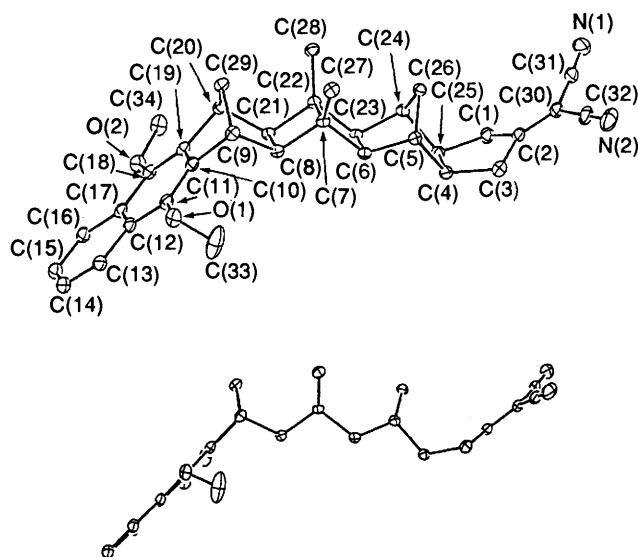


Fig. 3 ORTEP projections of compound **5**, as determined by single crystal X-ray diffraction. Hydrogen atoms are omitted for clarity.

Table 8 Edge-to-edge, R_e , and centre-to-centre, R_c , donor-acceptor distances (Å), and relative rate constants, k_{rel} , for photoinduced electron transfer for **1–5** in acetonitrile at 20 °C

Compd.	R_e	R_c	k_{rel}
1	6.8 ^a	9.0 ^a	114 ^b
2	9.4 ^c	11.8 ^c	13.6 ^d
3	6.5	9.8	16.4 ^b
4	9.0	12.1	1.0 ^b
5	9.5	12.6	2.7 ^e

^a Ref. 19. ^b Ref. 8. ^c Estimated from the corresponding ketone precursors; see ref. 19. ^d Ref. 5. ^e Ref. 10.

mixture was treated with ethanol (20 ml), to remove any unchanged sodium, followed by the addition of crushed ice (200 ml). Extraction with dichloromethane (3 × 75 ml) and evaporation of the organic extracts (after washing with water and drying) gave a solid (1.9 g) whose ¹H NMR spectrum revealed the presence of **11**, together with compounds resulting from partial reduction of the naphthalene ring.²¹ Rearomatization was achieved by treating this material with DDQ (2 g, 8.8 mmol) in benzene (150 ml) at room temperature for 18 h. The reaction mixture was filtered, and the filtrate was diluted with CH₂Cl₂ (50 ml) and washed with aqueous NaOH (100 ml). Evaporation of the dried filtrate gave a brownish solid which was subjected to column chromatography (silica; EtOAc-hexane, 30:70) to give **11** (1.25 g, 66%), m.p. 195–196 °C (methanol); δ_H (500 MHz; CDCl₃) 0.75 (1 H, d, J 10.5), 1.69 (1 H, d, J 10.5), 1.94 (2 H, s), 2.35 (2 H, s), 2.57 (2 H, AB q, J 12.4, 2 × 16-H), 2.58 (2 H, s), 2.92 (2 H, br s), 3.12 (3 H, s, 15-OCH₃), 3.25 (3 H, s, 15-OCH₃), 3.64 (2 H, s, 6-H, 13-H), 3.97 (6 H, s, 2 × OCH₃), 6.11 (2 H, t, J 2.1), 7.42 (2 H, m, aromatic) and 8.04 (2 H, m, aromatic) (Found: C, 78.6; H, 7.2. C₂₉H₃₂O₄ requires C, 78.35; H, 7.3%).

(1 α ,4 α ,4 α ,5 β ,5 β ,6 α ,13 α ,13 α β ,14 β ,14 α)-7,12,15,15-Tetramethoxy-1,2,3,4,4a,5,5a,6,13,13a,14,14a-dodecahydro-1,4:6,13-dimethanopentacene **12**.—A magnetically stirred mixture of **11** (1.0 g, 2.25 mmol), 10% Pd/C (100 mg) in ethyl acetate (200 ml) was hydrogenated at atmospheric pressure and 25 °C until no further uptake of hydrogen was observed. The mixture was

filtered and the filtrate evaporated to give **12** (1 g, 98%), m.p. 203–204 °C (ethyl acetate); δ_H (500 MHz; CDCl₃) 1.22 (1 H, d, J 11.0), 1.5–1.7 (5 H, m), 2.0–2.2 (5 H, m), 2.25 (1 H, d, J 11.0), 2.35 (4 H, br s), 3.28 (3 H, s, 15-OCH₃), 3.31 (3 H, s, 15-OCH₃), 3.59 (2 H, s, 6-H, 13-H), 3.97 (6 H, s, 2 × OCH₃), 7.41 (2 H, m, aromatic) and 8.03 (2 H, m, aromatic) (Found: C, 77.9; H, 7.5. C₂₉H₃₄O₄ requires C, 78.0; H, 7.7%).

(1 α ,4 α ,4 α ,5 β ,5 β ,6 α ,13 α ,13 α β ,14 β ,14 α)-7,12-Dimethoxy-1,2,3,4,4a,5,5a,6,13,13a,14,14a-dodecahydro-1,4:6,13-dimethanopentacene-15-one **13**.—A solution of **12** (0.85 g, 1.9 mmol) in THF (15 ml) and formic acid (10 ml) was stirred at room temperature for 18 h. Evaporation of the solvent under reduced pressure gave the ketone **13** (0.72 g, 94%), m.p. 240–241 °C (methanol); δ_H (500 MHz; CDCl₃) 1.39 (1 H, d, J 11.2), 1.66 (1 H, d, J 10.7), 1.76–1.78 (2 H, m), 1.91–1.95 (2 H, m), 2.02 (2 H, p, J 2.3), 2.07 (1 H, d, J 10.7), 2.15 (2 H, br s), 2.25 (1 H, d, J 11.2), 2.44 (2 H, br s), 2.56 (2 H, s), 3.62 (2 H, s, 6-H, 13-H), 3.97 (6 H, s, 2 × OCH₃), 7.43 (2 H, m, aromatic) and 8.04 (2 H, m, aromatic) (Found: C, 80.9; H, 7.1. C₂₇H₂₈O₃ requires C, 81.0; H, 7.05%).

(1 α ,4 α ,4 α ,5 β ,5 β ,6 α ,13 α ,13 α β ,14 β ,14 α)-7,12-Dimethoxy-1,2,3,4,4a,5,5a,6,13,13a,14,14a-dodecahydro-1,4:6,13-dimethanopentacene-15-ylidenepropanedinitrile **3**.—A solution of the ketone **13** (0.5 g, 1.25 mmol), malononitrile (0.2 g, 3.03 mmol), ammonium acetate (0.2 g, 2.6 mmol), and acetic acid (0.6 ml) in toluene (10 ml) was refluxed in a Dean-Stark apparatus for 24 h. The cooled reaction mixture was successively washed with saturated aqueous NaHCO₃ (50 ml) and water (50 ml). The dried organic extract was evaporated under reduced pressure to give **3** (0.52 g, 93%), m.p. 303–304 °C (ethyl acetate); δ_H (500 MHz; CDCl₃) 1.35 (1 H, d, J 11.5), 1.71 (3 H, br s + d, J 10.7), 1.94 (1 H, d, J 10.7), 2.01 (2 H, m), 2.09 (1 H, d, J 11.5), 2.14 (2 H, br s), 2.37 (2 H, br s), 2.58 (2 H, br s), 3.08 (2 H, t, J 2.2, 1-H, 4-H), 3.63 (2 H, s, 6-H, 13-H), 3.97 (6 H, s, 2 × OCH₃), 7.44 (2 H, m, aromatic), and 8.04 (2 H, m, aromatic); ν_{max} (Nujol)/cm⁻¹ 2240 (CN) (Found: C, 79.9; H, 6.2; N, 6.4. C₃₀H₂₈N₂O₂ requires C, 80.3; H, 6.3; N, 6.25%).

(1 α ,4 α ,4 α ,5 β ,5 β ,6 α ,13 α ,13 α β ,14 β ,14 α)-1,2,3,4,15,15-Hexachloro-7,12-dimethoxy-1,4,4a,5,5a,6,13,13a,14,14a-decahydro-1,4:6,13-dimethanopentacene **15**.—A solution of **8** (5.0 g, 15.7 mmol) and hexachlorocyclopentadiene **14** (4.5 g, 16.5 mmol) in xylene (20 ml) was refluxed for 24 h. Excess of methanol was added to the cooled reaction mixture and the resulting precipitate was collected and dried to give **15** (8.7 g, 94%), m.p. > 316 °C (methanol); δ_H (500 MHz; CDCl₃) 1.18 (1 H, d, J 12.2), 1.69 (1 H, d, J 12.2), 1.76 (1 H, d, J 11.0), 2.16 (2 H, d, J 2.6), 2.20 (1 H, d, J 11.0), 2.65 (2 H, br s), 3.05 (2 H, br s), 3.57 (2 H, s, 6-H, 13-H), 3.98 (6 H, s, 2 × OCH₃), 7.45 (2 H, m, aromatic) and 8.04 (2 H, m, aromatic) (Found: C, 54.6; H, 3.6. C₂₇H₂₂Cl₆O₂ requires C, 54.9; H, 3.75%).

(1 α ,4 α ,4 α ,5 β ,5 β ,6 α ,13 α ,13 α β ,14 β ,14 α)-7,12-Dimethoxy-1,4,4a,5,5a,6,13,13a,14,14a-decahydro-1,4:6,13-dimethanopentacene **16**.—Sodium pieces (3.0 g, 130 mmol) were added to a refluxing solution of **15** (3.0 g, 4.6 mmol) in THF (100 ml) and propan-2-ol (300 ml). Using an identical work-up procedure to that employed for the synthesis of **11**, gave a solid (1.6 g) whose ¹H NMR spectrum revealed the presence of **16**, together with reduced aromatic compounds. Rearomatization of this mixture with DDQ (2 g, 8.8 mmol) in benzene (150 ml), using the same technique described above for the synthesis of **11**, gave **16** (1.2 g, 83%), m.p. 180–181 °C (light petroleum-ethyl acetate); δ_H (500 MHz; CDCl₃) 0.65 (1 H, d, J 10.5), 1.23 (1 H, d, J 7.7), 1.38 (1 H, d, of t, J 1.8, 7.7), 1.65 (1 H, d, J 10.5), 1.92 (2 H, t, J 1.5), 2.34 (2 H, br s), 2.45 (1 H, d, J 10.3), 2.46 (2 H, s), 2.51

(1 H, d, *J* 10.3), 2.89 (2 H, t, *J* 1.7, 1-H, 4-H), 3.63 (2 H, s, 6-H, 13-H), 3.97 (6 H, s, 2 × OCH₃), 6.05 (2 H, t, *J* 2.0, 2-H, 3-H), 7.42 (2 H, m, aromatic) and 8.04 (2 H, m, aromatic) (Found: C, 84.2; H, 7.4. C₂₇H₂₈O₂ requires C, 84.3; H, 7.3%).

(1 α ,4 α ,4 $\alpha\alpha$,5 β ,5 $\alpha\beta$,6 α ,6 $\alpha\alpha$,7 β ,14 β ,14 $\alpha\alpha$,15 α ,15 $\alpha\beta$,16 β ,16 $\alpha\alpha$)-1,2,3,4-Tetrachloro-8,13,17,17-tetramethoxy-1,4,4a,5,5a,6,6a,7,14,14a,15,15a,16,16a-tetradecahydro-1,4:5,16:6,15:7,14-tetramethanohexacene **17**.—A mixture of **16** (1.2 g, 3.12 mmol) and tetrachlorodimethoxycyclopentadiene **9** (1.0 g, 3.79 mmol) in xylene (20 ml) was refluxed for 2 days. Using the same work-up procedure to that employed for the synthesis of **10** gave **17** (1.9 g, 93%), m.p. 244–246 °C (methanol); δ_{H} (500 MHz; CDCl₃) 0.96 (1 H, d, *J* 11.6), 1.21 (1 H, d, *J* 11.6), 1.55 (1 H, d, *J* 13.4), 1.62 (1 H, d, *J* 10.4), 2.03 (1 H, d, *J* 13.4), 2.06 (2 H, br s), 2.16 (1 H, d, *J* 10.4), 2.26 (2 H, br s), 2.46 (4 H, br s), 2.79 (2 H, s), 3.52 (3 H, s, 17-OCH₃), 3.57 (2 H, s, 7-H, 14-H), 3.58 (3 H, s, 17-OCH₃), 3.97 (6 H, s, 2 × OCH₃), 7.42 (2 H, m, aromatic) and 8.03 (2 H, m, aromatic) (Found: C, 62.8; H, 5.1. C₃₄H₃₄Cl₄O₄ requires C, 63.0; H, 5.3%).

(1 α ,4 α ,4 $\alpha\alpha$,5 β ,5 $\alpha\beta$,6 α ,6 $\alpha\alpha$,7 β ,14 β ,14 $\alpha\alpha$,15 α ,15 $\alpha\beta$,16 β ,16 $\alpha\alpha$)-8,13,17,17-Tetramethoxy-1,4,4a,5,5a,6,6a,7,14,14a,15,15a,16,16a-tetradecahydro-1,4:5,16:6,15:7,14-tetramethanohexacene **18**.—Reductive dechlorination of **17** (1.5 g, 2.31 mmol) with sodium pieces (4.0 g, 174 mmol) in refluxing THF (50 ml) and propan-2-ol (150 ml), using the same procedure to that employed for the synthesis of **11** gave, after aromatization with DDQ (1.0 g, 8.8 mmol) and subsequent column chromatography (silica; EtOAc–hexane, 30:70), crude **18** 0.95 g, 81%), m.p. 251–253 °C (light petroleum–ethyl acetate); δ_{H} (500 MHz; CDCl₃) 0.62 (1 H, d, *J* 10.2), 1.15 (1 H, d, *J* 11.1), 1.57 (1 H, d, *J* 10.6), 2.02 (2 H, t, *J* 1.7), 2.09 (2 H, s), 2.20 (1 H, d, *J* 10.2), 2.25 (2 H, br s), 2.27 (1 H, d, *J* 11.1), 2.39 (2 H, br s), 2.45 (2 H, br s), 2.50 (1 H, d, *J* 10.6), 2.84 (2 H, t, *J* 2.1), 3.08 (3 H, s, 17-OCH₃), 3.18 (3 H, s, 17-OCH₃), 3.55 (2 H, br s, 7-H, 14-H), 3.97 (6 H, s, 2 × OCH₃), 6.09 (2 H, t, *J* 2.4), 7.43 (2 H, m, aromatic) and 8.04 (2 H, m, aromatic) (Found: C, 80.1; H, 7.6. C₃₄H₃₈O₄ requires C, 80.0; H, 7.5%).

(1 α ,4 α ,4 $\alpha\alpha$,5 β ,5 $\alpha\beta$,6 α ,6 $\alpha\alpha$,7 β ,14 β ,14 $\alpha\alpha$,15 α ,15 $\alpha\beta$,16 β ,16 $\alpha\alpha$)-8,13,17,17-Tetramethoxy-1,2,3,4,4a,5,5a,6,6a,7,14,14a,15,15a,16,16a-hexadecahydro-1,4:5,16:6,15:7,14-tetramethanohexacene **19**.—A magnetically stirred mixture of **18** (0.3 g, 0.59 mmol) and 10% Pd/C (50 mg) in ethyl acetate (150 ml) was hydrogenated at atmospheric pressure and 25 °C until no further uptake of hydrogen was observed. The mixture was filtered and the filtrate evaporated to give **19** (0.3 g, 99%), m.p. 264–265 °C (light petroleum–ethyl acetate); δ_{H} (500 MHz; CDCl₃) 1.07–1.11 (2 H, m), 1.56–1.62 (3 H, m), 1.92 (1 H, d, *J* 11.1), 1.99–2.04 (6 H, m), 2.21–2.24 (8 H, m), 2.34 (2 H, s), 3.23 (3 H, s, 17-OCH₃), 3.24 (3 H, s, 17-OCH₃), 3.56 (2 H, br s, 7-H, 14-H), 3.97 (6 H, s, 2 × OCH₃), 7.41 (2 H, m, aromatic) and 8.03 (2 H, m, aromatic) (Found: C, 79.7; H, 8.0. C₃₄H₄₀O₄ requires C, 79.65; H, 7.9%).

(1 α ,4 α ,4 $\alpha\alpha$,5 β ,5 $\alpha\beta$,6 α ,6 $\alpha\alpha$,7 β ,14 β ,14 $\alpha\alpha$,15 α ,15 $\alpha\beta$,16 β ,16 $\alpha\alpha$)-8,13-Dimethoxy-1,2,3,4,4a,5,5a,6,6a,7,14,14a,15,15a,16,16a-hexadecahydro-1,4:5,16:6,15:7,14-tetramethanohexacene-17-one **20**.—A solution of **19** (295 mg, 0.58 mmol) in THF (10 ml) and formic acid (20 ml) was stirred at room temperature for ca. 18 h. Evaporation of the solvent under reduced pressure gave the ketone **20** (258 mg, 96%), m.p. 305–306 °C (methanol); δ_{H} (500 MHz; CDCl₃) 1.11 (1 H, d, *J* 11.3), 1.26 (1 H, d, *J* 11.1), 1.60 (1 H, d, *J* 10.5), 1.73 (3 H, m), 1.91–1.95 (4 H, m), 2.02 (2 H, t, *J* 1.7), 2.17 (2 H, near superposition of two doublets, *J* ca. 11–12 Hz), 2.30 (4 H, br s), 2.37 (2 H, br s), 2.45 (2 H, br s), 3.57 (2 H, br s), 3.96 (6 H, s, 2 × OCH₃), 7.42 (2 H, m, aromatic) and 8.04 (2

H, m, aromatic) (Found: C, 82.7; H, 7.6. C₃₂H₃₄O₃ requires C, 82.4; H, 7.3%).

(1 α ,4 α ,4 $\alpha\alpha$,5 β ,5 $\alpha\beta$,6 α ,6 $\alpha\alpha$,7 β ,14 β ,14 $\alpha\alpha$,15 α ,15 $\alpha\beta$,16 β ,16 $\alpha\alpha$)-8,13-Dimethoxy-1,2,3,4,4a,5,5a,6,6a,7,14,14a,15,15a,16,16a-hexadecahydro-1,4:5,16:6,15:7,14-tetramethanohexacene-17-ylidenepropanedinitrile **4**.—A solution of the ketone **20** (225 mg, 0.482 mmol), malononitrile (0.1 g, 1.57 mmol), ammonium acetate (100 mg, 1.3 mmol) and acetic acid (0.3 ml) in toluene (10 ml) was refluxed in a Dean–Stark apparatus for 24 h. The cooled reaction mixture was successively washed with saturated aqueous NaHCO₃ (40 ml) and water (40 ml). The dried organic extract was evaporated under reduced pressure to give **4** (200 mg, 81%), m.p. 263–264 °C (light petroleum–ethyl acetate); δ_{H} (500 MHz; CDCl₃) 1.15 (1 H, d, *J* 12.3), 1.23 (1 H, d, *J* 11.3), 1.58 (1 H, d, *J* 11.3), 1.61 (1 H, d, *J* 10.5), 1.66 (1 H, d, *J* 9.2), 1.98–2.02 (4 H, m), 2.04 (2 H, br s), 2.15 (1 H, d, *J* 10.5), 2.23 (2 H, br s), 2.29 (2 H, br s), 2.37 (2 H, br s), 2.47 (2 H, br s), 3.00 (2 H, t, *J* 2.2), 3.57 (2 H, s), 3.97 (6 H, s, 2 × OCH₃), 7.42 (2 H, m, aromatic) and 8.04 (2 H, m, aromatic) (Found: C, 81.5; H, 6.6; N, 5.5. C₃₅H₃₄N₂O₂ requires C, 81.7; H, 6.7; N, 5.4%).

(2 $\alpha\alpha$,3 β ,3 $\alpha\alpha$,3 $\beta\beta$,3 $\alpha\alpha$,4 β ,11 β ,11 $\alpha\alpha$,11 $\beta\beta$,11 $\alpha\alpha$,12 β ,12 $\alpha\alpha$)-2,2-Dichloro-5,10-dimethoxy-3b,11b-dimethyl-2a,3,3a,3c,4,11,11a,11c,12,12a-decahydro-3,12:4,11-dimethanocyclobuta[1'',2'':4'',5'']benzo[1'',2'':3',4']cyclobuta[1,2-b]anthracen-1-one **22**.—To a stirred mixture of compound **21**²¹ (4.96 g, 12.5 mmol) and zinc–copper couple (5.9 g, 90 mmol)²⁶ in anhydrous THF (160 ml), in a nitrogen atmosphere was slowly added dropwise trichloroacetyl chloride (4 ml, 35 mmol) in anhydrous THF (80 ml). The reaction mixture was stirred for 10 min whilst being irradiated with ultrasound. Addition of trichloroacetyl chloride took 15 h, after which time stirring was continued for a further 3 h. The reaction mixture was filtered through a Celite pad and evaporated to 100 ml. Light petroleum (b.p. 40–60 °C; 180 ml) was added and the solution was passed down a column of silica to remove the zinc salts and intractable tars. Evaporation of the eluant under reduced pressure gave the title compound **22** (4.50 g, 71%), m.p. 257–259 °C; δ_{H} (500 MHz; CDCl₃) 0.94 (3 H, s, 3b-CH₃), 0.99 (3 H, s, 11b-CH₃), 1.65 (1 H, br d, *J* 12, 13- or 14-H), 1.72 (1 H, br d, *J* 9.8, 13- or 14-H), 1.78 (1 H, br d, *J* 12, 13- or 14-H), 1.91 (1 H, br d, *J* 9.8, 13- or 14-H), 2.01 (2 H, br s, 3c- and 11a-H), 2.18 (1 H, br d, *J* 5.8, 3a-H), 2.20 (1 H, br d, *J* 5.8, 11c-H), 2.62 (1 H, br s, 3-H), 2.68 (1 H, br d, *J* 4.7, 2a-H), 2.69 (1 H, br s, 12-H), 3.48 (1 H, br d, *J* 4.7, 12a-H), 3.67 (1 H, br s, 4-H), 3.68 (1 H, br s, 11-H), 3.99 (3 H, s, 5-OCH₃), 4.00 (3 H, s, 10-OCH₃), 7.45 (2 H, m, aromatic) and 8.09 (2 H, m, aromatic); δ_{C} (122.725 MHz; CDCl₃) 9.45 (3b-CH₃), 9.52 (11b-CH₃), 31.50 (CH₂), 38.15 (CH), 39.41 (CH), 40.46 (CH), 42.68 (CH₂), 44.53 (3b-C), 44.59 (11b-C), 49.65 (CH), 50.42 (CH), 50.52 (CH), 50.70 (CH), 53.05 (2a-CH), 61.88 (2 × OCH₃), 64.17 (12a-CH), 87.46 (2-C), 122.00 (aromatic CH), 125.07 (aromatic CH), 127.85 (aromatic C), 134.75 (aromatic C), 134.81 (aromatic C), 144.30 (aromatic C) and 197.05 (1-C); ν_{max} (KBr)/cm⁻¹ 1808 (C=O) (Found: C, 70.5; H, 5.9. C₃₀H₃₀O₃Cl₂ requires C, 70.7; H, 5.9).

(3 $\alpha\alpha$,4 β ,4 $\alpha\alpha$,4 $\beta\beta$,4 $\alpha\alpha$,5 β ,12 β ,12 $\alpha\alpha$,12 $\beta\beta$,12 $\alpha\alpha$,13 β ,13 $\alpha\alpha$)-6,11-Dimethoxy-4b,12b-dimethyl-1,3,3a,4,4a,4c,5,12,12a,12c,13,13a-dodecahydro-4,13,5,12-dimethano-2H-indeno[5'',6'':3',4']cyclobuta[1'',2'':3,4]cyclobuta[1,2-b]anthracen-2-one **24**.—A solution of *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (5.3 g, 25 mmol) in diethyl ether (50 ml) was added dropwise with stirring, over 25 min, to a solution of potassium hydroxide (5.00 g) in distilled water (5 ml) and ethanol (25 ml), maintained at 62 °C. The generated diazomethane was simultaneously distilled into a foil-covered flask, containing a solution of compound **22** (2.0 g, 3.92

mmol) in anhydrous THF (50 ml) at 0 °C. After addition of diazomethane was complete, additional diethyl ether (20 ml) was added to the receiving flask and the latter was stoppered and left at room temperature for 20 h. After addition of acetic acid (2 ml), to destroy excess of diazomethane, the reaction mixture was successively washed with water (100 ml), aqueous NaHCO₃ (100 ml) and brine (100 ml). The dried (Na₂SO₄) solution was evaporated under reduced pressure to give an unstable yellow solid (2.0 g), presumed to be compound **23** [ν_{\max} (thin film) 1765 cm⁻¹], which was not purified further.

A vigorously stirred mixture of compound **23** (2.12 g, 4.03 mmol) and zinc powder (2.3 g, 35 mmol) in glacial acetic acid (14 ml) was refluxed for 19 h. The cooled reaction mixture was filtered. Dichloromethane (100 ml) was added to the filtrate and the resulting solution was extracted successively with water (6 × 100 ml), saturated aqueous NaHCO₃ (100 ml), and saturated brine (100 ml). The dried organic extract was evaporated to give a solid (1.85 g). Column chromatography (silica; benzene–diethyl ether; 90:10) gave the title compound **24** (0.94 g, 51%), (benzene–ethanol), m.p. 206–207 °C; δ_{H} (500 MHz; CDCl₃) 0.93 (6 H, s, 2 × CH₃), 1.32 (1 H, br d, *J* 11.3, 14- or 15-H), 1.57 (1 H, br d, *J* 11.3, 14- or 15-H), 1.69 (1 H, d, *J* 8.5, 14- or 15-H), 1.96 (3 H, multiplet consisting of the fourth methylene bridge proton and the 1- and 3- *exo* methylene protons), 1.99 (2 H, s), 2.03 (2 H, s), 2.15 (2 H, m), 2.20 (2 H, s), 2.46 (2 H, m, 1- and 3- *endo* H), 3.66 (2 H, s, 5- and 12-H), 3.99 (6 H, s, 2 × OCH₃), 7.44 (2 H, m, aromatic) and 8.08 (2 H, m, aromatic); δ_{C} (122.725 MHz; CDCl₃) 9.60 (2 × CH₃), 29.18 (CH₂), 40.48 (CH), 41.62 (CH), 42.73 (CH₂), 43.24 (CH), 43.43 (CH₂), 44.08 (4b- and 12b-C), 50.70 (CH), 51.71 (CH), 61.89 (2 × OCH₃), 121.88 (aromatic CH), 124.98 (aromatic CH), 127.83 (aromatic C), 135.19 (aromatic C), 144.25 (aromatic C) and 221.39 (2-C); ν_{\max} (KBr)/cm⁻¹ 1741 (C=O) (Found: C, 81.6; H, 7.5. C₃₁H₃₄O₃ requires C, 81.9; H, 7.5%).

(3 α ,4 β ,4 α ,4 β ,4 α ,5 β ,12 β ,12 α ,12 β ,12 α ,13 β ,13 α)-6,11-Dimethoxy-4b,12b-dimethyl-1,3,3a,4,4a,4c,5,12,12a,12c,-13,13a-dodecahydro-4,13,5,12-dimethano-2H-indeno[5',6'':3',4']cyclobuta[1',2':3,4]cyclobuta[1,2-b]anthracen-2-ylidene-propanedinitrile **5**.—A solution of the ketone **24** (280 mg, 0.62 mmol), malononitrile (0.1 g, 1.57 mmol), ammonium acetate (220 mg) and acetic acid (0.5 ml) in toluene (10 ml) was refluxed in a Dean–Stark apparatus for 24 h. The cooled reaction mixture was successively washed with saturated aqueous NaHCO₃ (40 ml) and water (40 ml). The dried organic extract was evaporated under reduced pressure to give compound **25** (120 mg, 40%), m.p. 242–244 °C (benzene–ethanol); δ_{H} (500 MHz; CDCl₃) 0.94 (6 H, s, 2 × CH₃), 1.16 (1 H, br d, *J* 9.2, 14- or 15-H), 1.58 (1 H, br d, *J* 9.2, 14- or 15-H), 1.71 (1 H, d, *J* 9.7, 14- or 15-H), 1.92 (1 H, d, *J* 9.7, 14- or 15-H), 1.99 (2 H, s), 2.05 (2 H, s), 2.19 (2 H, s), 2.20 (2 H, s), 2.58 (2 H, m, 1- and 3- *exo* H) 3.06 (2 H, m, 1- and 3- *endo* H), 3.67 (2 H, s, 5- and 12-H), 3.99 (6 H, s, 2 × OCH₃), 7.45 (2 H, m, aromatic) and 8.08 (2 H, m, aromatic); δ_{C} (122.725 MHz; CDCl₃) 9.62, 29.43, 40.51, 41.34, 42.72, 42.88, 44.08, 45.98, 50.72, 51.26, 61.92, 79.95, 111.84, 122.03, 125.06, 127.89, 135.08, 144.32, 193.08; ν_{\max} (KBr)/cm⁻¹ 2236 (CN), 1612 (Found: C, 81.5; H, 7.0; N, 5.2. C₃₄H₃₄O₂N₂ requires C, 81.3; H, 6.9; N, 5.5%).

X-Ray Crystallographic Determination.—Crystal data for compound **3**. C₃₀H₂₈N₂O₂, M = 448.6, monoclinic, space group P2₁/c, *a* = 9.157(4), *b* = 9.271(2), *c* = 29.960(14) Å, β = 107.65(1)°, *V* = 2424(2) Å³, *D_c* = 1.23, *D_m* = 1.22 g cm⁻³, *Z* = 4, μ_{Mo} = 0.72 cm⁻¹. Crystal from ethyl acetate, size 0.14 × 0.15 × 0.16 mm, $2\theta_{\max}$ = 46°, max. and min. transmission factors 0.98 and 0.99. The number of reflections was 1934 considered observed out of 3362 unique data, with *R_{merge}* =

0.011 for 46 pairs of equivalent *hk0* reflections. Final residuals *R*, *R_w* were 0.040, 0.050.

Crystal data for compound 4. C₃₅H₃₄N₂O₂·CH₃COOC₂H₅, M = 602.8, monoclinic, space group P2₁/c, *a* = 11.018(5), *b* = 19.679(3), *c* = 17.729(8) Å, β = 123.81(2)°, *V* = 3194(2) Å³, *D_c* = 1.25, *D_m* = 1.26 g cm⁻³, *Z* = 4, μ_{Mo} = 0.75 cm⁻¹. Crystal from ethyl acetate, size 0.14 × 0.15 × 0.17 mm, $2\theta_{\max}$ = 46°, max. and min. transmission factors 0.98 and 0.99. Standard reflection declined by ca. 10% during measurement and correction was applied during processing. The number of reflections was 2088 considered observed out of 4421 unique data, with *R_{merge}* = 0.018 for 83 pairs of equivalent *hk0* reflections. Final residuals *R*, *R_w* were 0.037, 0.044.

Crystal data for compound 5. C₃₄H₃₄N₂O₂·(CH₃CN)_{1/2}, M = 523.2, monoclinic, space group C2/c, *a* = 21.241(4), *b* = 16.441(1), *c* = 16.850(4) Å, β = 105.74(1)°, *V* = 5661(1) Å³, *D_c* = 1.23, *D_m* = 1.23 g cm⁻³, *Z* = 8, μ_{Cu} = 5.61 cm⁻¹. Crystal from acetonitrile, size 0.18 × 0.19 × 0.39 mm, $2\theta_{\max}$ = 120°, max. and min. transmission factors 0.85 and 0.91. Standard reflection declined by ca. 30% during measurement and correction was applied during processing. The number of reflections was 3325 considered observed out of 4204 unique data, with *R_{merge}* = 0.065 for 138 pairs of equivalent *hk0* reflections. Final residuals *R*, *R_w* were 0.059, 0.082, the high values probably due to the poor quality and unstable crystal.

Structure Determination.—Reflection data were measured with an Enraf–Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite monochromatized molybdenum radiation (λ = 0.710 69 Å) for **3** and **4** and nickel-filtered copper radiation (λ = 1.540 56 Å) for **5**. Data were corrected for absorption. Reflections with *I* > 3 σ (*I*) were considered observed. The structures were determined by direct phasing and Fourier methods. Hydrogen atoms were located in difference Fouriers for **3** and **4**, included in calculated positions for **5**, and were assigned thermal parameters equal to those of the atom to which bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full matrix least squares. The solvent molecules in **4** and **5** were disordered. In the case of **5** the disordered acetonitrile was not resolved, probably due to the short C–N distance and proximity to the 2-fold axis, and the Fourier transform of the electron density in its region was used as its contribution to the calculated structure factor. The ethyl acetate in **4** had recognizable two-fold disorder about its approximate centre, with the ethyl carbons of one orientation superimposed on the acetyl carbons of the other, and with the oxygen atoms resolved. The residual electron density in the region of the solvent after using this model was included as for **5**. Reflection weights used were 1/ $\sigma^2(F_0)$, with $\sigma(F_0)$ being derived from $\sigma(I_0) = [\sigma^2(I_0) + (0.04I_0)^2]^{1/2}$. The weighted residual is defined as $R_w = (\sum \Delta^2 / \sum w F_0^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography.³⁵ Structure solution was by MULTAN 80³⁶ and refinement used BLOCKLS, a local version of ORFLS.³⁷ ORTEP-II³⁸ running on a Macintosh IICx was used for the structural diagrams, and an IBM 3090 computer was used for calculations.

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