

## Synthesis of Rigidly Linked Donor–Acceptor Systems Designed to Test the Effect of Orbital Symmetry on the Dynamics of Long-range Intramolecular Electron Transfer Processes

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The synthesis of the novel rigid bichromophoric systems, **3**, **4**, **6**, together with the monochromophoric system, **5**, is described. Such systems are characterized in terms of each possessing a polynorbornyl bridge, one end of which is terminally fused to a bicyclo[2.2.2]octene unit. Deacetalization of the dimethoxyacetal, **7**, with formic acid gave the ketone, **9**, which readily underwent thermal decarbonylation to give the diene **11**. Diels–Alder reaction of **11** with dicyanoacetylene or dimethylacetylene dicarboxylate readily gave the adducts, **13** and **15**, respectively, resulting from *endo*-attack by the dienophile on the diene. Catalytic hydrogenation of **13** and **15** gave **3** and **6** respectively. In a similar manner, **4** and **5** were synthesized starting from the dimethoxyacetals, **8** and **19a**, respectively. Single crystal X-ray structures of **3** and **6** were determined and are consistent with the structures shown.

Recently, a great deal of experimental evidence has been accumulated demonstrating that both thermal and photo-induced electron transfer between a donor and acceptor can take place over distances that are considerably greater than the sum of the van der Waals radii of the donor and acceptor groups. These studies are providing a detailed 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.<sup>1</sup> In this respect, studies on intramolecular electron transfer play a pivotal role because the attachment of donor and acceptor groups to a rigid hydrocarbon bridge enables the unambiguous delineation of the dependence of electron transfer dynamics on donor–acceptor distance and orientation to be determined.<sup>1–25</sup> A variety of hydrocarbon bridges, covalently linked to the donor and acceptor groups have been used in such studies, including polynorbornyl (norbornylogous) bridges,<sup>2–16</sup> cyclohexane, decalin and steroid systems,<sup>17–22</sup> oligobicyclo[2.2.2]octanes,<sup>23</sup> triptycenes<sup>24</sup> and polyspirocyclobutanes.<sup>25</sup>

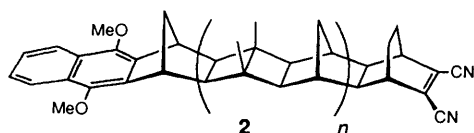
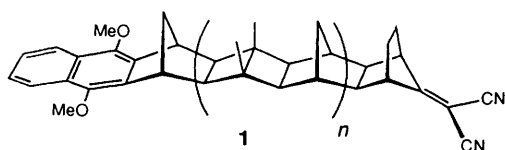
The norbornylogous bridge systems, synthesized by our group, have proven to be particularly useful in the study of long-range intramolecular electron transfer processes, on account of their total rigidity and symmetry. Thus, we have synthesized several members of the organic donor–acceptor compounds, **1**, in which the donor–acceptor separation ranges, from *ca.* 6 Å, for

the 4-bond system, **1** ( $n = 0$ ), to *ca.* 14 Å, for the 12-bond system, **1** ( $n = 2$ ). Photoinduced and pulse radiolysis electron transfer studies on **1** have revealed that intramolecular electron transfer can take place extremely rapidly over large distances. For example, the rate of photoinduced electron transfer in the 12-bond system **1** ( $n = 2$ ), occurring from the locally electronically excited state of the dimethoxynaphthalene donor (D) to the dicyanoethene acceptor (A), is about  $10^9$  s<sup>-1</sup>.<sup>5</sup>

Recently, Reimers and Hush drew attention to the likelihood that photoinduced electron transfer in **1** is actually electronically forbidden in that the reactant state (involving locally electronically excited dimethoxynaphthalene) and the resulting charge separated product state, D<sup>+</sup>–A<sup>-</sup>, in **1** have opposite symmetries.<sup>26</sup> This would mean that the coupling matrix element for the electron transfer process would be zero and that the electron transfer rate should likewise be zero. However, because the observed rates of photoinduced electron transfer in **1** are, in fact, extremely rapid, it was suggested that although the electron transfer was electronically forbidden, it was vibronically allowed.<sup>26</sup>

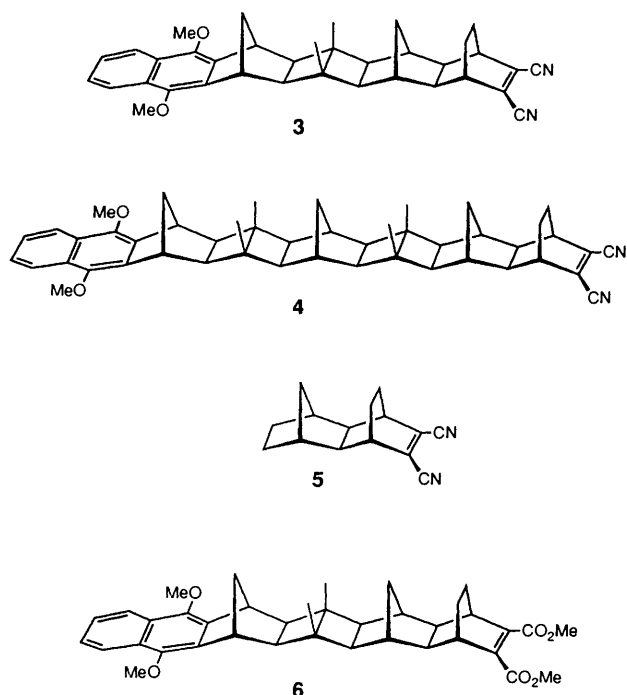
One way of exploring this problem experimentally is to compare the rates of the so-called electronically forbidden, but vibronically allowed photoinduced electron transfer for the series, **1**, with a similar series of molecules but in which the electron transfer is known to be electronically allowed. One such possible series of bichromophoric molecules is shown by **2**, in which the double bond of the dicyanoethene acceptor has been rotated 90° with respect to the corresponding double bond in **1**. This rotation makes the symmetry of the charge separated product state, D<sup>+</sup>–A<sup>-</sup>, in **2** the same as that of the electronically excited reactant state.<sup>27</sup>

In this paper, we describe the synthesis of two members of this new series of molecules, **2**, namely the 8-bond and 12-bond compounds, **3** and **4** respectively, together with the model system, **5**. The synthesis of the 8-bond diester, **6**, is also reported.



### Results and Discussion

The synthetic strategy is outlined in Scheme 1. The heart of Scheme 1 is the synthesis of the dienes, **11** and **12**, and their subsequent Diels–Alder reactions with either dicyanoacetylene or dimethylacetylene dicarboxylate (DMAD). It was expected that approach of dienophile to either diene should occur from the *endo* face of the diene, rather than from the *exo* face, to give



the desired diastereomer, *e.g.* **13**, since this approach involves the least steric congestion in the ensuing transition structure. This is demonstrated by the profile, **16**, of the molecular mechanics-optimized structure of the methanonaphthalene, **20**, in which it is obvious that *exo* approach of the dienophile results in severe steric crowding between the approaching dienophile and the methylene bridge of the norbornyl unit.

The dienes should be accessible from the ketones, **9** and **10**, through thermal cheletropic loss of carbon monoxide, since norborn-2-en-7-ones are known to be prone to this reaction.<sup>28</sup> This expectation was borne out. Thus, deacetalization of the known<sup>5,15</sup> dimethoxyacetals, **7** and **8**, using formic acid (room temperature), smoothly gave the respective ketones, **9** and **10** in high yields. Ketones **9** and **10** are thermally labile and readily underwent cheletropic loss of CO in refluxing toluene, to give the dienes, **11** and **12**, respectively.

Diels–Alder reaction of dienes **11** and **12** with dicyanoacetylene<sup>29</sup> was carried out at  $-5-0^{\circ}\text{C}$  and, in each case, led to the formation of a single adduct, **13** and **14**, respectively. These

adducts were unstable with respect to thermal retro-Diels–Alder reaction,<sup>30</sup> leading to the formation of significant amounts of the appropriate ene compound, **17a** (in the case of **13**) or **17b** (in the case of **14**), and 1,2-dicyanobenzene, **18a**, even at  $40^{\circ}\text{C}$ . Consequently, adducts **13** and **14** were not purified but were immediately subjected to controlled catalytic hydrogenation (room temperature) to give good yields of the desired monohydrogenated compounds, **3** and **4**, respectively.

Diels–Alder reaction of the diene, **11**, with the less reactive dienophile, DMAD, required heating at  $40-50^{\circ}\text{C}$ , and, consequently, the resulting adduct, **15**, was contaminated with small amounts of **17a** and dimethylphthalate, **18b**, resulting from the retro-Diels–Alder reaction. Controlled catalytic hydrogenation of the crude adduct, **15**, gave **6**. In a similar fashion, **5** was synthesized from the dimethoxyacetal, **19a**, *via* **19b-21**.

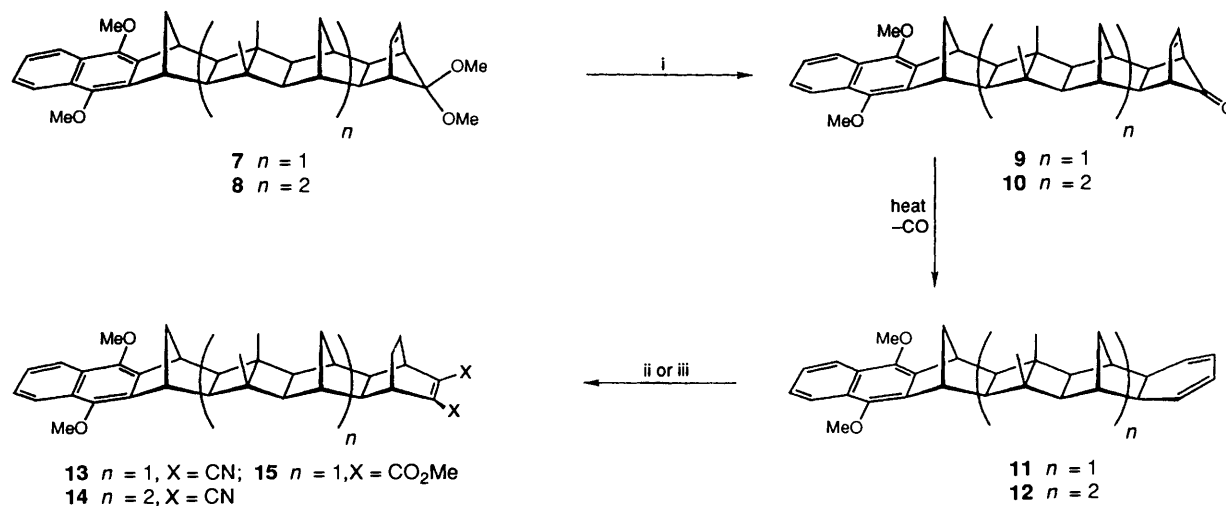
X-ray crystal structures of **3** and **6** were determined (see Experimental section for details). Fractional coordinates for the non-hydrogen atoms are given in Tables 1 and 2. ORTEP drawings for **3** and **6** are given in Figs. 1 and 2, respectively. In these figures, the hydrogen atoms have been omitted for clarity. Tables of final fractional coordinates for all atoms (including hydrogen) and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

The results of the two X-ray crystal structure determinations are consistent with the expected stereochemistry and connectivities. The important conclusion to be drawn from these structures is that the Diels–Alder addition of both dicyanoacetylene and DMAD to **11** did, indeed occur from the *endo* side of the diene.

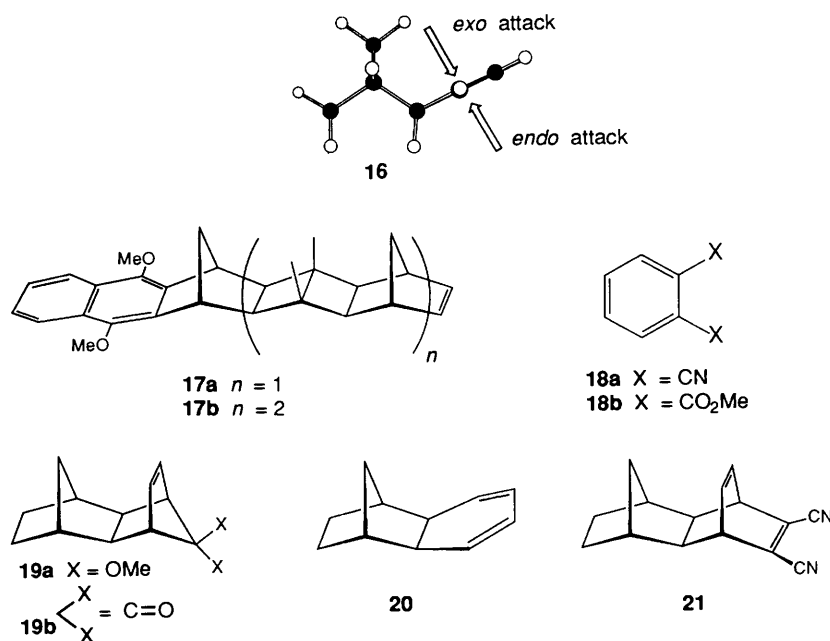
In conclusion, the cheletropic loss of CO from norbornenones and subsequent Diels–Alder reaction with the resulting dienes, provide an efficient route to rigid polynorbornyl bridges terminally fused to a substituted bicyclo[2.2.2]octene unit. This methodology will enable the synthesis of a variety of novel donor–bridge–acceptor systems for the study of long-range intramolecular electron transfer processes. A preliminary account of the dynamics of photoinduced electron transfer in **3** and **6** has recently appeared elsewhere.<sup>27</sup>

## Experimental

*General.*—M.p.s were taken on a Koffler hot-stage and are uncorrected.  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker AM-500 spectrometer operating at 500 and 122.725 MHz, respectively. All NMR spectra were



**Scheme 1** Reagents: i,  $\text{HCO}_2\text{H}-\text{THF}$ ; ii, dicyanoacetylene; iii, DMAD

**Table 1** Non-hydrogen atomic parameters for **3**, esd in parentheses

|       | <i>x</i>  | <i>y</i>  | <i>z</i>  |
|-------|-----------|-----------|-----------|
| O(1)  | 0.8892(2) | 0.9896(2) | 0.5188(2) |
| O(2)  | 0.6232(2) | 0.7236(2) | 0.3550(1) |
| N(1)  | 0.0826(3) | 0.7097(3) | 0.8847(2) |
| N(2)  | 0.2984(3) | 0.8602(3) | 1.0330(2) |
| C(1)  | 0.3453(3) | 0.5831(3) | 0.8540(2) |
| C(2)  | 0.4058(3) | 0.5163(3) | 0.9125(2) |
| C(3)  | 0.4866(3) | 0.5803(3) | 0.9614(2) |
| C(4)  | 0.4815(3) | 0.6903(3) | 0.9344(2) |
| C(5)  | 0.5087(2) | 0.7034(2) | 0.8479(1) |
| C(6)  | 0.6239(2) | 0.6706(2) | 0.8190(2) |
| C(7)  | 0.6345(2) | 0.7143(2) | 0.7383(1) |
| C(8)  | 0.7361(2) | 0.6827(2) | 0.6890(2) |
| C(9)  | 0.7442(2) | 0.7552(2) | 0.6201(2) |
| C(10) | 0.8543(3) | 0.7581(2) | 0.5725(2) |
| C(11) | 0.8204(2) | 0.8183(2) | 0.5020(2) |
| C(12) | 0.8312(3) | 0.9171(2) | 0.4812(2) |
| C(13) | 0.7724(3) | 0.9529(2) | 0.4159(2) |
| C(14) | 0.7745(3) | 1.0560(3) | 0.3957(2) |
| C(15) | 0.7114(4) | 1.0909(3) | 0.3375(2) |
| C(16) | 0.6440(4) | 1.0270(3) | 0.2950(2) |
| C(17) | 0.6413(3) | 0.9262(3) | 0.3110(2) |
| C(18) | 0.7038(3) | 0.8874(2) | 0.3729(2) |
| C(19) | 0.6953(2) | 0.7855(2) | 0.3956(2) |
| C(20) | 0.7504(2) | 0.7535(2) | 0.4583(2) |
| C(21) | 0.7417(3) | 0.6565(2) | 0.5025(2) |
| C(22) | 0.6661(2) | 0.6861(2) | 0.5710(2) |
| C(23) | 0.6543(3) | 0.6127(2) | 0.6392(2) |
| C(24) | 0.5543(2) | 0.6470(2) | 0.6897(2) |
| C(25) | 0.5072(3) | 0.5731(2) | 0.7495(2) |
| C(26) | 0.4279(3) | 0.6374(2) | 0.7991(2) |
| C(27) | 0.2904(3) | 0.6666(3) | 0.8989(2) |
| C(28) | 0.3605(3) | 0.7199(3) | 0.9421(2) |
| C(29) | 0.6090(3) | 0.5588(2) | 0.8019(2) |
| C(30) | 0.8437(3) | 0.6536(3) | 0.7284(2) |
| C(31) | 0.6658(3) | 0.5013(2) | 0.6226(2) |
| C(32) | 0.8579(3) | 0.6525(2) | 0.5383(2) |
| C(33) | 0.1731(3) | 0.6907(3) | 0.8927(2) |
| C(34) | 0.3250(3) | 0.7986(3) | 0.9921(2) |
| C(35) | 0.9740(4) | 0.9671(3) | 0.5692(3) |
| C(36) | 0.6764(4) | 0.6588(4) | 0.3030(2) |

measured using  $\text{CDCl}_3$  as solvent. 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.

**Table 2** Non-hydrogen atomic parameters for **6**, esd in parentheses

|       | <i>x</i>   | <i>y</i>  | <i>z</i>   |
|-------|------------|-----------|------------|
| O(1)  | 0.0438(2)  | 0.1031(1) | 0.8262(2)  |
| O(2)  | -0.0794(2) | 0.0457(1) | 0.7298(2)  |
| O(3)  | 0.1968(2)  | 0.0300(1) | 0.9874(2)  |
| O(4)  | 0.4297(2)  | 0.0448(1) | 1.0385(2)  |
| O(5)  | 1.0238(2)  | 0.2702(1) | 0.6805(3)  |
| O(6)  | 0.4885(2)  | 0.3330(1) | 0.3856(2)  |
| C(1)  | 0.1635(2)  | 0.0585(1) | 0.5971(2)  |
| C(2)  | 0.2062(3)  | 0.0140(1) | 0.5622(3)  |
| C(3)  | 0.3530(3)  | 0.0011(1) | 0.6575(3)  |
| C(4)  | 0.4058(2)  | 0.0363(1) | 0.7600(2)  |
| C(5)  | 0.4248(2)  | 0.0791(1) | 0.6986(2)  |
| C(6)  | 0.5261(2)  | 0.0814(1) | 0.6153(2)  |
| C(7)  | 0.5536(2)  | 0.1291(1) | 0.6068(2)  |
| C(8)  | 0.6296(2)  | 0.1457(1) | 0.5114(2)  |
| C(9)  | 0.6812(2)  | 0.1920(1) | 0.5500(2)  |
| C(10) | 0.7876(3)  | 0.2123(1) | 0.4885(3)  |
| C(11) | 0.7909(3)  | 0.2594(1) | 0.5240(3)  |
| C(12) | 0.8890(3)  | 0.2844(1) | 0.6079(3)  |
| C(13) | 0.8560(3)  | 0.3280(1) | 0.6216(2)  |
| C(14) | 0.9557(3)  | 0.3560(1) | 0.7067(3)  |
| C(15) | 0.9222(3)  | 0.3977(1) | 0.7161(3)  |
| C(16) | 0.7892(3)  | 0.4136(1) | 0.6426(3)  |
| C(17) | 0.6893(3)  | 0.3876(1) | 0.5600(3)  |
| C(18) | 0.7194(3)  | 0.3444(1) | 0.5479(2)  |
| C(19) | 0.6183(3)  | 0.3166(1) | 0.4618(2)  |
| C(20) | 0.6541(3)  | 0.2755(1) | 0.4492(2)  |
| C(21) | 0.5735(3)  | 0.2390(1) | 0.3682(2)  |
| C(22) | 0.5320(3)  | 0.2098(1) | 0.4649(2)  |
| C(23) | 0.4784(3)  | 0.1639(1) | 0.4215(2)  |
| C(24) | 0.4051(2)  | 0.1460(1) | 0.5166(2)  |
| C(25) | 0.3142(2)  | 0.1051(1) | 0.4811(2)  |
| C(26) | 0.2776(2)  | 0.0937(1) | 0.6032(2)  |
| C(27) | 0.1622(2)  | 0.0550(1) | 0.7345(2)  |
| C(28) | 0.2874(2)  | 0.0431(1) | 0.8187(2)  |
| C(29) | 0.4271(3)  | 0.0719(1) | 0.4782(2)  |
| C(30) | 0.7320(3)  | 0.1163(1) | 0.4735(3)  |
| C(31) | 0.4052(3)  | 0.1557(1) | 0.2792(3)  |
| C(32) | 0.6987(3)  | 0.2148(1) | 0.3461(3)  |
| C(33) | 0.0294(2)  | 0.0660(1) | 0.7641(2)  |
| C(34) | -0.0782(4) | 0.1168(1) | 0.8627(4)  |
| C(35) | 0.3152(3)  | 0.0397(1) | 0.9587(2)  |
| C(36) | 0.2078(4)  | 0.0297(1) | 1.1223(3)  |
| C(37) | 1.0421(8)  | 0.2446(4) | 0.7792(11) |
| C(37) | 1.1209(11) | 0.2559(5) | 0.6295(15) |
| C(38) | 0.3716(4)  | 0.3279(1) | 0.4279(4)  |

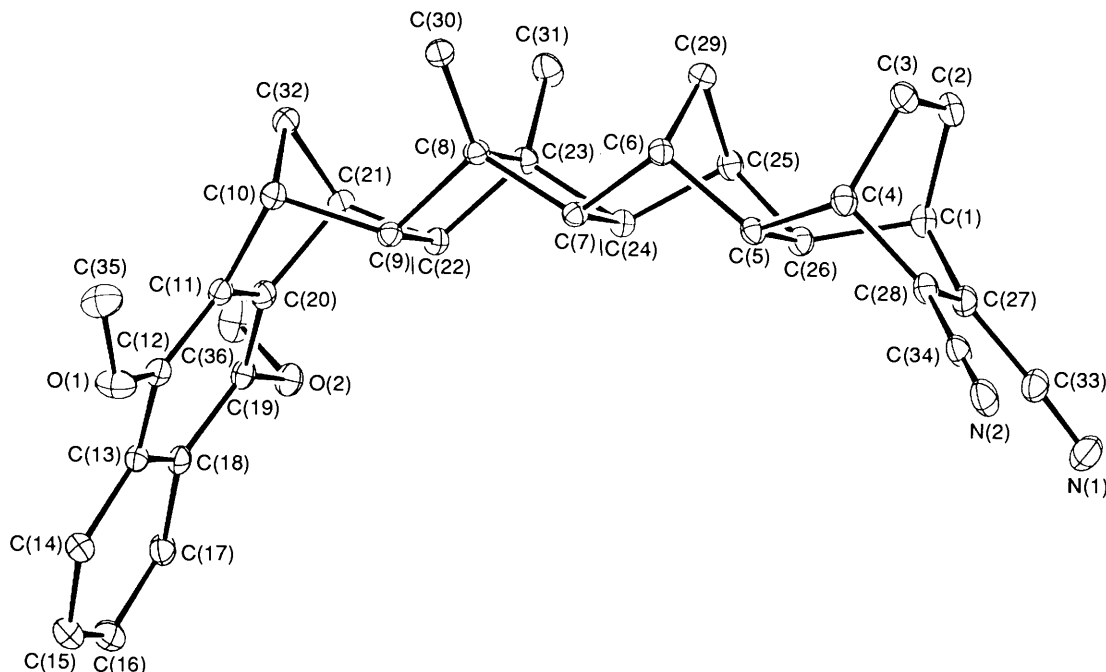


Fig. 1 ORTEP projection of compound **3**, as determined by single crystal X-ray diffraction. Hydrogen atoms are omitted for clarity.

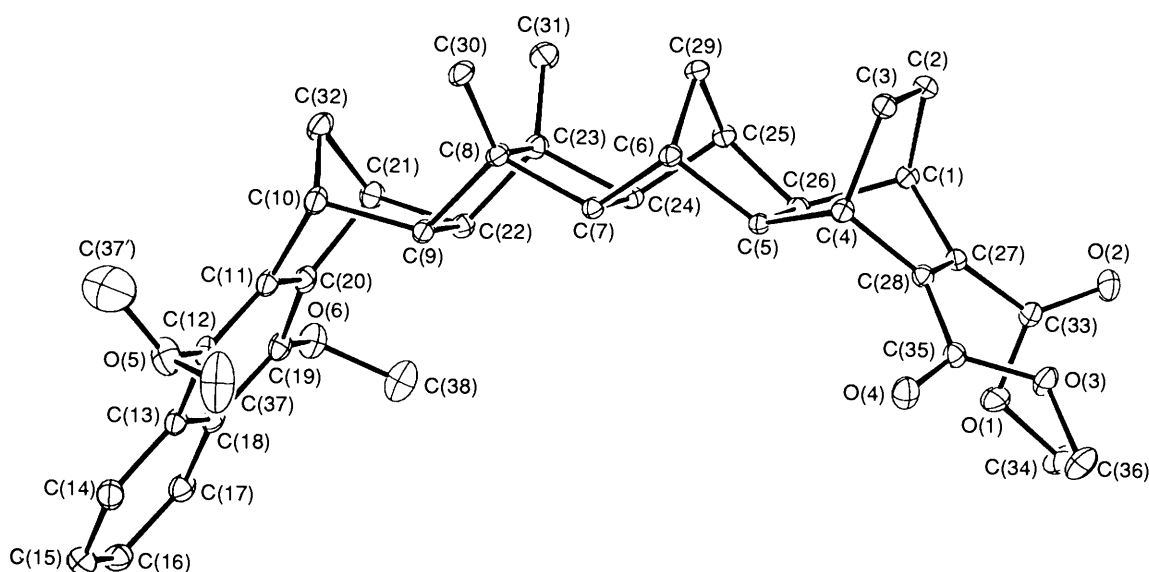


Fig. 2 ORTEP projection of compound **6**, as determined by single crystal X-ray diffraction. Hydrogen atoms are omitted for clarity.

(4 $\alpha$ ,5 $\beta$ ,5 $\alpha\alpha$ ,5 $\beta\beta$ ,5 $c\alpha$ ,6 $\beta$ ,13 $\beta$ ,13 $\alpha\alpha$ ,13 $\beta\beta$ ,13 $c\alpha$ ,14 $\beta$ ,14 $\alpha\alpha$ )-4 $\alpha$ ,5,5 $\alpha$ ,5 $c$ ,6,13,13 $\alpha$ ,13 $c$ ,14,14 $\alpha$ -Decahydro-7,12-dimethoxy-5b,13b-dimethyl-5,14:6,13-dimethanonaphtho[2'',3'':3',4']cyclobuta[1',2':3,4]cyclobuta[1,2-b]anthracene **11**.—A solution of the acetal **7** (5 g, 9.5 mmol)<sup>15</sup> in formic acid (50 cm<sup>3</sup>) and THF (20 cm<sup>3</sup>) was stirred at room temperature for 18 h. The mixture was extracted with dichloromethane (100 cm<sup>3</sup>) and successively washed with water (2  $\times$  50 cm<sup>3</sup>) and NaHCO<sub>3</sub> (2  $\times$  50 cm<sup>3</sup>). The extract was dried over Na<sub>2</sub>SO<sub>4</sub> and the dichloromethane evaporated to give crude **9** (4 g, 88%). This material was quite unstable and could not be purified sufficiently for analysis. However, a partial <sup>1</sup>H NMR spectrum (60 MHz; CDCl<sub>3</sub>) revealed the loss of both OCH<sub>3</sub> signals ( $\delta$  3.0, 3.1) that were present in **7**, and the IR spectrum showed a strong C=O absorption at 1780 cm<sup>-1</sup>.

A solution of crude **9** (4 g, 8.35 mmol) in toluene (20 cm<sup>3</sup>) was

neated under reflux for 18 h. The solvent was removed under reduced pressure. The residue was recrystallised from ethyl acetate–pentane (10:90) to give the diene **11** (2.9 g, 77%), m.p. 189 °C;  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>) 0.94 (6 H, s, 2  $\times$  CH<sub>3</sub>), 1.65 (2 H, m), 1.70 (2 H, m), 1.97 (2 H, s), 2.15 (2 H, s), 2.18 (2 H, s), 2.38 (2 H, s), 3.64 (2 H, s), 3.97 (6 H, s, 2  $\times$  OCH<sub>3</sub>), 5.35 (2 H, m), 5.57 (2 H, m), 7.43 (2 H, m, aromatic) and 8.06 (2 H, m, aromatic) (Found: C, 85.0; H, 7.65. C<sub>32</sub>H<sub>34</sub>O<sub>2</sub> requires C, 85.3; H, 7.6%).

1 $\alpha$ ,4 $\alpha$ ,4 $\alpha\beta$ ,5 $\alpha$ ,5 $\alpha\beta$ ,5 $\beta\alpha$ ,5 $\beta\beta$ ,6 $\alpha$ ,13 $\alpha$ ,13 $\alpha\beta$ ,13 $\beta\alpha$ ,13 $\beta\beta$ ,14 $\alpha$ ,14 $\alpha\beta$ )-1,4,4 $\alpha$ ,5,5 $\alpha$ ,5 $c$ ,6,13,13 $\alpha$ ,13 $c$ ,14,14 $\alpha$ -Dodecahydro-7,12-dimethoxy-5b,13b-dimethyl-1,4-ethano-5,14:16,13-dimethanonaphtho[2'',3'':3',4']cyclobuta[1',2':3,4]cyclobuta[1,2-b]anthracene-2,3-dicarbonitrile **3**.—Dicyanoacetylene<sup>29</sup> (100 mg, 1.45 mmol) was added very slowly to an ice-cold solution of the diene **11**

(300 mg, 0.67 mmol) in THF (10 cm<sup>3</sup>). (**CAUTION!** The reaction is extremely exothermic. Higher reaction temperatures caused the product to undergo a retro-Diels–Alder reaction.) The mixture was stirred magnetically for 15 min after the addition was complete. Methanol (15 cm<sup>3</sup>) was added to the stirred solution and compound **13** was precipitated. The crude product **13** (290 mg, ca. 82%) was filtered, and immediately hydrogenated.

A solution of the crude adduct **13** (290 mg, 0.55 mmol) in ethyl acetate (20 cm<sup>3</sup>) was hydrogenated at 1 atm. and 25 °C using 10% Pd/C (50 mg) until uptake of one equivalent of hydrogen had occurred. The catalyst was filtered off, and the solvent removed under reduced pressure. Column chromatography (silica, EtOAc–hexane 30:70) of the residue gave pure **3** (0.232 g, 80%), m.p. 243–245 °C (decomp.) (EtOAc–pentane 10:90);  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>) 0.95 (6 H, s, 2 × CH<sub>3</sub>), 1.30 (2 H, d, *J* 8.7), 1.38 (2 H, s), 1.60 (2 H, m), 1.68 (1 H, d, *J* 9.7), 1.80 (1 H, d, *J* 11.8), 1.88 (4 H, m), 2.11 (2 H, s), 2.14 (2 H, s), 2.96 (2 H, s), 3.66 (2 H, s), 3.96 (6 H, s, 2 × OCH<sub>3</sub>), 7.44 (2 H, m, aromatic) and 8.07 (2 H, m, aromatic);  $\delta_{\text{C}}$ (122.725 MHz; CDCl<sub>3</sub>) 9.71 (CH<sub>3</sub>), 20.52 (CH<sub>2</sub>), 30.59 (CH<sub>2</sub>), 37.51 (CH), 38.61 (CH), 40.46 (CH), 42.71 (CH<sub>2</sub>), 43.64 (CH), 44.17 (C), 50.59 (CH), 53.69 (CH), 61.66 (OCH<sub>3</sub>), 114.31 (CN), 121.99 (CH, aromatic), 125.03 (CH, aromatic), 127.85 (C, aromatic), 132.90 (C=C), 134.90 (C, aromatic) and 144.29 (C, aromatic);  $\nu_{\text{max}}$  (thin film)/cm<sup>-1</sup> 2217 (C=O) (Found: C, 81.4; H, 7.0; N, 5.2. C<sub>36</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub> requires C, 81.8; H, 6.9; N, 5.3%).

*Dimethyl* (1 $\alpha$ ,4 $\alpha$ ,4 $\alpha\beta$ ,5 $\alpha$ ,5 $\alpha\beta$ ,5 $\beta\alpha$ ,5 $\beta$ ,6 $\alpha$ ,13 $\alpha$ ,13 $\beta$ ,13 $\beta\alpha$ ,13 $\beta$ ,14 $\alpha$ ,14 $\alpha\beta$ )-1,4,4 $\alpha$ ,5,5 $\alpha$ ,5 $\beta$ ,6,13,13 $\alpha$ ,13 $\beta$ ,14,14 $\alpha$ -*Dodecahydro-7,12-dimethoxy-5b,13b-dimethyl-1,4-ethano-5,14:6,13-dimethanonaphtho*[1<sup>'''</sup>,3<sup>'''</sup>:3',4']*cyclobuta*[1',2':3,4']*cyclobuta*[1,2-b]*anthracene-2,3-dicarbonylate* **6**.—A magnetically stirred solution of **11** (2.0 g, 4.44 mmol) and DMAD (0.70 g, 4.9 mmol) in benzene (20 cm<sup>3</sup>) was maintained at 40–50 °C for 36 h. Methanol (30 cm<sup>3</sup>) was added to the cooled room temp.) reaction mixture, and the crude solid **15** (1.55 g, 68%) was separated by filtration. The product was unstable, and was not characterized.

Crude product **15** (1.55 g, 2.6 mmol) in EtOAc (30 cm<sup>3</sup>) was hydrogenated at 1 atm. and 25 °C, using 10% Pd/C (60 mg) until uptake of one equivalent of hydrogen had occurred. Standard workup procedure gave crude **6** which was purified by column chromatography (silica, EtOAc–hexane 30:60) to give pure compound **6**, (1.05 g, 67%), m.p. 186 °C (from EtOAc–pentane 30:70);  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>) 0.94 (6 H, s, 2 × CH<sub>3</sub>), 1.25 (2 H, d, *J* 8.9), 1.38 (2 H, s), 1.52 (2 H, m), 1.65 (1 H, d, *J* 9.7), 1.78 (1 H, d, *J* 8.5), 1.88 (4 H, m), 2.07 (2 H, s), 2.12 (2 H, s), 2.96 (2 H, s), 3.64 (2 H, s), 3.75 (6 H, s, 2 × OCH<sub>3</sub>), 3.97 (6 H, s, 2 × OCH<sub>3</sub>), 7.43 (2 H, m, aromatic) and 8.07 (2 H, m, aromatic);  $\delta_{\text{C}}$ (122.725 MHz; CDCl<sub>3</sub>); 9.76 (CH<sub>3</sub>), 20.95 (CH<sub>2</sub>), 30.49 (CH<sub>2</sub>), 36.02 (CH), 37.58 (CH), 40.50 (CH), 42.77 (CH<sub>2</sub>), 44.17 (C), 44.21 (CH), 50.66 (CH), 52.00 (CH<sub>3</sub>), 53.69 (CH), 61.63 (OCH<sub>3</sub>), 121.98 (CH, aromatic), 124.96 (CH, aromatic), 127.63 (C, aromatic), 135.18 (C, aromatic), 142.90 (C=C), 144.90 (C, aromatic) and 166.78 (C=O) (Found: C, 76.7; H, 7.3. C<sub>38</sub>H<sub>42</sub>O<sub>6</sub> requires C, 76.7; H, 7.1%).

(4 $\alpha$ ,5 $\beta$ ,5 $\alpha$ ,5 $\beta$ ,5 $\alpha$ ,5 $\beta$ ,5 $\alpha$ ,6 $\beta$ ,6 $\alpha$ ,6 $\beta$ ,6 $\alpha$ ,7 $\beta$ ,14 $\beta$ ,14 $\alpha$ ,14 $\beta$ ,14 $\alpha$ ,15 $\beta$ ,15 $\alpha$ ,15 $\beta$ ,15 $\alpha$ ,16 $\beta$ ,16 $\alpha$ )-4 $\alpha$ ,5,5 $\alpha$ ,5 $\beta$ ,6 $\alpha$ ,6 $\beta$ ,7,14,14 $\alpha$ ,14 $\beta$ ,15,15 $\alpha$ ,15 $\beta$ ,16,16 $\alpha$ -*Hexadecahydro-8,13-dimethoxy-5b,6b,14b,15b-tetramethyl-5,16:6,15:7,14-trimethanonaphtho*[2<sup>'''</sup>,3<sup>'''</sup>:3<sup>'''</sup>,4<sup>'''</sup>]*cyclobuta*[1<sup>'''</sup>,2<sup>'''</sup>:3<sup>'''</sup>,4<sup>'''</sup>]*cyclobuta*[1<sup>'''</sup>,2<sup>'''</sup>:4<sup>'''</sup>,5<sup>'''</sup>]-*benzo*[1<sup>''</sup>,2<sup>''</sup>:3',4']*cyclobuta*[1',2':3,4]*cyclobuta*[1,2-b]*anthracene* **12**.—A solution of the acetal **8** (5 g, 7.7 mmol)<sup>5</sup> in THF (20 cm<sup>3</sup>) and formic acid (60 cm<sup>3</sup>) was magnetically stirred at room temperature for 18 h. Standard workup procedure gave crude ketone **10** (4.3 g, 89%) whose partial <sup>1</sup>H NMR spectrum (60

MHz; CDCl<sub>3</sub>) revealed the loss of both OCH<sub>3</sub> signals ( $\delta$  3.0, 3.1) that were present in **8**.

A solution of the crude ketone **10** (4.3 g, 6.9 mmol) in toluene (30 cm<sup>3</sup>) was heated under reflux for 18 h. The toluene was removed under reduced pressure, and the residue recrystallised from EtOAc–pentane (10:90) to give the diene **12** (3.05 g, 74%), m.p. 232–234 °C;  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>) 0.79 (6 H, s, 2 × CH<sub>3</sub>), 0.94 (6 H, s, 2 × CH<sub>3</sub>), 1.63–1.79 (6 H, m), 1.86–1.92 (4 H, m), 2.01–2.09 (4 H, m), 2.13–2.17 (6 H, m), 3.64 (2 H, br s), 3.98 (6 H, s, 2 × OCH<sub>3</sub>), 5.35 (2 H, m), 5.57 (2 H, m), 7.43 (2 H, m, aromatic) and 8.06 (2 H, m, aromatic) (Found: C, 86.0; H, 8.2. C<sub>43</sub>H<sub>48</sub>O<sub>2</sub> requires C, 86.5; H, 8.1%).

(1 $\alpha$ ,4 $\alpha$ ,4 $\alpha\beta$ ,5 $\alpha$ ,5 $\alpha\beta$ ,5 $\beta\alpha$ ,5 $\beta$ ,6 $\alpha$ ,6 $\beta$ ,6 $\alpha$ ,6 $\beta$ ,7 $\alpha$ ,14 $\alpha$ ,14 $\alpha\beta$ ,14 $\beta\alpha$ ,14 $\beta$ ,15 $\alpha$ ,15 $\alpha\beta$ ,15 $\beta\alpha$ ,15 $\beta$ ,16 $\alpha$ ,16 $\alpha\beta$ )-1,4,4 $\alpha$ ,5,5 $\alpha$ ,5 $\beta$ ,6,6 $\alpha$ ,6 $\beta$ ,7,14,14 $\alpha$ ,14 $\beta$ ,15,15 $\alpha$ ,15 $\beta$ ,16,16 $\alpha$ -*Octadecahydro-8,13-dimethoxy-5b,6b,14b,15b-tetramethyl-1,4-ethano-5,16:16,15:7,14-trimethanonaphtho*[2<sup>'''</sup>,3<sup>'''</sup>:3<sup>'''</sup>,4<sup>'''</sup>]*cyclobuta*[1<sup>'''</sup>,2<sup>'''</sup>:3<sup>'''</sup>,4<sup>'''</sup>]*cyclobuta*[1<sup>'''</sup>,2<sup>'''</sup>:4<sup>'''</sup>,5<sup>'''</sup>]*benzo*[1<sup>''</sup>,2<sup>''</sup>:3',4']*cyclobuta*[1',2':3,4]*cyclobuta*[1,2-b]*anthracene-2,3-dicarbonitrile* **4**.—Dicyanoacetylene (0.7 g, 0.99 mmol)<sup>29</sup> was added dropwise to an ice-cold solution of the diene **12** (0.250 g, 0.4 mmol) in THF (15 cm<sup>3</sup>). After stirring for 15 min., methanol (20 cm<sup>3</sup>) was introduced and the mixture filtered to obtain crude adduct **14** (255 mg), which was immediately hydrogenated.

A magnetically stirred solution of **14** (255 mg, 0.38 mmol) in EtOAc (30 cm<sup>3</sup>) was catalytically hydrogenated using 10% Pd/C (50 mg) at 1 atm. and 25 °C until uptake of one equivalent of hydrogen had occurred. The catalyst was filtered off, and the solvent evaporated to give crude product which was purified using column chromatography (silica, EtOAc–hexane 30:70) to give pure **4** (0.165 g, 65%), m.p. 285–286 °C (decomp.) (from EtOAc–pentane 30:70);  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>) 0.78 (6 H, s, 2 × CH<sub>3</sub>), 0.94 (6 H, s, 2 × CH<sub>3</sub>), 1.27 (2 H, m), 1.40 (2 H, s), 1.51–1.74 (6 H, overlapping m), 1.84 (2 H, s), 1.86 (1 H, d, *J* 8.8), 1.88 (2 H, s), 1.90 (2 H, s), 1.91 (1 H, d, *J* 9.6), 2.01 (2 H, s), 2.03 (2 H, s), 2.16 (2 H, s), 2.94 (2 H, s), 3.63 (2 H, s), 3.97 (6 H, s, 2 × OCH<sub>3</sub>), 7.43 (2 H, m, aromatic) and 8.07 (2 H, m, aromatic);  $\delta_{\text{C}}$ (122.725 MHz; CDCl<sub>3</sub>) 9.68 (CH<sub>3</sub>), 9.86 (CH<sub>3</sub>), 20.57 (CH<sub>2</sub>), 30.60 (CH<sub>2</sub>), 31.30 (CH<sub>2</sub>), 36.07 (CH), 37.45 (CH), 38.72 (CH), 40.54 (CH), 42.78 (CH<sub>2</sub>), 43.74 (CH), 44.81 (C), 45.53 (C), 50.78 (CH), 51.42 (CH), 51.47 (CH), 53.92 (CH), 61.88 (OCH<sub>3</sub>), 114.37 (CN), 122.01 (CH, aromatic), 124.97 (CH, aromatic), 127.85 (C, aromatic), 132.93 (C=C), 135.34 (C, aromatic) and 144.24 (C, aromatic);  $\nu_{\text{max}}$ (thin film)/cm<sup>-1</sup> 2215 (C≡N) (Found: C, 80.0; H, 7.3; N, 4.0. C<sub>47</sub>H<sub>50</sub>N<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O requires C, 79.4; H, 7.7; N, 3.95%).

(1 $\alpha$ ,4 $\alpha$ ,4 $\alpha\beta$ ,5 $\alpha$ ,8 $\alpha$ ,8 $\alpha\beta$ )-1,4,4 $\alpha$ ,5,6,7,8,8 $\alpha$ -*Octahydro-1,4-ethano-5,8-methanonaphthalene-2,3-dicarbonitrile* **5**.—A solution of acetal, **19a** (4 g, 18.2 mmol)<sup>31</sup> in THF (10 cm<sup>3</sup>) and formic acid (50 cm<sup>3</sup>) was magnetically stirred for 18 h. Standard workup procedure gave crude ketone **19b** (3.0 g, 95%) whose <sup>1</sup>H NMR spectrum showed the absence of the two OCH<sub>3</sub> groups that were present in **19a**.

Crude ketone **19b** (3.0 g, 17.2 mmol) in toluene (20 cm<sup>3</sup>) was heated under reflux for 18 h. Evaporation of toluene under reduced pressure gave a yellowish oil (2.5 g, 75%) which was subjected to column chromatography (silica, EtOAc–hexane 10:90). Although the eluted product (2.0 g, semi-solid) resisted further purification, its <sup>1</sup>H NMR spectrum revealed that it consisted of ca. 95% of **20**;  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>) 1.25 (1 H, d of pent, *J* 1.5, 9.6), 1.38 (2 H, m), 1.53–1.59 (2 H, m), 1.79 (1 H, d of pent, *J* 1.9, 9.6), 2.04 (2 H, m), 2.49 (2 H, m), 5.37–5.41 (2 H, m) and 5.54–5.58 (2 H, m).

Dicyanoacetylene (150 mg, 1.97 mmol)<sup>29</sup> was added dropwise to an ice-cold solution of diene **20** (150 mg, 1.03 mmol) in THF (10 cm<sup>3</sup>). When addition was complete, methanol (15 cm<sup>3</sup>)

was introduced, giving the crude solid adduct, **21** (200 mg, 87%) which was immediately hydrogenated.

Crude **21** (200 mg, 0.9 mmol) in EtOAc (20 cm<sup>3</sup>) was hydrogenated using identical conditions as for the synthesis of **3**, giving after workup a light yellow solid. Purification by column chromatography (silica, EtOAc-hexane 10:90) and recrystallisation from EtOAc-pentane (10:90) gave pure **5** (158 mg, 79%), m.p. 165–166 °C (from EtOAc-pentane 10:90);  $\delta_{\text{H}}$  (500 MHz; CDCl<sub>3</sub>) 1.10 (2 H, m), 1.16 (1 H, d, *J* 11.1), 1.25 (1 H, d, *J* 4.7), 1.27 (1 H, d, *J* 4.7), 1.54 (2 H, s), 1.58 (2 H, m), 1.76 (1 H, d, *J* 9.9), 1.82 (2 H, d, *J* 9.2), 2.14 (2 H, s) and 2.97 (2 H, s);  $\delta_{\text{C}}$  (122.725 MHz; CDCl<sub>3</sub>) 20.27 (CH<sub>2</sub>), 30.60 (CH<sub>2</sub>), 34.62 (CH<sub>2</sub>), 37.29 (CH), 38.89 (CH), 44.97 (CH), 114.38 (CN) and 133.04 (C=C);  $\nu_{\text{max}}$  (thin film)/cm<sup>-1</sup> 2219 (C≡N) (Found: C, 80.0; H, 7.3; N, 12.3. C<sub>15</sub>H<sub>16</sub>N<sub>2</sub> requires C, 80.3; H, 7.2; N, 12.5%).

*X-Ray Crystallographic Determination.*—Crystal data for compound **3**. C<sub>36</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>, *M* 528.7, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>1, *a* 11.9812(5), *b* 13.3931(7), *c* 17.5105(7) Å, *V* 2809.8(2) Å<sup>3</sup>, *D<sub>c</sub>* 1.25 g cm<sup>-3</sup>, *Z* 4,  $\mu_{\text{Cu}}$  5.65 cm<sup>-1</sup>, crystal size 0.19 by 0.22 by 0.29 mm,  $2\theta_{\text{max}}$  140°. The number of reflexions was 2520 considered observed out of 3002 unique data. Final residuals *R*, *R<sub>w</sub>* were 0.038, 0.059.

*Crystal data for compound 6*. C<sub>38</sub>H<sub>42</sub>O<sub>6</sub>, *M* 594.8, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* 9.830(1), *b* 31.423(1), *c* 10.969(1) Å,  $\beta$  108.594(5)°, *V* 3211.5(5) Å<sup>3</sup>, *D<sub>c</sub>* 1.23 g cm<sup>-3</sup>, *Z* 4,  $\mu_{\text{Cu}}$  6.21 cm<sup>-1</sup>, crystal size 0.09 by 0.11 by 0.45 mm,  $2\theta_{\text{max}}$  140°. The number of reflexions was 3720 considered observed out of 4754 unique data, with *R<sub>merge</sub>* 0.011 for 218 pairs of equivalent *hk0* reflexions. Final residuals *R*, *R<sub>w</sub>* were 0.049, 0.068.

*Structure determination.* Reflexion data were measured with an Enraf-Nonius CAD-4 diffractometer in  $\theta/2\theta$  scan mode using nickel filtered copper radiation ( $\lambda$  1.5418 Å). Data were corrected for absorption using Gaussian integration on a 12 × 12 × 12 grid. Reflexions with *I* > 3 $\sigma$ (*I*) were considered observed. The structures were determined by direct phasing and Fourier methods. Hydrogen atoms were included in calculated positions, 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. Reflexion weights used were 1/ $\sigma^2(F_o)$ , with  $\sigma(F_o)$  being derived from  $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{\frac{1}{2}}$ . The weighted residual is defined as  $R_w = (\Sigma w\Delta^2 / \Sigma wF_o^2)^{\frac{1}{2}}$ . Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography.<sup>32</sup> Structure solution was by MULTAN80<sup>33</sup> and refinement used BLOCKLS, a local version of ORFLS,<sup>34</sup> ORTEP-II<sup>35</sup> running on a Macintosh IIcx was used for the structural diagrams, and an IBM 3090 computer was used for calculations.

The structures and atom numbering schemes for **3** and **6** are shown in Figs. 1 and 2 respectively, with hydrogen atoms omitted for clarity. One methoxy carbon atom in **6** is disordered over two positions, labelled C(37) and C(37)'. Atomic parameters for the non-hydrogen atoms are given in Tables 1 and 2. Material deposited at the Cambridge Crystallographic Data Centre comprises all positional and thermal parameters, interatomic distances, angles and torsional angles.\*

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\* For full details of the CCDC deposition scheme see, 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1993, Issue 1.

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