A Synthetic Strategy for the Construction of a Novel Series of Rigid Supramolecular Triads

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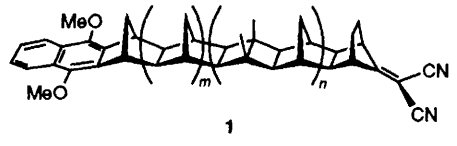
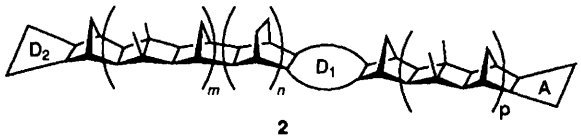
A method is described for constructing totally rigid triad (trichromophoric) supramolecular systems, D_2–B_1–D_1–B_2–A, in which the chromophores D_2 (dimethylaniline), D_1 (dimethoxynaphthalene), and A (dicyanovinyl) are fused to bridges, B_1 and B_2, consisting of linearly fused norbornyl and bicyclo[2.2.0]hexanyl units.

The central role played by electron transfer (ET) in a multitude of chemical and biological reactions ensures that it remains the focus of research activity.[1,2] A major activity in this area is the investigation of the dynamics of long range ET processes in covalently linked Donor–Bridge–Acceptor dyads (D–B–A).[1–3] In this respect, we have found that rigid norbornylogous bridges, consisting of linearly fused norbornyl and bicyclo[2.2.0]hexanyl units, mediate intramolecular photoinduced ET processes in dyads, such as **1**, with unprecedented speed and efficiency, over distances as large as 13 Å.[3]

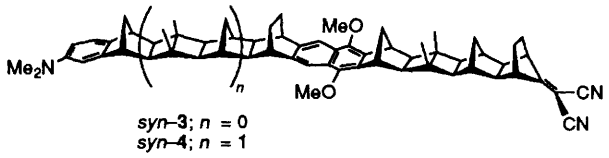
The norbornylogous bridge could offer promise in the construction of molecular photovoltaic devices if ways could be found to acheive both efficient charge separation and longevity of the resulting charge separated state.[1c] This can be accomplished using polychromophoric systems, such as triads, D_2–D_1–A, tetrads, *etc.*[1b,c] Triads **2**, built around rigid norbornylogous bridges, would offer a number of important advantages over bridges currently being used in polychromophoric systems[1b,c] namely, their rigidity and symmetry, coupled with the synthetic ease by which both the length and configuration of the bridges may be systematically altered.[4] A general strategy for synthesizing triads **2**, in which D_1 is a naphthalene group, has been accomplished, illustrative of which is the synthesis of the triads **3**–**5**.



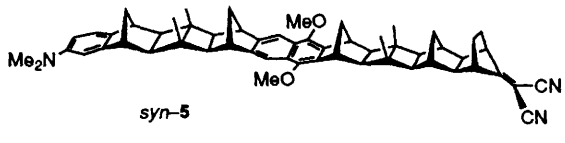
1



2



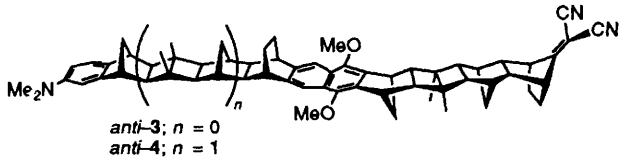
syn-**3**; *n* = 0
syn-**4**; *n* = 1



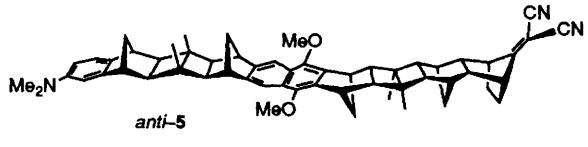
syn-**5**

The key feature of the strategy is shown in Scheme 1. The left-hand and right-hand bridges, generalized by **6** and **7**, are synthesized such that one terminus of each bridge bears appropriate functionality for conversion into one of the chromophores, D_2 or A, and the other terminus bears either a diene or a quinone group. Triad construction is then acheived through a Diels–Alder reaction between bridges, **6** and **7**, which also forms the central naphthalene chromophore, **8**–**11**.

Two strategies have been developed for the synthesis of the diene bearing bridge, depending on whether the diene is part of a bicyclo[2.2.2]octanyl unit or a norbornyl unit (Scheme 2). The former case is illustrated by the synthesis of **18**. Diels–Alder reaction of **12** with dimethoxytetrachlorocyclopentadiene, followed by reductive dechlorination of the adduct[5a] and subsequent deketalization with formic acid gave **13**. Ketone **13** is thermally labile to cheletropic loss of CO and

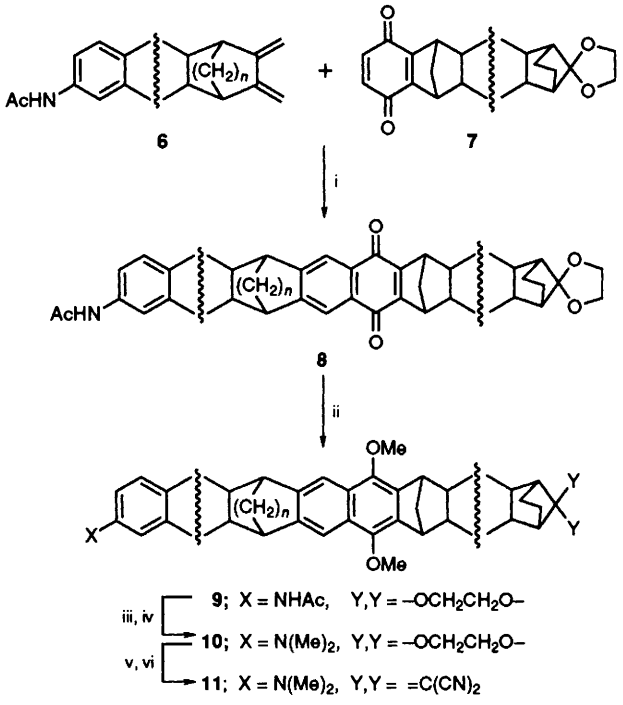


anti-**3**; *n* = 0
anti-**4**; *n* = 1



anti-**5**

the resulting 1,3-diene was trapped *in situ* by dimethyl fumarate to give a Diels–Alder adduct which afforded bisacetoxymethyl compound **15** after catalytic hydrogenation, reduction of the ester groups and subsequent acetylation.



Scheme 1 *Reagents and conditions*: i, PbO_2, THF, reflux, 4 days; ii, $Na_2S_2O_4$, $NaHCO_3$, TEBAC; then KOH; then Me_2SO_4, 90 min; iii, KOH, EtOH–H_2O (5:1), reflux, 36 h; iv, $NaBH_4$, $H_2C{=}O$, H_2SO_4, THF, EtOH, 15–20 °C, 30 min; v, HCO_2H–THF (3:4), 90 °C, 12 h; vi, $CH_2(CN)_2$, NaOAc, AcOH, toluene, reflux, 15 h (THF = tetrahydrofuran; TEBAC = tribenzyl ammonium chloride)

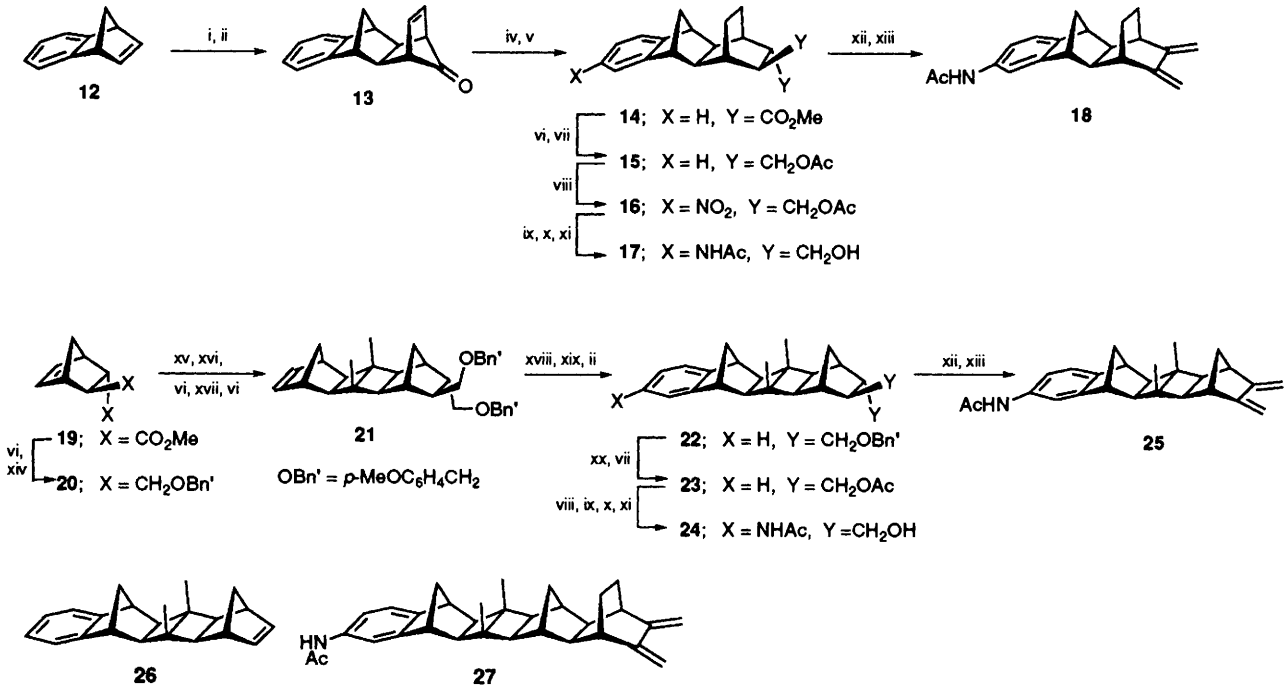
Nitration of **15** occurred at the position indicated, in accordance with precedent,[4b] and the product was converted into **17** using standard prcedures. Bistosylation of **17** followed by bisdehydrotosylation gave diene **18** in 13% overall yield from **12**. The 8-bond amide diene **27** was prepared in a similar fashion from **26** which was obtained from **12** using standard bridge extension methodology.[4]

In the strategy just described, the incipient chromophore (D_2) is already present in the bridge prior to its elaboration to the diene. The reverse procedure is used for the construction of bismethylenenorbornyl bearing bridges, such as **25**. In this approach the *p*-methoxybenzyl derivative **20** of the *trans* dial was converted into **21** through application of the four-bond bridge extension technique.[4] Benzene annelation of this compound using the tetrachlorothiophene 1,1-dioxide approach[4f,5b] gave **22**, and this was readily converted into **23** through deprotection (DDQ) and acetylation. Conversion of **23** into diene **25** followed the same procedures that were used for the synthesis of **18**.

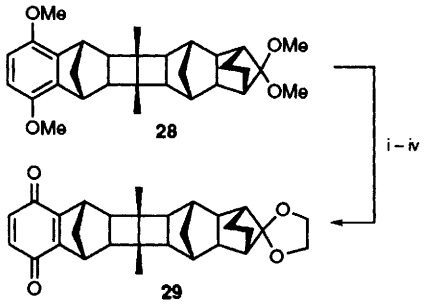
The quinone bearing bridge **29** was prepared in 52% yield from **28** using standard reactions (Scheme 3). Compound **28** was obtained in several steps from the Diels–Alder adduct of *p*-benzoquinone and cyclopentadiene, using procedures previously employed in the synthesis of the corresponding dimethoxynaphthalene system.[3a,4f]

The triads were obtained as outlined by the general Scheme 1. Diels–Alder reaction of the amide dienes **6** (**18**, **25** or **27**) with the bridge quinone **7** (**29**), in the presence of PbO_2, led, in each case, to the direct formation of the corresponding naphthoquinone triad **8** (82–90%), as an inseparable mixture of two diastereoisomers, *syn* and *anti*. As expected, the diastereoisomers were formed in equal amounts using the bicyclo[2.2.2]octanediylidene bridges **18** and **27**; however, the cycloaddition reaction involving the norbornanediylidene bridge **25** was more selective, and resulted in the formation of a 70:30 mixture of diastereoisomers.

Reductive methylation of each of the quinones **8** gave the



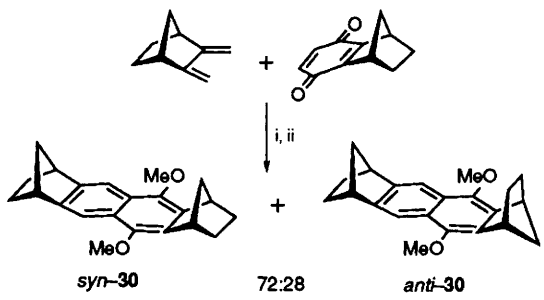
Scheme 2 *Reagents and conditions* (reactions at room temperature unless otherwise noted): i, dimethoxytetrachlorocyclopentadiene, 100 °C, 16 h; ii, Na, Pr^iOH, THF, reflux 17 h; iii, HCO_2H, THF (1:2), 18 h; iv, dimethyl fumarate, toluene, reflux, 14 h; v, H_2, 10% Pd/C, EtOAc, 1 atm; vi, $LiAlH_4$, THF, reflux; vii, Ac_2O, Py, 22 h; viii, $Cu(NO_3)_2{\cdot}3H_2O$, Ac_2O, CH_2Cl_2, 17 h; ix, H_2, 5% Pd/C, EtOAc–EtOH (5:1), 1 atm; x, Ac_2O, CH_2Cl_2, 30 min; xi, $LiBH_4$, THF, 6.5 days; xii, TsCl, Py, −5 °C, 36 h; xiii, $KOBu^t$, DMSO, 14 h; xiv, *p*-methoxybenzyl chloride, NaI, NaH, monoglyme–DMF (1:2), 24 h; xv, DMAD, $RuH_2CO(PPh_3)_3$, benzene, reflux (Ar), 5 days; xvi, quadricyclane, 125 °C, 4 days; xvii, MsCl, Py, −5 °C, 3 days; xviii, tetrachlorothiophene-1,1-dioxide, toluene, reflux, 4 days; xix, KOH, EtOH–THF (3:2), reflux, 18 h; xx, DDQ, CH_2Cl_2–H_2O (15:1), 2 h (Py = pyridine; Ts = *p*-$MeC_6H_4SO_2$; DMSO = dimethyl sulfoxide; DMF = dimethylformamide; DMAD = dimethyl acetylenedicarboxylate; Ms = $MeSO_2$; DDQ = dichlorodicyanobenzoquinone)



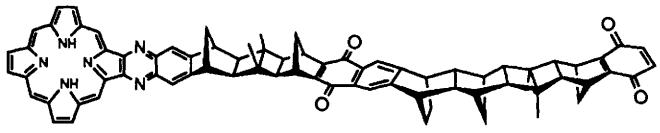
Scheme 3 *Reagents and conditions*: i, HCO_2H, THF, room temp., 24 h; ii, BBr_3, CH_2Cl_2, room temp., 18 h; iii, $HOCH_2CH_2OH$, TsOH, toluene, reflux, 18 h; iv, DDQ, CH_2Cl_2, room temp., 2 h

corresponding dimethoxynaphthalene triad **9** which could be separated (TLC) into the two diastereoisomers; **H** (the material having the higher R_f value) being stereoisomerically pure, and **L** (the material with the lower R_f value) containing a small amount (*ca.* 5%) of the **H** form.

Conversion of the diastereoisomers of each triad system **9** into the final triads **11** (*syn* and *anti* forms of **3–5**) was straightforward.† We cannot yet make unequivocal stereochemical assignment, *syn* or *anti*, to the **H** and **L** isomers of **3–5**, owing to the similarity between the NMR spectra of these isomers,† and to our inability to obtain suitable crystals for X-ray crystallography. However, the **H** and **L** isomers of **5** are tentatively assigned as *anti*-**5** and *syn*-**5** respectively, on the basis of the known stereochemical outcome of the Diels–



Scheme 4 *Reagents and conditions*: i, PbO_2, THF, reflux, 4 days; ii, $Na_2S_2O_4$, $NaHCO_3$, TEBAC, then KOH, then Me_2SO_4, 17 h, room temp.



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Alder reaction between 2,3-bismethylenenorbornane and norbornylbenzoquinone (Scheme 4). This reaction gave a 72 : 28 mixture of *syn*-**30** and *anti*-**30** (*cf.* 70 : 30 mixture of **L-5** and **H-5**). The identity of the major diastereoisomer as *syn*-**30** was confirmed by X-ray crystallography.[6] For these reasons, we assign the major isomer, **L-5**, as *syn*-**5**.

The photophysics of **3–5** will be described elsewhere; suffice to say here is that stepwise photoinduced charge separation is observed for both *syn*-**3** and *anti*-**3** with near unit efficiency, to yield giant dipole states.[7]

The synthetic strategy described here is capable of broad application and allows for the construction of novel porphyrin –quionone triads, such as **31**, from readily synthesizable porphyrin and quinone bridge components.[4b] Such systems are being currently synthesized in our laboratory.

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† All compounds gave satisfactory elemental analysis. Melting points and ^1H NMR spectroscopic data for triads **3–5** are as follows:

H-3: m.p. >250 °C (decomp.); ^1H NMR (500 MHz, $CDCl_3$) δ 0.94 (s, 6H), 1.42 (d br, *J* 8.5 Hz, 2H), 1.60–1.68 (m, 5H), 1.73 (s, 2H), 1.77 (d, *J* 10.0 Hz, 1H), 1.85 (d, *J* 10.0 Hz, 1H), 1.87 (s, 2H), 1.92 (d, *J* 11.7 Hz, 2H), 2.02–2.9 (m, 4H), 2.08 (s, 2H), 2.31 (s, 2H), 2.48 (d, *J* 10.0 Hz, 1H), 2.84 (s, 6H), 2.98 (s, 2H), 3.21 (s, 1H), 3.23 (s, 3H), 3.60 (s, 2H), 3.94 (s, 6H), 6.37 (dd, *J* 8.0 Hz, *J* 1.9 Hz, 1H), 6.70 (d *J* 1.9 Hz, 1H), 6.97 (d, *J* 8.0 Hz, 1H), 7.75 (s, 2H).

L-3: m.p. >250 °C (decomp.). ^1H NMR (500 MHz, $CDCl_3$) δ 0.94 (s, 6H), 1.45 (d br, *J* 7.8 Hz, 2H), 1.60 (s, 2H), 1.64 (s, 2H), 1.66 (d, *J* 6.9 Hz, 1H), 1.72 (s, 2H), 1.77 (d, *J* 9.4 Hz, 1H), 1.86 (d, *J* 10.2 Hz, 1H), 1.88 (s, 2H), 1.92 (d, *J* 11.8 Hz, 2H), 2.02–2.08 (m, 4H), 2.10 (s, 2H), 2.30 (s, 2H), 2.48 (d, *J* 9.7 Hz, 1H), 2.84 (s, 6H), 2.97 (s, 2H), 3.21 (s, 1H), 3.22 (s, 3H), 3.60 (s, 2H), 3.94 (s, 6H), 6.35 (dd, *J* 8.0 Hz, *J* 1.9 Hz, 1H), 6.68 (d, *J* 1.9 Hz, 1H), 6.96 (d, *J* 8.0 Hz, 1H), 7.75 (s, 2H).

H-4; m.p. 286 °C (decomp.). ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (s, 6H), 0.94 (s, 6H), 1.30 (d br, *J* 8.2 Hz, 2H) 1.39 (s, 2H), 1.53–1.61 (m, 3H), 1.64–1.74 (m, 6H), 1.78 (s, 2H), 1.86 (d, *J* 6.9 Hz, 1H), 1.87 (s, 4H), 1.92 (d, *J* 14.0 Hz, 1H), 2.02–2.07 (m, 4H), 2.10 (s, 2H), 2.13 (d, *J* 9.7 Hz, 1H), 2.18 (s, 2H), 2.31 (s, 2H), 2.88 (s, 6H), 2.98 (s, 2H), 3.05 (s, 2H), 3.14 (s, 1H), 3.16 (s, 1H), 3.61 (s, 2H), 3.97 (s, 6H), 6.44 (s br, 1H), 6.69 (s br, 1H) 7.00 (d, *J* 8.0 Hz, 1H), 7.76 (s, 2H).

L-4; m.p. 278 °C (decomp.). ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (s, 6H), 0.94 (s, 6H), 1.34 (d br, *J* 8.2 Hz, 2H), 1.36 (s, 2H), 1.54–1.67 (m, 7H), 1.73 (s, 2H), 1.78 (s, 2H), 1.87–1.88 (m, 5H), 1.93 (d, *J* 14.0 Hz, 1H), 2.02–2.07 (m, 4H), 2.09 (s, 2H), 2.13 (d, *J* 9.7 Hz, 1H), 2.18 (s, 2H), 2.30 (s, 2H), 2.89 (s, 6H), 2.98 (s, 2H), 3.05 (s, 2H), 3.14 (s, 1H), 3.16 (s, 1H), 3.62 (s, 2H), 3.97 (s, 6H), 6.44 (d, *J* 8.0 Hz, 1H), 6.69 (s br, 1H), 7.00 (d, *J* 8.0 Hz, 1H), 7.76 (s, 2H).

H-5; m.p. 280 °C (decomp.). ^1H NMR (500 MHz, $CDCl_3$) δ 0.94 (s, 6H), 1.02 (s, 6H), 1.60–1.65 (m, 3H), 1.66–1.69 (m, 3H), 1.73 (s, 2H), 1.83 (d, *J* 7.7 Hz, 1H), 1.85 (d, *J* 8.8 Hz, 1H), 1.88 (s, 2H), 1.89 (s, 2H), 1.93 (d, *J* 11.8 Hz, 1H), 1.97 (s, 2H), 1.97 (d, *J* 8.0 Hz, 1H), 2.05 (d, *J* 8.4 Hz, 2H), 2.11 (s, 2H), 2.31 (s, 2H), 2.89 (s, 6H), 2.98 (s, 2H), 3.20 (s, 1H), 3.22 (s, 1H), 3.38 (s, 2H), 3.60 (s, 2H), 3.94 (s, 6H), 6.44 (dd, *J* 8.0 Hz, *J* 1.9 Hz, 1H), 6.70 (d, *J* 1.9 Hz, 1H), 7.00 (d, *J* 8.0 Hz, 1H), 7.77 (s, 2H).

L-5; m.p. >250 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 0.94 (s, 6H), 1.02 (s, 6H), 1.59–1.67 (m, 6H), 1.71 (s, 2H), 1.82–1.86 (m, 2H), 1.86 (s, 2H), 1.87 (s, 2H), 1.92 (d, *J* 11.8 Hz, 1H), 1.94 (s, 2H), 1.97 (d, *J* 9.4 Hz, 1H), 2.04 (d, *J* 8.7 Hz, 2H), 2.10 (s, 2H), 2.30 (s, 2H), 2.89 (s, 6H), 2.98 (s, 2H), 3.20 (s, 1H), 3.21 (s, 1H), 3.38 (s, 2H), 3.61 (s, 2H), 3.94 (s, 6H), 6.42 (dd, *J* 8.0 Hz, *J* 1.9 Hz, 1H), 6.68 (d, *J* 1.9 Hz, 1H), 6.99 (d, *J* 8.0 Hz, 1H), 7.77 (s, 2H).

References

1 (*a*) M. A. Fox and M. Chanon, ed., *Photoinduced Electron Transfer*, Parts A–D, Elsevier, Amsterdam, 1988; (*b*) M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435; (*c*) D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 1993, **26**, 198.

2 (*a*) L. T. Calcaterra, G. L. Closs and J. R. Miller, *J. Am. Chem. Soc.*, 1983, **105**, 670; (*b*) A. D. Joran, B. A. Leland, G. G. Geller, J. J. Hopfield and P. B. Dervan, *J. Am. Chem. Soc.*, 1984, **106**, 6090; (*c*) M. R. Wasielewski, M. P. Niemczyk, W. A. Svec and E. B. Pewitt, *J. Am. Chem. Soc.*, 1985, **107**, 5562.

3 (*a*) H. Oevering, M. N. Paddon-Row, M. Heppener, A. M. Oliver, E. Cotsaris, J. W. Verhoeven and N. S. Hush, *J. Am. Chem. Soc.*, 1987, **109**, 3258; (*b*) A. M. Oliver, D. C. Craig, M. N. Paddon-Row, J. Kroon and J. W. Verhoeven, *Chem. Phys. Lett.*, 1988, **150**, 366.

4 (*a*) A. Golka, P. J. Keyte and M. N. Paddon-Row, *Tetrahedron*, 1992, **48**, 7663; (*b*) M. Antolovich, A. M. Oliver and M. N. Paddow-Row, *J. Chem. Soc., Perkin Trans. 2*, 1989, 783; (*c*) D. C. Craig, A. M. Oliver and M. N. Paddow-Row, *J. Chem. Soc., Perkin Trans. 1*, 1993, 197; (*d*) A. M. Oliver and M. N. Paddon-Row, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1145; (*e*) D. C. Craig, J. M. Lawson, A. M. Oliver and M. N. Paddow-Row, *J. Chem. Soc., Perkin Trans. 1*, 1990, 3305; (*f*) M. N. Paddon-Row, E. Cotsaris and H. K. Patney, *Tetrahedron*, 1986, **42**, 1779; (*g*) R. N. Warrener, I. G. Pitt and D. N. Butler, *J. Chem. Soc., Chem. Commun.*, 1983, 1340.

5 (*a*) B. V. Lap and M. N. Paddon-Row, *J. Org. Chem.*, 1979, **44**, 4979; (*b*) M. S. Raasch, *J. Org. Chem.*, 1980, **45**, 856.

6 D. C. Craig, J. M. Lawson and M. N. Paddon-Row, unpublished results.

7 J. M. Lawson, M. N. Paddon-Row, W. Schuddeboom, J. M. Warman, A. H. Clayton and K. P. Ghiggino, *J. Phys. Chem.*, in the press.