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Crystal Structures of Three Long, Rigid, Norbornylogous Compounds of Relevance to Distance-Dependence Studies of Long-Range Intramolecular Electron-Transfer Processes

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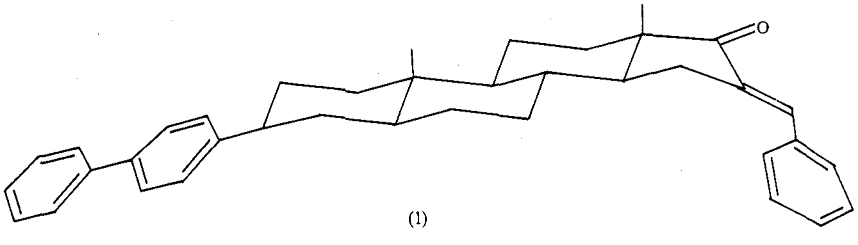
Abstract

Results of previous studies revealed that photoinduced intramolecular electron transfer between the dimethoxynaphthalene donor and dicyanomethylene acceptor groups in the series of rigid alicyclic compounds (2a)–(6a) is extremely rapid. As the first step towards determining the distance dependence of the rate of photoinduced intramolecular electron transfer in these molecules, crystal structures of (3a), (4b) and (5b), have been measured. The edge-to-edge distance between the two chromophores in (3a), (4b) and (5b) is 6·8, 9·4, and 11·5 Å respectively. The estimated centre-to-centre separation between the chromophores in (2a)–(6a) ranges from *c.* 7·1 Å in (2a) to *c.* 14·9 Å in (6a). From these results, dipole moments of the charge-separated states of (2a)–(6a), following photoinduced intramolecular electron transfer, could be estimated. These predicted values were in excellent agreement with those determined experimentally by using the time-resolved microwave conductivity technique. An interesting structural feature of (3a), (4b) and (5b) is the pronounced curvature of the molecular backbone in these molecules. It is predicted that approximately 24 linearly fused norbornyl and bicyclo[2.2.0] units would complete a circle, forming a member of a novel class of macrocycles, tentatively called dogcollaranes.

Introduction

Single electron transfer is the most fundamental of all chemical reactions and plays a pivotal role in a variety of thermal[1] and photochemical[2] processes, the most spectacular of which occur in biological systems. A wealth of evidence



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has been gathered that shows that both thermally induced[1] and photoinduced[3-11] 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. Indeed, many biological electron transfer processes involve such long-range events. This is dramatically illustrated by the primary steps in photosynthesis[12] in which extremely rapid (subnanosecond) photoinduced electron transfer occurs along a gradient of redox centres which are rigidly embedded in a lipid membrane and separated from each other by well defined distances of 10 Å or greater.[13,14]

Recent studies on a number of modified biological and non-biological systems, containing redox centres at widely different distances, have revealed electron transfer rates ranging from the picosecond regime to many seconds.[15-27] Miller and coworkers have provided some superb examples of rapid, long-range, thermal intramolecular electron transfer occurring over large distances.[26,27] Thus, the rate constant for intramolecular electron transfer from the biphenyl donor to the cinnamoyl acceptor in the anion radical of (1) was found to be greater than 10^9 s^{-1}, notwithstanding a donor–acceptor edge-to-edge distance of *c*. 10 Å.[26,27]

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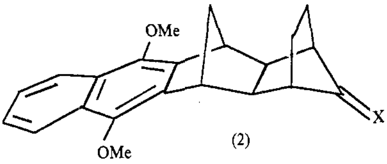
A central issue in electron transfer dynamics is the question of the mechanism of long-range electron transfer in which the donor and acceptor groups are situated at least 6 Å apart, either as separate entities, or connected to each other through a non-conjugated sigma-bonded framework. Does it occur via direct electron tunnelling through space, or does it occur via a through-bond mechanism?[28–30] Some sort of through-space electron tunnelling has, until recently, been the favoured mechanism, being proposed, for example, to account for the rapid rates of intramolecular electron transfer observed in anion radicals such as (1)[26] (but which was subsequently rejected in favour of a through-bond mechanism).[27]

The through-bond mechanism involves coupling of the donor and acceptor π (or π^*) orbitals with the σ (and σ^*) orbitals of the interconnecting sigma-bonded framework. Although this mechanism has been occasionally advocated,[9,30–34] it has not, until recently, enjoyed much popularity. This is largely due to the widely held belief that coupling between sigma and pi orbitals is too weak to allow through-bond mediated electron transfer to occur.



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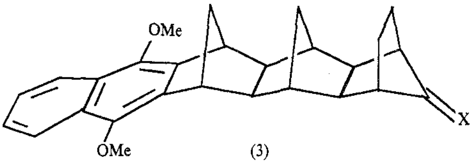

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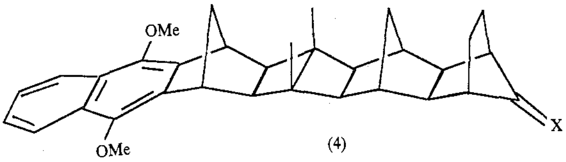

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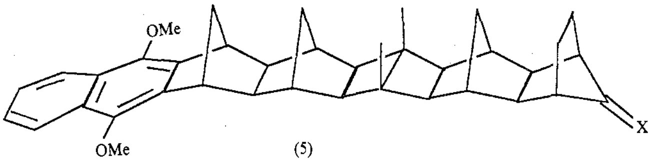
(a) X = C(CN)$_2$
(b) X = O



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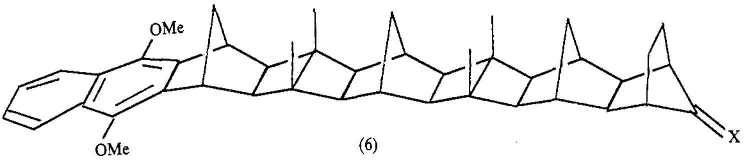

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In order to investigate more fully the role played by through-bond interactions in long-range intramolecular electron transfer processes, it is necessary to make a more thorough and systematic study of the distance dependence of the rates of electron transfer in well defined systems in which the donor and acceptor groups are held rigidly with respect to each other at various distances. Several recent studies have addressed this challenge[25,27,35,36] but the model compounds employed all suffered from one or more disadvantages such as the lack of molecular symmetry, or the presence of conformational mobility, which allowed the chromophores to rotate with respect to each other. More seriously, the molecular backbones of the model systems did not offer much scope in terms of varying their lengths, thereby severely restricting the range of the distance dependence studies to two or three different donor–acceptor separations.

Recently, we have successfully overcome these objections through the synthesis of the series of rigid systems (2a)–(6a),[34,37] along which the dimethoxynaphthalene donor and dicyanomethylene acceptor groups are separated by 4, 6, 8, 10 and 12 sigma bonds.

Picosecond time-resolved studies on (2a)–(6a) revealed that the rate constants for photoinduced intramolecular electron transfer from the first electronically excited state of the dimethoxynaphthalene donor to the dicyanomethylene acceptor in these compounds are very large indeed,[3-6,37] being *c.* 10^{10} s^{-1} and 10^9 s^{-1} (in benzene solution) for (5a) and (6a) respectively.

An important goal of our electron transfer studies is to obtain a quantitative distance dependence of the rates of electron transfer. In a step towards realizing this objective, we have measured the crystal structures of (3a), (4b) and (5b) in which the chromophores are separated by 6, 8, and 10 bonds respectively. Herein, we present the results of these crystal studies.

Synthesis

The synthesis of these compounds has been reported elsewhere: (3a),[37] (4b),[34] (5b).[34]

Crystallography

Crystal data for (3a).—$C_{30}H_{28}N_2O_2$, M 448·6, orthorhombic, space group $P2_12_12_1$, a 11·899(1), b 12·685(1), c 15·502(1) Å, V 2339·9(2) Å^3, D_m 1·25, D_c 1·27 g cm^{-3}, Z 4, μ_{Cu} 5·92 cm^{-1}. Crystal size 0·20 by 0·26 by 0·31 mm, $2\theta_{max}$ 140°, number of reflections was 2064 considered observed out of 2515 measured. Final residuals R, R_w were 0·041, 0·057.

Crystal data for (4b).—$C_{33}H_{36}O_3$, M 480·6, orthorhombic, space group $Pnma$, a 21·454(2), b 11·471(1), c 20·315(2) Å, V 4999·5(7) Å^3, D_m 1·27, D_c 1·28 g cm^{-3}, Z 8, μ_{Cu} 5·89 cm^{-1}. Crystal size 0·11 by 0·18 by 0·56 mm, $2\theta_{max}$ 120°, number of reflections was 2374 considered observed out of 3917 measured. Final residuals R, R_w were 0·051, 0·068. The structure consists of molecules with perfect mirror symmetry lying across the planes located at $y = 1/4$ and $3/4$, making the asymmetric unit two independent half molecules.

Crystal data for (5b).—$C_{38}H_{42}O_3$, M 546·8, monoclinic, space group $P2_1/c$, a 19·125(2), b 12·408(1), c 12·398(2) Å, β 91·72(1)°, V 2940·8(6) Å^3, D_m 1·25, D_c 1·23 g cm^{-3}, Z 4,

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μ_{Cu} 5·58 cm^{-1}. Crystal size 0·12 by 0·14 by 0·40 mm, $2\theta_{max}$ 140°, number of reflections was 3551 considered observed out of 5561 measured. Final residuals R, R_w were 0·048, 0·068.

Structure determination.—Reflection data for crystals of rather poor quality were measured with an Enraf–Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode, nickel-filtered copper radiation (λ 1·54056 Å) being used. Data were corrected for absorption. Reflections with $I > 3\sigma(I)$

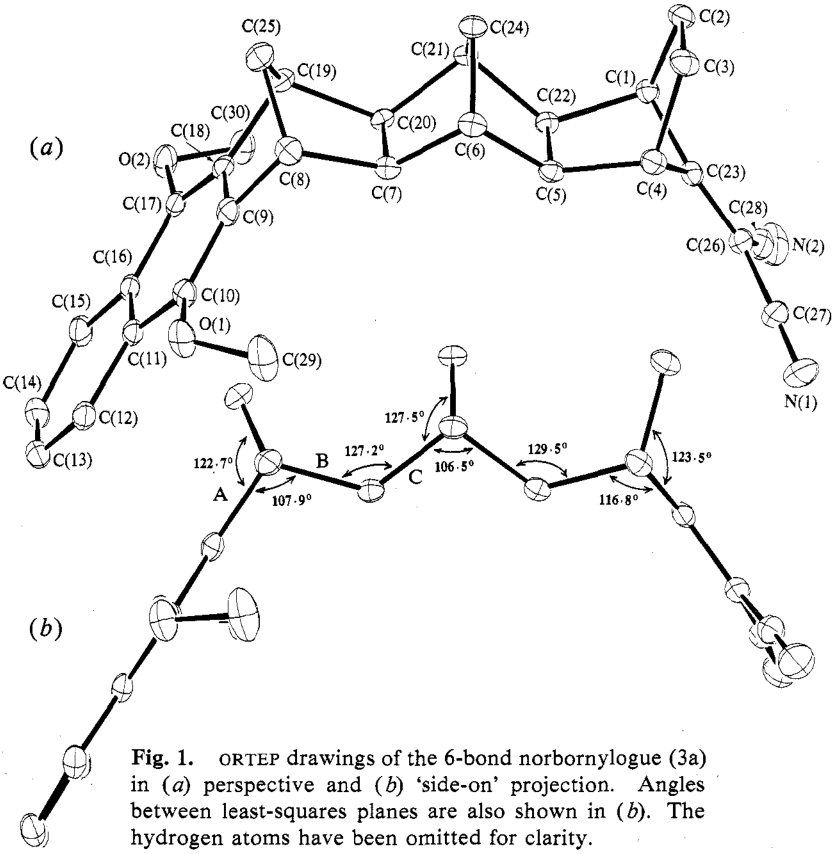

Fig. 1. ORTEP drawings of the 6-bond norbornylogue (3a) in (*a*) perspective and (*b*) 'side-on' projection. Angles between least-squares planes are also shown in (*b*). The hydrogen atoms have been omitted for clarity.

Table 1. Non-hydrogen atomic parameters for (3a)

E.s.d. in parentheses in this and subsequent Tables

Atom	x	y	z	Atom	x	y	z
O(1)	0·6251(3)	0·1958(2)	0·5133(1)	C(14)	0·7843(3)	0·1230(3)	0·8043(2)
O(2)	0·4588(2)	0·0007(2)	0·8087(1)	C(15)	0·6780(3)	0·0794(3)	0·8064(2)
N(1)	0·5485(3)	−0·4427(4)	0·2460(3)	C(16)	0·6065(3)	0·0866(2)	0·7329(2)
N(2)	0·4348(4)	−0·5883(3)	0·4908(3)	C(17)	0·4972(3)	0·0429(2)	0·7325(2)
C(1)	0·2558(2)	−0·3477(2)	0·4582(2)	C(18)	0·4336(2)	0·0496(2)	0·6602(2)
C(2)	0·1498(2)	−0·3281(3)	0·4036(2)	C(19)	0·3163(2)	0·0100(2)	0·6368(2)
C(3)	0·1927(3)	−0·2708(3)	0·3217(2)	C(20)	0·3412(2)	−0·0859(2)	0·5759(2)
C(4)	0·3210(3)	−0·2650(3)	0·3360(2)	C(21)	0·2467(2)	−0·1570(2)	0·5405(2)
C(5)	0·3569(2)	−0·1894(2)	0·4102(2)	C(22)	0·3121(2)	−0·2459(2)	0·4943(2)
C(6)	0·3112(2)	−0·0761(2)	0·4204(2)	C(23)	0·3390(2)	−0·3662(2)	0·3859(2)
C(7)	0·3863(2)	−0·0307(2)	0·4918(2)	C(24)	0·1983(2)	−0·0932(3)	0·4655(2)
C(8)	0·3820(3)	0·0886(2)	0·5173(2)	C(25)	0·2798(3)	0·0993(3)	0·5772(3)
C(9)	0·4746(3)	0·0999(2)	0·5837(2)	C(26)	0·4149(3)	−0·4419(3)	0·3760(2)
C(10)	0·5812(3)	0·1422(2)	0·5824(2)	C(27)	0·4892(3)	−0·4437(4)	0·3037(3)
C(11)	0·6484(3)	0·1382(2)	0·6577(2)	C(28)	0·4266(3)	−0·5248(3)	0·4383(3)
C(12)	0·7580(3)	0·1834(2)	0·6611(2)	C(29)	0·6265(5)	0·1486(4)	0·4334(3)
C(13)	0·8223(3)	0·1760(3)	0·7321(2)	C(30)	0·4320(3)	−0·1063(3)	0·8112(2)

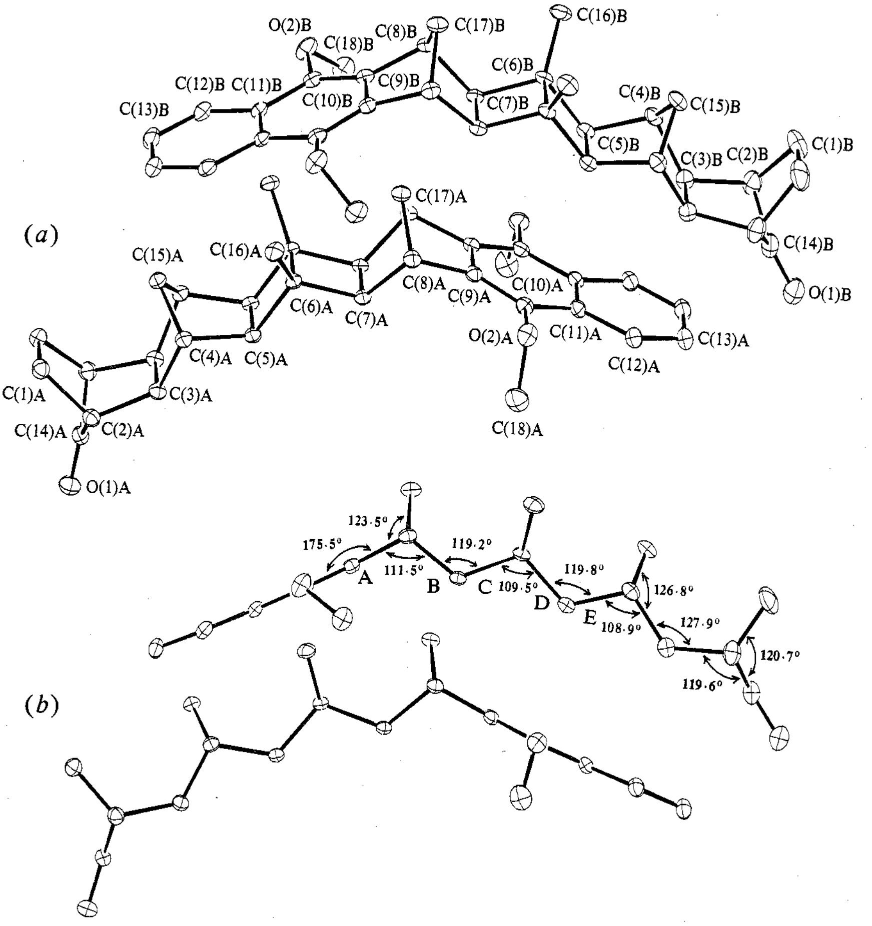

Fig. 2. ORTEP drawings of the 8-bond norbornylogue (4b) in (*a*) perspective and (*b*) 'side-on' projection. Angles between least-squares planes are also shown in (*b*). The hydrogen atoms have been omitted for clarity.

Table 2. Non-hydrogen atomic parameters for (4b)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(1)A	0·4756(2)	0·2500	0·6812(2)	O(1)B	0·2902(2)	0·2500	−0·1211(2)
O(2)A	0·2994(1)	0·4935(2)	0·1779(1)	O(2)B	0·0191(1)	0·0071(2)	0·3620(1)
C(1)A	0·3251(2)	0·3170(3)	0·6967(2)	C(1)B	0·1448(3)	0·1834(5)	−0·1441(2)
C(2)A	0·3771(2)	0·3504(3)	0·6497(2)	C(2)B	0·1907(2)	0·1489(4)	−0·0908(2)
C(3)A	0·3634(2)	0·3190(3)	0·5768(2)	C(3)B	0·1694(2)	0·1813(3)	−0·0206(2)
C(4)A	0·3010(1)	0·3487(3)	0·5424(2)	C(4)B	0·1030(2)	0·1515(3)	0·0040(2)
C(5)A	0·3127(1)	0·3185(3)	0·4695(2)	C(5)B	0·1022(1)	0·1815(2)	0·0772(2)
C(6)A	0·2574(1)	0·3195(3)	0·4200(1)	C(6)B	0·0385(1)	0·1790(3)	0·1133(2)
C(7)A	0·2836(1)	0·3185(3)	0·3489(2)	C(7)B	0·0487(1)	0·1816(3)	0·1886(2)
C(8)A	0·2390(1)	0·3487(3)	0·2914(2)	C(8)B	−0·0070(1)	0·1517(3)	0·2330(2)
C(9)A	0·2724(1)	0·3121(3)	0·2289(2)	C(9)B	0·0108(1)	0·1877(3)	0·3018(2)
C(10)A	0·2987(2)	0·3720(3)	0·1784(2)	C(10)B	0·0226(1)	0·1275(3)	0·3587(2)
C(11)A	0·3237(2)	0·3124(3)	0·1231(2)	C(11)B	0·0334(1)	0·1879(3)	0·4182(2)
C(12)A	0·3473(2)	0·3715(4)	0·0673(2)	C(12)B	0·0428(2)	0·1291(3)	0·4788(2)
C(13)A	0·3702(2)	0·3116(3)	0·0147(2)	C(13)B	0·0505(2)	0·1884(3)	0·5357(2)
C(14)A	0·4214(3)	0·2500	0·6641(2)	C(14)B	0·2364(4)	0·2500	−0·1020(3)
C(15)A	0·2584(2)	0·2500	0·5639(2)	C(15)B	0·0629(3)	0·2500	−0·0245(3)
C(16)A	0·2017(2)	0·3972(3)	0·4357(2)	C(16)B	−0·0098(2)	0·0941(4)	0·0877(2)
C(17)A	0·1904(2)	0·2500	0·2961(3)	C(17)B	−0·0539(2)	0·2500	0·2177(3)
C(18)A	0·3576(2)	0·5417(4)	0·1966(2)	C(18)B	0·0631(2)	−0·0577(3)	0·3258(2)

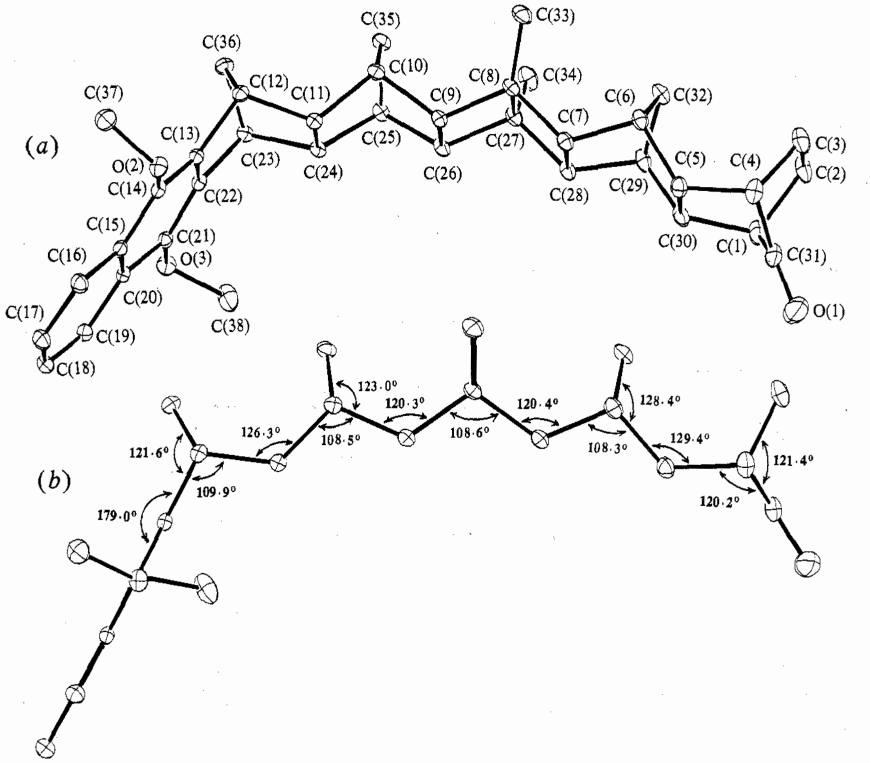

Fig. 3. ORTEP drawings of the 10-bond norbornylogue (5b) in (*a*) perspective and (*b*) 'side-on' projection. Angles between least-squares planes are also shown in (*b*). The hydrogen atoms have been omitted for clarity.

Table 3. Non-hydrogen atomic parameters for (5b)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(1)	0·2467(2)	0·3802(2)	0·1102(3)	C(19)	0·9513(1)	0·6819(2)	0·2562(2)
O(2)	0·8520(1)	0·5155(2)	0·5721(1)	C(20)	0·9189(1)	0·5923(2)	0·3045(2)
O(3)	0·9187(1)	0·4943(2)	0·1367(1)	C(21)	0·9019(1)	0·4971(2)	0·2441(2)
C(1)	0·3280(2)	0·2369(3)	0·0542(2)	C(22)	0·8733(1)	0·4119(2)	0·2951(2)
C(2)	0·2962(2)	0·1251(3)	0·0740(3)	C(23)	0·8504(1)	0·3007(2)	0·2577(2)
C(3)	0·2776(2)	0·1289(3)	0·1958(3)	C(24)	0·7690(1)	0·3047(2)	0·2551(2)
C(4)	0·3001(2)	0·2429(3)	0·2322(3)	C(25)	0·7257(1)	0·2073(2)	0·2158(2)
C(5)	0·3805(2)	0·2584(2)	0·2352(2)	C(26)	0·6499(1)	0·2483(2)	0·2125(2)
C(6)	0·4321(1)	0·1776(2)	0·2874(2)	C(27)	0·5898(1)	0·1668(2)	0·1906(2)
C(7)	0·5035(1)	0·2350(2)	0·2859(2)	C(28)	0·5220(1)	0·2312(2)	0·1633(2)
C(8)	0·5714(1)	0·1720(2)	0·3171(2)	C(29)	0·4587(2)	0·1715(2)	0·1114(2)
C(9)	0·6317(1)	0·2532(2)	0·3357(2)	C(30)	0·3991(2)	0·2544(2)	0·1127(2)
C(10)	0·7002(1)	0·2158(2)	0·3924(2)	C(31)	0·2835(2)	0·3021(3)	0·1293(3)
C(11)	0·7518(1)	0·3106(2)	0·3782(2)	C(32)	0·4410(1)	0·0914(2)	0·2002(2)
C(12)	0·8251(1)	0·3096(2)	0·4347(2)	C(33)	0·5654(2)	0·0795(2)	0·3963(2)
C(13)	0·8572(1)	0·4174(2)	0·4072(2)	C(34)	0·6058(2)	0·0692(3)	0·1218(2)
C(14)	0·8710(1)	0·5076(2)	0·4655(2)	C(35)	0·7253(1)	0·1303(2)	0·3127(2)
C(15)	0·9032(1)	0·5979(2)	0·4155(2)	C(36)	0·8698(1)	0·2378(2)	0·3621(2)
C(16)	0·9199(1)	0·6930(2)	0·4735(2)	C(37)	0·9049(2)	0·4829(3)	0·6475(3)
C(17)	0·9525(2)	0·7773(2)	0·4244(3)	C(38)	0·8609(2)	0·5007(3)	0·0639(2)
C(18)	0·9676(2)	0·7719(2)	0·3158(3)				

were considered observed. The structures were solved by using direct phasing and Fourier methods. Hydrogen atoms were located in difference Fouriers and assigned thermal parameters equal to those of the atom to which bonded. Positional and anisotropic thermal parameters were refined for the non-hydrogen atoms. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o)+(0\cdot04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w = (\Sigma w(\Delta F)^2/\Sigma wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography.[38] Structure solution was by MULTAN 80,[39] and refinement used BLOCKLS, a local version of ORFLS.[40] ORTEP-II[41] was used for the preparation of the structural diagrams. A Cyber 171 computer was used for all calculations.

ORTEP drawings[41] of (3a), (4b) and (5b) are given in Figs 1–3 respectively. For purposes of clarity, the hydrogen atoms have been omitted. Non-hydrogen atom coordinates for (3a),

Table 4. Bond lengths (Å) for (3a)

Atoms	Distance	Atoms	Distance	Atoms	Distance
C(1)–C(2)	1·540(4)	C(11)–C(16)	1·427(4)	C(23)–C(26)	1·326(4)
C(2)–C(3)	1·549(5)	C(12)–C(13)	1·344(5)	C(26)–C(27)	1·428(5)
C(3)–C(4)	1·545(4)	C(13)–C(14)	1·382(5)	C(27)–N(1)	1·139(5)
C(4)–C(5)	1·557(4)	C(14)–C(15)	1·381(5)	C(26)–C(28)	1·435(5)
C(5)–C(6)	1·545(4)	C(15)–C(16)	1·424(5)	C(28)–N(2)	1·149(5)
C(5)–C(22)	1·580(4)	C(16)–C(17)	1·414(4)	C(6)–C(24)	1·530(4)
C(6)–C(7)	1·535(4)	C(17)–C(18)	1·355(4)	C(21)–C(24)	1·529(4)
C(7)–C(8)	1·565(4)	C(18)–C(19)	1·528(4)	C(8)–C(25)	1·535(5)
C(7)–C(20)	1·574(4)	C(19)–C(20)	1·567(4)	C(19)–C(25)	1·524(5)
C(8)–C(9)	1·515(5)	C(20)–C(21)	1·543(4)	C(10)–O(1)	1·372(4)
C(9)–C(10)	1·377(4)	C(21)–C(22)	1·546(4)	O(1)–C(29)	1·375(5)
C(9)–C(18)	1·431(4)	C(22)–C(1)	1·558(4)	C(17)–O(2)	1·375(4)
C(10)–C(11)	1·416(4)	C(1)–C(23)	1·515(4)	O(2)–C(30)	1·394(4)
C(11)–C(12)	1·425(4)	C(4)–C(23)	1·515(5)		

Table 5. Bond lengths (Å) for molecules A and B of (4b)

$^{\mathrm{I}}$ refers to the symmetry transformation x, $1/2-y$, z

Atoms	A	B	Atoms	A	B
C(1)–C(2)	1·518(5)	1·516(6)	C(9)–C(9)$^{\mathrm{I}}$	1·425(6)	1·430(6)
C(1)–C(1)$^{\mathrm{I}}$	1·538(7)	1·529(11)	C(10)–C(11)	1·421(4)	1·412(4)
C(2)–C(3)	1·552(4)	1·544(5)	C(11)–C(12)	1·415(5)	1·417(4)
C(3)–C(4)	1·548(4)	1·549(5)	C(11)–C(11)$^{\mathrm{I}}$	1·431(7)	1·425(6)
C(3)–C(3)$^{\mathrm{I}}$	1·583(6)	1·577(7)	C(12)–C(13)	1·363(5)	1·353(5)
C(4)–C(5)	1·541(4)	1·525(4)	C(13)–C(13)$^{\mathrm{I}}$	1·413(8)	1·412(8)
C(5)–C(6)	1·556(4)	1·551(4)	C(2)–C(14)	1·521(5)	1·536(6)
C(5)–C(5)$^{\mathrm{I}}$	1·572(6)	1·572(6)	C(14)–O(1)	1·213(6)	1·216(7)
C(6)–C(7)	1·548(4)	1·545(4)	C(4)–C(15)	1·519(4)	1·533(5)
C(6)–C(6)$^{\mathrm{I}}$	1·595(6)	1·628(6)	C(6)–C(16)	1·526(4)	1·514(4)
C(7)–C(8)	1·550(4)	1·535(4)	C(8)–C(17)	1·542(5)	1·543(5)
C(7)–C(7)$^{\mathrm{I}}$	1·571(6)	1·570(6)	C(10)–O(2)	1·393(4)	1·385(4)
C(8)–C(9)	1·518(4)	1·508(5)	O(2)–C(18)	1·418(5)	1·408(4)
C(9)–C(10)	1·357(4)	1·370(4)			

[38] Ibers, J. A., and Hamilton, W. C., (Eds) 'International Tables for X-Ray Crystallography' Vol. 4 (Kynoch Press: Birmingham 1974).

[39] Main, P., 'MULTAN 80' University of York, England, 1980.

[40] Busing, W. R., Martin, K. O., and Levy, H. A., 'ORFLS' Oak Ridge National Laboratory, Tennessee, U.S.A., 1962.

[41] Johnson, C. K., 'ORTEP-II' Oak Ridge National Laboratory, Tennessee, U.S.A., 1976.

(4b) and (5b) are given in Tables 1–3 respectively. Non-hydrogen interatomic distances for (3a), (4b) and (5b) are given in Tables 4–6 respectively, and the corresponding interatomic angles (Tables 7–9) are also listed. Angles between least-squares planes for (3a), (4b) and (5b) are shown in Figs 1 *b*, 2 *b* and 3 *b*, respectively. Material deposited† with this Journal includes all atom and thermal parameters and all interatomic distances, angles, torsional angles and structure factors. *In the following discussion, the crystallographic numbering schemes shown in Figs 1–3 will be used to describe atom positions in (3a), (4b) and (5b) respectively.*

Table 6. Bond lengths (Å) for (5b)

Atoms	Distance	Atoms	Distance	Atoms	Distance
C(1)–C(2)	1·537(4)	C(13)–C(22)	1·434(3)	C(30)–C(1)	1·537(4)
C(2)–C(3)	1·563(4)	C(14)–C(15)	1·429(3)	C(1)–C(31)	1·515(5)
C(3)–C(4)	1·542(5)	C(15)–C(16)	1·414(3)	C(4)–C(31)	1·499(5)
C(4)–C(5)	1·549(4)	C(15)–C(20)	1·419(3)	O(1)–C(31)	1·217(4)
C(5)–C(6)	1·536(4)	C(16)–C(17)	1·370(4)	C(6)–C(32)	1·533(4)
C(5)–C(30)	1·572(4)	C(17)–C(18)	1·387(4)	C(29)–C(32)	1·528(4)
C(6)–C(7)	1·541(3)	C(18)–C(19)	1·370(4)	C(8)–C(33)	1·516(3)
C(7)–C(8)	1·553(4)	C(19)–C(20)	1·414(3)	C(27)–C(34)	1·517(4)
C(7)–C(28)	1·572(3)	C(20)–C(21)	1·431(3)	C(10)–C(35)	1·537(3)
C(8)–C(9)	1·544(3)	C(21)–C(22)	1·357(3)	C(25)–C(35)	1·535(3)
C(8)–C(27)	1·619(3)	C(22)–C(23)	1·516(3)	C(12)–C(36)	1·543(3)
C(9)–C(10)	1·539(3)	C(23)–C(24)	1·555(3)	C(23)–C(36)	1·547(3)
C(9)–C(26)	1·577(3)	C(24)–C(25)	1·537(3)	C(14)–O(2)	1·385(3)
C(10)–C(11)	1·549(3)	C(25)–C(26)	1·536(4)	O(2)–C(37)	1·415(3)
C(11)–C(12)	1·548(3)	C(26)–C(27)	1·548(3)	C(21)–O(3)	1·379(3)
C(11)–C(24)	1·573(3)	C(27)–C(28)	1·552(4)	O(3)–C(38)	1·408(4)
C(12)–C(13)	1·514(3)	C(28)–C(29)	1·543(3)		
C(13)–C(14)	1·354(3)	C(29)–C(30)	1·536(4)		

Discussion

The results of the three structure determinations are consistent with the expected stoichiometries and connectivities. Both (3a) and (4b) have C_s point group symmetry, the latter being crystallographically exact. The rigid framework of (5b) also possesses this symmetry, but the two methoxy groups adopt conformations that reduce the overall molecular symmetry of this molecule to C_1. The bond lengths, bond angles and interplanar angles of the norbornyl units in (3a), (4b) and (5b) resemble those for the norbornyl ring found in a variety of molecules, such as norbornane,[42] aldrin,[43] (7a)–(7c),[33] and related compounds.[44] The average envelope angle of the six-membered ring of the norbornyl unit (that is, the angle between the planes C and D in Fig. 2 *b*) in (3a), (4b) and (5b) is *c.* 108°, and the average distance between the midpoints of the ethano bonds, as indicated by the dashed lines in (8), is about 2·45 Å.

The internal angles between the carbon atoms of the bicyclo[2.2.0] units in (4b) and (5b) are close to 90°. As expected, the angles made by the methyl groups in the bicyclo[2.2.0] group are substantially larger than the tetrahedral value. For example,

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† Available on application to the Australian Journal of Chemistry, 314 Albert Street, East Melbourne, Vic. 3002.

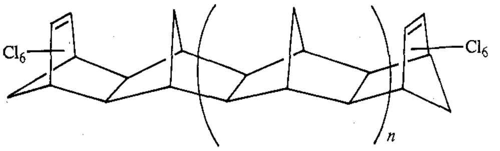
[42] Dallinga, G., and Toneman, L. H., *Recl Trav. Chim. Pays-Bas*, 1968, **87**, 795.

[43] DeLacy, T. P., and Kennard, C. H. L., *J. Chem. Soc., Perkin Trans. 2*, 1972, 2153.

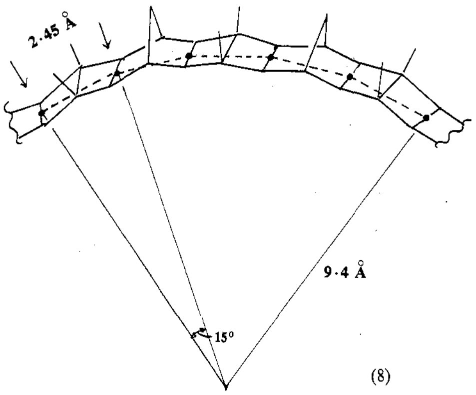
[44] Craig, D. C., Paddon-Row, M. N., and Patney, H. K., *Aust. J. Chem.*, 1986, **39**, 1587.

Table 7. **Interatomic angles (degrees) for (3a)**

Atoms	Angle	Atoms	Angle
C(10)–O(1)–C(29)	119·5(3)	C(13)–C(14)–C(15)	120·9(4)
C(17)–O(2)–C(30)	118·6(2)	C(14)–C(15)–C(16)	120·2(3)
C(2)–C(1)–C(22)	114·6(2)	C(11)–C(16)–C(15)	118·3(3)
C(2)–C(1)–C(23)	98·8(2)	C(11)–C(16)–C(17)	119·8(3)
C(22)–C(1)–C(23)	96·5(2)	C(15)–C(16)–C(17)	121·8(3)
C(1)–C(2)–C(3)	104·9(2)	O(2)–C(17)–C(16)	117·0(3)
C(2)–C(3)–C(4)	103·3(3)	O(2)–C(17)–C(18)	123·3(3)
C(3)–C(4)–C(5)	114·0(3)	C(16)–C(17)–C(18)	119·5(3)
C(3)–C(4)–C(23)	99·9(3)	C(9)–C(18)–C(17)	121·5(3)
C(5)–C(4)–C(23)	96·0(2)	C(9)–C(18)–C(19)	105·2(3)
C(4)–C(5)–C(6)	123·5(2)	C(17)–C(18)–C(19)	133·3(3)
C(4)–C(5)–C(22)	103·8(2)	C(18)–C(19)–C(20)	103·0(2)
C(6)–C(5)–C(22)	102·6(2)	C(18)–C(19)–C(25)	99·2(3)
C(5)–C(6)–C(7)	102·6(2)	C(20)–C(19)–C(25)	105·4(2)
C(5)–C(6)–C(24)	102·9(2)	C(7)–C(20)–C(19)	102·6(2)
C(7)–C(6)–C(24)	103·5(2)	C(7)–C(20)–C(21)	102·4(2)
C(6)–C(7)–C(8)	121·7(2)	C(19)–C(20)–C(21)	122·0(2)
C(6)–C(7)–C(20)	103·4(2)	C(20)–C(21)–C(22)	102·9(2)
C(8)–C(7)–C(20)	102·1(2)	C(20)–C(21)–C(24)	103·6(2)
C(7)–C(8)–C(9)	103·8(2)	C(22)–C(21)–C(24)	102·9(2)
C(7)–C(8)–C(25)	105·3(3)	C(1)–C(22)–C(5)	103·0(2)
C(9)–C(8)–C(25)	99·0(3)	C(1)–C(22)–C(21)	123·6(2)
C(8)–C(9)–C(10)	134·1(3)	C(5)–C(22)–C(21)	102·8(2)
C(8)–C(9)–C(18)	105·8(3)	C(1)–C(23)–C(4)	98·9(2)
C(10)–C(9)–C(18)	120·0(3)	C(1)–C(23)–C(26)	130·0(3)
O(1)–C(10)–C(9)	123·7(3)	C(4)–C(23)–C(26)	130·6(3)
O(1)–C(10)–C(11)	116·5(3)	C(6)–C(24)–C(21)	95·3(2)
C(9)–C(10)–C(11)	119·6(3)	C(8)–C(25)–C(19)	94·4(2)
C(10)–C(11)–C(12)	122·2(3)	C(23)–C(26)–C(27)	121·6(4)
C(10)–C(11)–C(16)	119·5(3)	C(23)–C(26)–C(28)	121·2(3)
C(12)–C(11)–C(16)	118·3(3)	C(27)–C(26)–C(28)	117·1(3)
C(11)–C(12)–C(13)	121·5(3)	N(1)–C(27)–C(26)	178·3(5)
C(12)–C(13)–C(14)	120·7(3)	N(2)–C(28)–C(26)	177·3(4)



(7a) $n = 0$
(7b) $n = 1$
(7c) $n = 2$



(8)

the C(33)–C(8)–C(7) and C(33)–C(8)–C(27) angles in (5b) are 117·6° and 128·3° respectively. The peripheral bond lengths are comparable in both the bicyclo[2.2.0] and norbornyl units, being only marginally longer in the former ring.

A notable feature of all three crystal structures is a strong tendency towards curvature of the molecular framework that connects the two chromophores. This is most easily seen in the 'side-on' projections in Figs 1*b*–3*b*. This curvature is a consequence of the difference in the magnitude between two different kinds of interplanar angles, as shown in these Figures. Thus, the angle between the two planes that define the envelope of the six-membered ring *within* a norbornyl unit (e.g., planes A and B of Fig. 1*b*), or bicyclo[2.2.0] unit (e.g., planes C and D of Fig. 2*b*), is only *c.* 109°, whereas that between corresponding planes on adjacent norbornyl or bicyclo[2.2.0] units (e.g., planes B and C of Fig. 1*b*) is 10–15° larger. This effect is typical of norbornylogous systems and is also evident, for example, in the crystal structures of aldrin,[43] and 7(a–c).[33]

Table 8. Interatomic angles (degrees) for molecules A and B of (4b)
$^{\text{I}}$ refers to the symmetry transformation $x, \frac{1}{2} - y, z$

Atoms	A	B	Atoms	A	B
C(10)–O(2)–C(18)	113·4(3)	117·7(3)	C(6)–C(7)–C(7)$^{\text{I}}$	90·4(2)	91·1(2)
C(1)$^{\text{I}}$–C(1)–C(2)	104·6(2)	105·1(3)	C(6)–C(7)–C(8)	118·5(2)	117·9(2)
C(1)–C(2)–C(14)	98·5(3)	96·4(4)	C(8)–C(7)–C(7)$^{\text{I}}$	103·0(2)	102·9(2)
C(1)–C(2)–C(3)	113·7(3)	113·9(4)	C(7)–C(8)–C(9)	106·1(2)	106·6(2)
C(14)–C(2)–C(3)	97·3(3)	98·3(4)	C(7)–C(8)–C(17)	101·9(3)	103·0(3)
C(2)–C(3)–C(3)$^{\text{I}}$	103·4(2)	103·9(2)	C(9)–C(8)–C(17)	99·6(3)	98·7(3)
C(2)–C(3)–C(4)	122·9(3)	121·2(3)	C(8)–C(9)–C(9)$^{\text{I}}$	106·1(2)	105·9(2)
C(4)–C(3)–C(3)$^{\text{I}}$	102·7(2)	102·7(2)	C(8)–C(9)–C(10)	133·5(3)	133·8(3)
C(3)–C(4)–C(5)	104·1(3)	105·9(3)	C(10)–C(9)–C(9)$^{\text{I}}$	120·4(2)	120·3(2)
C(3)–C(4)–C(15)	103·1(3)	103·4(3)	C(9)–C(10)–O(2)	121·1(3)	122·2(3)
C(5)–C(4)–C(15)	101·9(3)	101·3(3)	C(9)–C(10)–C(11)	120·7(3)	120·3(3)
C(4)–C(5)–C(5)$^{\text{I}}$	103·0(2)	103·0(2)	C(11)–C(10)–O(2)	118·1(3)	117·2(3)
C(4)–C(5)–C(6)	119·7(3)	117·8(3)	C(10)–C(11)–C(11)$^{\text{I}}$	118·8(2)	119·4(2)
C(6)–C(5)–C(5)$^{\text{I}}$	90·4(2)	91·0(2)	C(10)–C(11)–C(12)	122·6(3)	122·2(3)
C(5)–C(6)–C(6)$^{\text{I}}$	89·6(2)	89·0(2)	C(12)–C(11)–C(11)$^{\text{I}}$	118·7(2)	118·4(2)
C(5)–C(6)–C(7)	109·1(2)	110·1(2)	C(11)–C(12)–C(13)	121·0(4)	121·4(4)
C(5)–C(6)–C(16)	117·8(3)	116·8(3)	C(12)–C(13)–C(13)$^{\text{I}}$	120·3(2)	120·2(2)
C(7)–C(6)–C(6)$^{\text{I}}$	89·6(2)	88·9(2)	O(1)–C(14)–C(2)	130·8(2)	130·8(3)
C(7)–C(6)–C(16)	118·9(3)	116·6(3)	C(2)–C(14)–C(2)$^{\text{I}}$	98·4(4)	98·0(6)

Interestingly, the curvature of the molecular backbone is roughly the same for all three compounds and may be schematized by (8). The dashed lines that connect the midpoints of the indicated carbon–carbon bonds of the norbornyl or bicyclo[2.2.0] units constitute a series of chords of identical lengths (*c.* 2·45 Å), around which may be circumscribed a circle of radius *c.* 9·4 Å. Each chord subtends an angle of approximately 15° at the centre.

Amusingly, a system of 24 units, containing equal numbers of alternating norbornyl and bicyclo[2.2.0] moieties linearly fused to each other, would complete the circle. Joining the two ends of such a molecule would produce a most interesting macrocyclic structure which may be regarded as a member of the unknown class of compounds jocularly termed dogcollaranes. Progressive replacement of bicyclo[2.2.0] units with norbornyl moieties would lead to dogcollaranes of steadily diminishing diameters. This is the result of the larger interplanar angle between two adjacent norbornyl groups (e.g., between the planes B and C of Fig. 1*b*) compared to that between a norbornyl group and a bicyclo[2.2.0] group (e.g., between the planes B and C of Fig. 2*b*). Crystal data for (3a) and (5b), taken in conjunction with those for (7c), containing three linearly fused norbornyl units,[33] would suggest that the smallest possible dogcollarane would consist of only 16 norbornyl units.

Table 9. Interatomic angles (degrees) for (5b)

Atoms	Angle	Atoms	Angle
C(14)–O(2)–C(37)	114·1(2)	C(15)–C(16)–C(17)	120·6(3)
C(21)–O(3)–C(38)	114·6(2)	C(16)–C(17)–C(18)	120·4(3)
C(2)–C(1)–C(30)	113·7(3)	C(17)–C(18)–C(19)	120·8(3)
C(2)–C(1)–C(31)	98·8(3)	C(18)–C(19)–C(20)	120·5(3)
C(30)–C(1)–C(31)	98·1(2)	C(15)–C(20)–C(19)	118·7(2)
C(1)–C(2)–C(3)	103·3(3)	C(15)–C(20)–C(21)	119·7(2)
C(2)–C(3)–C(4)	103·9(3)	C(19)–C(20)–C(21)	121·5(2)
C(3)–C(4)–C(5)	112·9(3)	O(3)–C(21)–C(20)	118·0(2)
C(3)–C(4)–C(31)	98·7(3)	O(3)–C(21)–C(22)	122·7(2)
C(5)–C(4)–C(31)	98·3(3)	C(20)–C(21)–C(22)	119·2(2)
C(4)–C(5)–C(6)	123·6(3)	C(13)–C(22)–C(21)	121·1(2)
C(4)–C(5)–C(30)	103·0(2)	C(13)–C(22)–C(23)	105·7(2)
C(6)–C(5)–C(30)	103·1(2)	C(21)–C(22)–C(23)	133·2(2)
C(5)–C(6)–C(7)	104·5(2)	C(22)–C(23)–C(24)	104·9(2)
C(5)–C(6)–C(32)	104·0(2)	C(22)–C(23)–C(36)	98·2(2)
C(7)–C(6)–C(32)	101·3(2)	C(24)–C(23)–C(36)	104·4(2)
C(6)–C(7)–C(8)	119·8(2)	C(11)–C(24)–C(23)	102·7(2)
C(6)–C(7)–C(28)	102·9(2)	C(11)–C(24)–C(25)	102·6(2)
C(8)–C(7)–C(28)	90·9(2)	C(23)–C(24)–C(25)	120·7(2)
C(7)–C(8)–C(9)	108·9(2)	C(24)–C(25)–C(26)	104·3(2)
C(7)–C(8)–C(27)	89·1(2)	C(24)–C(25)–C(35)	104·9(2)
C(7)–C(8)–C(33)	117·6(2)	C(26)–C(25)–C(35)	101·6(2)
C(9)–C(8)–C(27)	89·2(2)	C(9)–C(26)–C(25)	102·9(2)
C(9)–C(8)–C(33)	117·9(2)	C(9)–C(26)–C(27)	90·6(2)
C(27)–C(8)–C(33)	128·3(2)	C(25)–C(26)–C(27)	118·9(2)
C(8)–C(9)–C(10)	119·6(2)	C(8)–C(27)–C(26)	89·2(2)
C(8)–C(9)–C(26)	90·9(2)	C(8)–C(27)–C(28)	89·2(2)
C(10)–C(9)–C(26)	102·8(2)	C(8)–C(27)–C(34)	129·0(2)
C(9)–C(10)–C(11)	104·8(2)	C(26)–C(27)–C(28)	108·2(2)
C(9)–C(10)–C(35)	101·1(2)	C(26)–C(27)–C(34)	117·3(2)
C(11)–C(10)–C(35)	103·8(2)	C(28)–C(27)–C(34)	118·0(2)
C(10)–C(11)–C(12)	121·0(2)	C(7)–C(28)–C(27)	90·9(2)
C(10)–C(11)–C(24)	103·2(2)	C(7)–C(28)–C(29)	102·8(2)
C(12)–C(11)–C(24)	103·0(2)	C(27)–C(28)–C(29)	118·9(2)
C(11)–C(12)–C(13)	105·0(2)	C(28)–C(29)–C(30)	104·3(2)
C(11)–C(12)–C(36)	104·6(2)	C(28)–C(29)–C(32)	101·6(2)
C(13)–C(12)–C(36)	98·2(2)	C(30)–C(29)–C(32)	104·3(2)
C(12)–C(13)–C(14)	133·1(2)	C(1)–C(30)–C(5)	103·8(2)
C(12)–C(13)–C(22)	106·0(2)	C(1)–C(30)–C(29)	123·1(3)
C(14)–C(13)–C(22)	120·9(2)	C(5)–C(30)–C(29)	102·7(2)
O(2)–C(14)–C(13)	121·1(2)	O(1)–C(31)–C(1)	129·7(4)
O(2)–C(14)–C(15)	119·2(2)	O(1)–C(31)–C(4)	131·5(4)
C(13)–C(14)–C(15)	119·7(2)	C(1)–C(31)–C(4)	98·7(3)
C(14)–C(15)–C(16)	121·8(2)	C(6)–C(32)–C(29)	95·0(2)
C(14)–C(15)–C(20)	119·3(2)	C(10)–C(35)–C(25)	94·7(2)
C(16)–C(15)–C(20)	118·9(2)	C(12)–C(36)–C(23)	94·2(2)

Because of the inherent curvature of the molecular framework connecting the pair of chromophores in (3)–(5), it would seem that the maximum spatial separation of the dimethoxynaphthalene and dicyanomethylene groups that could be realized in this series is approximately 19 Å. This would correspond to a semicircular homologue having a total of about 15 norbornyl and bicyclo[2.2.0] units.

Two important molecular metric properties of relevance to electron transfer dynamics are the edge-to-edge (R_e) and centre-to-centre (R_c) distances between the chromophores. The former 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 (3a). R_c refers to the distance between the approximate 'centres of gravity' of the chromophores, that is, between C(26) and the midpoint of the C(11)–C(16) bond vector of (3a). The R_c and R_e values for (2a)–(6a) are given in Table 10. The R_e values for (4a) and (5a) are taken to be the same as those determined for the corresponding carbonyl analogues, (4b) and (5b), respectively. This is reasonable, since the geometry of the norbornyl group that contains the dicyanomethylene chromophore in (3a) is very similar to that containing the carbonyl group in both (4b) and (5b). R_c values for (4a) and (5a) were estimated from the R_e values for the ketones (4b) and (5b) and from the C(23)–C(26) bond length of the dicyanomethylene group of (3a). Approximate R_e and R_c values for (2a) and (6a) were obtained from extrapolation of the curvature of the molecular framework, as indicated by (8).

Table 10. Estimated edge-to-edge R_e and centre-to-centre R_c distances between the chromophores in (2a)–(6a), and estimated dipole moments p_c and measured dipole moments p^* of the charge-separated states, D^+–A^-, of (2a)–(6a)

Compound	R_e (Å)	R_c (Å)	p^* (D)[A]	p_c (D)
(2a)	4·6[B]	7·1[B]	25[C]	34
(3a)	6·8	9·0	37[C]	43
(4a)	9·4[D]	11·8[E]	55[C]	57
(5a)	11·5[D]	13·3[E]	67[C]	64
(6a)	13·5[B]	14·9[B]	77[F]	72

[A] Measured by the time-resolved microwave conductivity technique[45] in benzene solvent.
[B] Estimated values based on extrapolation of the curvature of the molecular backbone [see (8)].
[C] Ref. 4.
[D] R_e for (4a) and (5a) assumed to be equal to R_e for the carbonyl analogues (4b) or (5b) respectively.
[E] Estimated from the R_e values for (4b) and (5b) and the C(23)–C(26) bond length in (3a).
[F] Ref. 5.

An example of the usefulness of these distance values is the ability to predict with confidence the magnitude of the dipole moment of the charge-separated state, D^+–A^-, of (3a)–(6a) after photoinduced electron transfer. Assuming that the charges in D^+–A^- are separated by R_c, the predicted dipole moments, p_c, of Table 10 are calculated. The experimental dipole moments, p^*, for the charge-separated states of (3a)–(6a) following photoinduced electron transfer were obtained by using the time-resolved microwave conductivity technique,[45] and the data are given in

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[45] De Haas, M. P., and Warman, J. M.. *Chem. Phys.*, 1982, 73, 35.

Table 10.[4,5] The correspondence between the predicted (p_c) and experimental (p^*) values is excellent and reinforces our belief that photoinduced electron transfer is essentially complete in these molecules.

In order to determine the precise nature of the distance dependence of photoinduced intramolecular electron transfer, crystal structures of (2a) and (6a) should also be obtained. In addition, higher members of the series (2a)–(6a) must be synthesized and studied. To this end, we have synthesized a homologue of (6a) in which the chromophores are separated by *sixteen* bonds.[46] The results of crystal structure determinations and photoinduced intramolecular electron-transfer rate measurements on this, and other compounds, will form the subject of future publications.

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[46] Oliver, A. M., and Paddon-Row, M. N., unpublished data.