

Synthesis, electrochemistry and *ab initio* molecular orbital calculations on some norbornane- and bicyclo[2.2.2]octane-fused 5,12-bis(dicyanomethylidene)naphthalene systems

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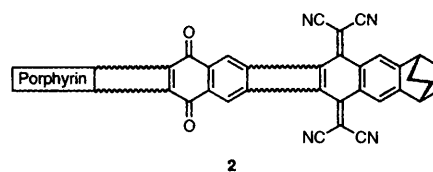
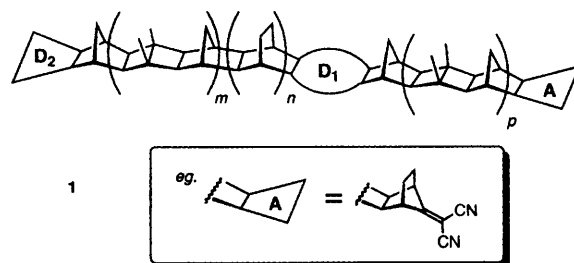
A series of norbornane- and bicyclo[2.2.2]octane-fused tetracyanonaphthoquinodimethane (benzo-TCNQ) derivatives, 4, 6, 8, 10 and 12 has been synthesized. Cyclic voltammetry measurements revealed two one-electron reduction waves for the benzo-TCNQ systems 4, 8 and 10 which possess either a cyclobutane or a norbornane moiety fused to the quinonoid ring, but a single (presumably two-electron) reduction wave for 6 and 12 which possess a bicyclo[2.2.2]octane group fused to the quinonoid ring. The benzo-TCNQ systems were found to be potent electron acceptors. The results of (U)HF/3-21G calculations carried out on representative benzo-TCNQ derivatives suggest that steric interactions between the quinonoid ring and its adjacent fused alicyclic group are largely responsible for the observed decrease in the electron affinities along the series: $8 > 4 > 6$. The MO calculations further suggest that LUMO energies of neutral TCNQ derivatives are qualitatively reliable predictors of electron affinities. The calculated (gas phase) internal reorganization energies, λ_i , for the benzo-TCNQ systems are *ca.* 54 kJ mol⁻¹ and are comparable to that calculated for the dicyanovinyl (DCV) system, 27. The similarity between the λ_i values for the benzo-TCNQ systems and 27, together with the experimental finding that benzo-TCNQ systems are reduced at *ca.* 1.7 V less negative potentials than 27, should make the norbornane- and bicyclo[2.2.2]octane-benzo-TCNQ systems superior to the DCV moiety as acceptor chromophores in giant multichromophoric systems.

Introduction

An important aim in chemistry is the rational design of molecules and supramolecular assemblies that are capable of achieving photoinduced charge separation over large distances and with high quantum efficiency.¹⁻⁵ Such molecular photovoltaic systems would have widespread applications in molecular electronic devices.⁵ A major approach towards achieving this goal is the construction of rigid multichromophoric systems in which the chromophores (redox active centres) are connected *via* a series of saturated bridges.^{2,3} An example of a trichromophoric system is D_2-D_1-A , in which the primary donor group, D_1 , is connected to the secondary donor, D_2 , by a bridge and to the acceptor, A, by a different bridge. In such systems, light-induced intramolecular electron transfer (ET) takes place *via* a cascade of redox processes to give the final giant charge separated state, ${}^+D_2-D_1-A^-$.

Our efforts in this area have concentrated on synthesizing the novel triads, **1**, in which the primary donor group, D_1 , is connected to the secondary donor group, D_2 , and to the acceptor group, A, by bridges comprising linearly fused norbornane and bicyclo[2.2.0]hexane groups (norbornylogous bridges). The chromophores used in our first successfully synthesized series of triads, **1**, were dimethoxynaphthalene ($D_1 = DMN$), *N,N*-dimethylaniline ($D_2 = DMA$), and the dicyanovinyl acceptor group (A = DCV; see inset to structure **1**).^{6,7}

Preliminary photophysical studies were encouraging in that the giant charge-separated state, ${}^+(DMA)-(DMN)-(DCV)^-$, was formed following flash photolysis of these systems.^{8,9} However, the efficiency of formation of the giant charge-separated states was not high, particularly in low polarity solvents, because of the moderate driving force† for the



process.⁸ We hoped to overcome the driving force problem by replacing the dicyanovinyl acceptor group with chromophores based on the tetracyanoquinodimethane (TCNQ) system, in particular, the tetracyanonaphthoquinodimethane [bis-(dicyanomethylidene)naphthalene] (benzo-TCNQ) group, as shown by **2**. TCNQ derivatives are potent acceptors and the benzo-TCNQ moiety should be stronger than the dicyanovinyl group by more than 1 V. Indeed, Wasielewski *et al.* have successfully demonstrated the efficacy of a benzo-TCNQ derivative as an acceptor in a porphyrin-based triad.¹⁰

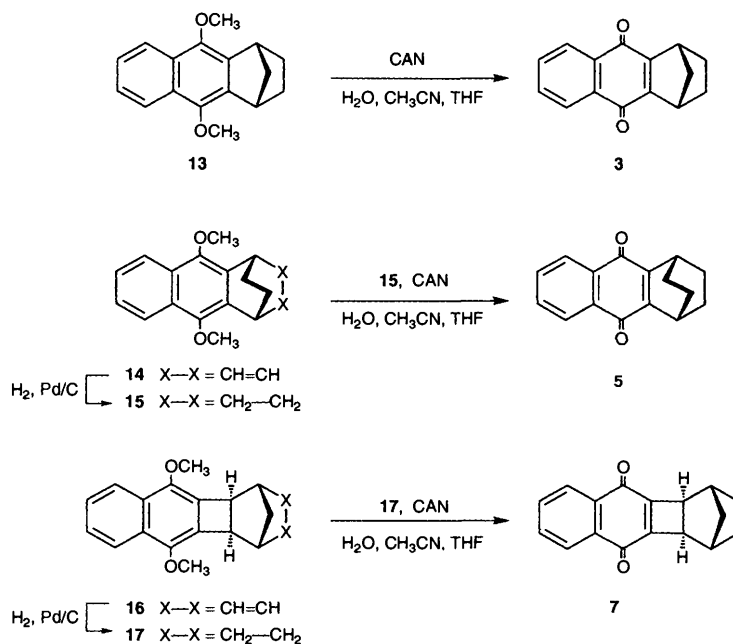
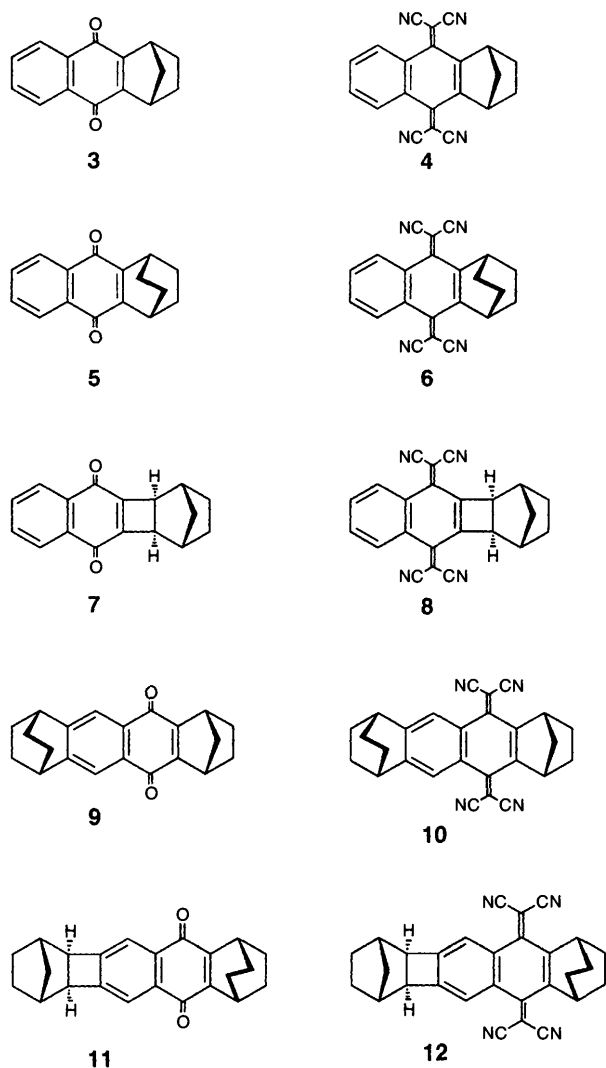
In this paper we report the synthesis and electrochemistry of some novel quinones and benzo-TCNQ derivatives, **3-12**, which serve as suitable models for the benzo-TCNQ component in triads, such as **2**. Molecular orbital calculations have also been carried out on some of these benzo-TCNQ systems in order to shed light on the electrochemical data.

† The driving force is the negative of the free energy change for the process: $D_2-D_1-A \longrightarrow {}^+D_2-D_1-A^-$

Results and discussion

Synthesis

Quinones **3**, **5** and **7** were readily synthesized in high yield (>90%) by oxidation of the corresponding 1,4-dimethoxy-



Scheme 1

naphthalene compounds with cerium(IV) ammonium nitrate (CAN),¹¹ as shown in Scheme 1. Quinone **3** has previously been prepared by oxidation of the corresponding 1,4-dihydroxynaphthalene.¹²

The quinone **9** was conveniently obtained (61% yield) in a one-pot reaction by carrying out the Diels–Alder reaction between quinone **18** and diene **19** in the presence of lead dioxide, in refluxing benzene (Scheme 2). The lead dioxide serves to oxidize the adduct **20** directly to **9**.⁷

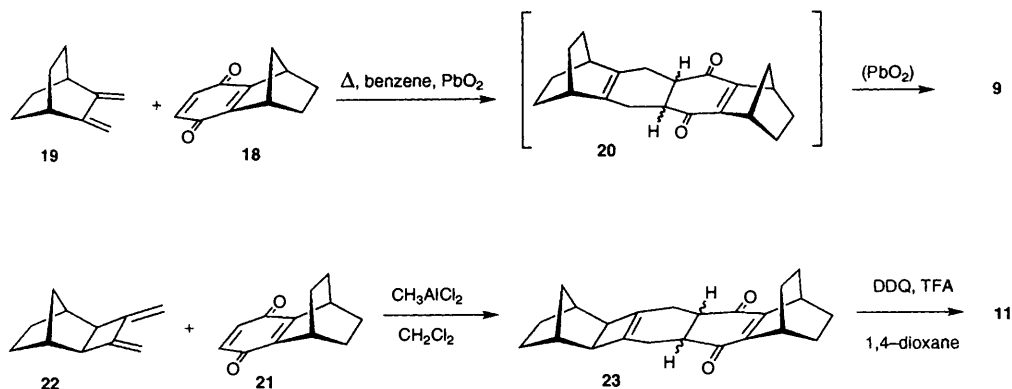
Application of the lead dioxide strategy to the synthesis of quinone **11** from **21** and **22** failed on account of the thermal instability and low enophilicity of the diene **22**. However, a high yield (95%) of the adduct **23** was obtained by carrying out the Diels–Alder reaction under Lewis acid-catalysed conditions (CH_3AlCl_2 as Lewis acid) at 0 °C. Adduct **23**, as a mixture of stereoisomers (see Scheme 2), was readily oxidized to the quinone **11** using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with trifluoroacetic acid.

Access to the benzo-TCNQ compounds was achieved through reaction of the quinones with malononitrile (Scheme 3), using Lehnert's procedure (CH_2Cl_2 , TiCl_4 , pyridine).^{13,14} After some experimentation with relative proportions of reagents and quinone substrate, it was found that optimum yields of the benzo-TCNQ compounds (>90%) were obtained using a quinone– TiCl_4 –malononitrile–pyridine ratio of 1:2.5:5:5. This reagent ratio is similar to that used by Kini *et al.* in their synthesis of TCNQ analogues,¹⁵ with the exception that the proportion of malononitrile was doubled in the present study (using the proportion of malononitrile employed by Kini *et al.* led to the formation of mixtures of unreacted substrate, the monocondensation product, and the desired benzo-TCNQ biscondensation product).

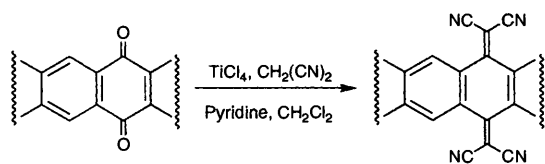
Electrochemistry

Cyclic voltammetry (CV) measurements were carried out on the quinones and benzo-TCNQ compounds in acetonitrile solvent, using a glassy carbon working electrode with tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The half-wave potentials, relative to a quasireference Ag/AgCl electrode (see Experimental section), are presented in Table 1.

The series of naphthoquinones, **3**, **5**, **7**, **9** and **11** each exhibited two reversible one-electron reduction waves which correspond to the anion radical and dianion. As to be expected, the reduction potentials for these naphthoquinones are



Scheme 2



Scheme 3

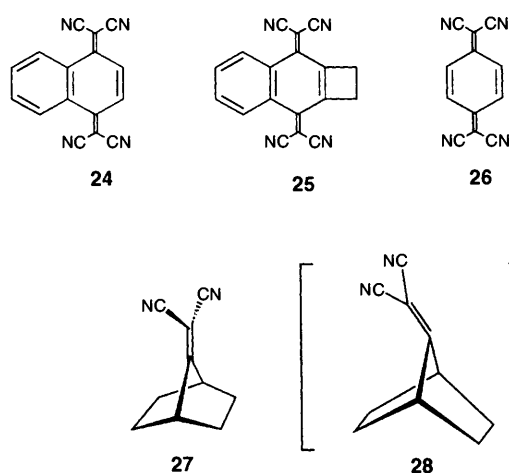


Table 1 Cyclic voltammetric data for quinones and benzo-TCNQ derivatives

Compound	$E_{\frac{1}{2}}^1/V^a$	$E_{\frac{1}{2}}^2/V^a$
Quinones		
3	-0.69	-1.20
5	-0.75	-1.20
7	-0.62	-1.13
9	-0.74	-1.14
11	-0.77	-1.195
Benzo-TCNQ derivatives		
4	-0.05	-0.15
6		-0.10
8	0.075	-0.32
10	-0.10	-0.21
12		-0.14
24	0.08 ^b	-0.48 ^b
25	-0.10 ^c	-0.47 ^c

^a Glassy carbon working electrode vs. Ag/AgCl reference electrode (Fc/Fc⁺ redox couple as internal reference), Pt wire auxiliary electrode, MeCN/0.1 mol dm⁻³ Bu₄NBF₄, scan rate 100 mV s⁻¹. ^b Dropping mercury working electrode vs. SCE, LiClO₄ as supporting electrolyte.¹⁷ ^c Glassy carbon working electrode vs. SCE, MeCN/0.1 mol dm⁻³ Et₄NClO₄, scan rate 100 mV s⁻¹.¹⁸

comparable to those for the parent 1,4-naphthoquinone. The $E_{\frac{1}{2}}^1$ values for the series span ca. 0.15 V, whereas the $E_{\frac{1}{2}}^2$ values

cover only a half of this range. The nature of the ring fused to the quinone segment affects only the first reduction potential, which moves to more negative values along the series 7 > 3 > 5; that is, a norbornane ring decreases the $E_{\frac{1}{2}}^1$ value by 75 mV, relative to a cyclobutane ring (cf. 3 vs. 7), and a bicyclo[2.2.2]ring further decreases the potential by 52 mV (cf. 5 vs. 3).

It is well known^{16,17} that TCNQ and benzo-TCNQ systems are significantly stronger electron acceptors than the corresponding quinones and a cursory glance at the first reduction potentials presented in Table 1 demonstrate that our benzo-TCNQ systems are indeed reduced at significantly less negative potentials than the corresponding quinones, by about 0.65 V.

Although 4, 8 and 10, together with the parent benzo-TCNQ 24¹⁷ and the cyclobutabeno-TCNQ 25,¹⁸ each displayed two reversible one-electron reduction waves, compounds 6 and 12 each exhibited a single reversible reduction wave with a value lying approximately midway between the two waves for 10. Presumably, the single reduction wave observed for these two compounds corresponds to a two-electron reduction to the dianion although, perhaps surprisingly, the separation between the anodic and cathodic peaks for both compounds is ca. 70 mV, instead of ca. 30 mV, expected for a two-electron reduction. Nevertheless, there are many unequivocal examples of ring fused benzo-TCNQ derivatives that show only a single two-electron reduction wave.^{16,17,19-21} Even for 4 and 10, which do show two reduction waves, the difference between $E_{\frac{1}{2}}^1$ and $E_{\frac{1}{2}}^2$ is only ca. 100 mV.

As observed for the corresponding quinones, $E_{\frac{1}{2}}^1$ for the benzo-TCNQ derivatives moves to progressively more negative values upon changing the fused alicyclic ring from cyclobutane to norbornane to bicyclo[2.2.2]octane; i.e. 8 > 4 > 6.

Molecular orbital calculations

In order to gain knowledge of the geometries and energies of the benzo-TCNQ systems studied herein and their anion radicals, *ab initio* MO calculations were carried out on 4, 6, 24 and 25.²² Cyclobutabeno-TCNQ 25, was used as a model for 8. Additional calculations were also carried out on TCNQ 26 and the 7-(dicyanomethylidene)norbornane (DCV) system 27 and their corresponding anion radicals. The DCV system 27 has been included since this moiety has been frequently used as an acceptor group in ET studies.^{4,8,9}

Full geometry optimizations of all species were carried out, with no symmetry constraints, using the Hartree-Fock theoretical model and the 3-21G basis set²³ (HF/3-21G). In the case of the open-shell anion radicals, the unrestricted Hartree-Fock method was employed (UHF/3-21G).

It was found that geometry optimization of 4, 6, 24 and 25, and their anion radicals, led to structures possessing C_s symmetry. Geometry optimization of TCNQ 26 and its anion radical gave D_{2h} (planar) structures and harmonic frequency calculations confirmed that these structures correspond to true

Table 2 Geometrical parameters for HF/3-21G optimized structures of TCNQ derivatives

Parameter ^a	24	25	4	6	26 ^b
r_1	1.481	1.494	1.490	1.489	1.462
r_2	1.408	1.418	1.405	1.402	1.328
r_3	1.471	1.451	1.465	1.478	
r_4	1.323	1.330	1.338	1.331	
r_5	1.346	1.347	1.346	1.342	1.347
r_6	1.424	1.425	1.427	1.427	1.424
a_1	125.6	126.0	123.6	123.6	121.5
a_2	119.0	121.3	123.5	123.3	
ϕ	154.2	157.4	147.8	142.4	180.0
τ^c	4.4	5.5	4.3	0.0	0.0

^a Bond lengths in Å and bond angles in degrees. ^b D_{2h} geometry. ^c Average value. A positive value for τ designates twisting in the direction depicted in Fig. 1.

Table 3 Geometrical parameters for UHF/3-21G optimized structures of anion radicals of TCNQ derivatives

Parameter ^a	24 ⁻	25 ⁻	4 ⁻	6 ⁻	26 ^{-b}
r_1	1.460	1.473	1.469	1.466	1.422
r_2	1.425	1.431	1.412	1.415	1.357
r_3	1.409	1.395	1.403	1.421	
r_4	1.358	1.367	1.389	1.376	
r_5	1.415	1.412	1.415	1.408	1.409
r_6	1.408	1.409	1.414	1.414	1.409
a_1	126.5	126.6	121.8	123.0	121.9
a_2	117.8	120.6	124.0	123.3	
ϕ	174.7	172.7	161.0	153.0	180.0
τ^c	5.2	10.3	19.0	-8.2 ^d	0.0

^a Bond lengths in Å and bond angles in degrees. ^b D_{2h} geometry. ^c Average value. A positive value for τ designates twisting in the direction depicted in Fig. 1. ^d Rigid twisting of both C-CN bonds of each =C(CN)₂ group about its double bond does not occur; instead, the right-hand C-CN bond of each group rotates downwards (in the direction opposite to that depicted by τ in Fig. 1) and the left-hand C-CN bond of each group remains coplanar with the double bond and the double bond ligands associated with the quinonoid ring.

energy minima. The minimum energy structure for the norbornane-DCV system **27** possesses C_{2v} symmetry in which the C=C double bond is locally planar. The anion radical of this molecule **27⁻** possesses C_s symmetry, in which there is strong pyramidalization about C7, as depicted by **28**.[†] The C(CN)₂ group in **27⁻** is locally planar. Mulliken population analysis on **27⁻** reveals that the C7 centre carries a large proportion of the unpaired spin density (1.0 au) and therefore has strong radical character, whereas most of the excess negative charge density (0.9 e) is delocalized over the C(CN)₂ moiety.

Selected geometrical parameters[‡] for **4**, **6**, **24**, **25** and **26**, and their anion radicals are presented in Tables 2 and 3, respectively. These parameters are defined in Fig. 1. The changes in the magnitudes of the geometrical parameters, upon going from the neutral species to the anion radical, are given in Table 4. Energies of the systems are presented in Table 5. Perspectives of the optimized structures for **24**, **25**, **4** and **6**, and their anion radicals, are given in Figs. 2–5, respectively.

It would have been preferable to have carried out the

[†] The degree of pyramidalization at C7, measured by the angle between the C7–C8 bond and the plane defined by the atoms C1, C4 and C7, is 36.3°.

[‡] Complete lists of coordinates for all energy-minimized structures, including **26** and **27** and their corresponding anion radicals are available as supplementary data (suppl. No. 57128) from the British Library. For details of the supplementary publications scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1. Electronic versions of these data may be obtained from M.N.P.-R. e-mail: M.PaddonRow@unsw.edu.au.

Table 4 Differences between the optimized geometrical parameters for the neutral TCNQ derivatives and their corresponding anion radicals

$\Delta(\text{Parameter})^{a,b}$	24	25	4	6	26 ^c
Δr_1	-0.021	-0.021	-0.021	-0.023	-0.040
Δr_2	0.017	0.013	0.007	0.013	0.029
Δr_3	-0.062	-0.056	-0.062	-0.057	
Δr_4	0.035	0.037	0.051	0.045	
Δr_5	0.069	0.065	0.069	0.066	0.062
Δr_6	-0.016	-0.016	-0.013	-0.013	-0.015
Δa_1	0.9	0.6	-1.8	-0.6	0.4
Δa_2	-1.2	-0.7	0.5	0.0	
$\Delta \phi$	20.5	15.3	13.2	10.6	0.0
$\Delta \tau^d$	0.8	4.8	14.7	-8.2 ^e	0.0

^a (Geometrical parameter of anion radical) – (geometrical parameter of respective neutral). ^b Bond lengths in Å and bond angles in degrees. ^c D_{2h} geometry. ^d Average value. ^e See footnote *d* of Table 3.

Table 5 Energies of neutral TCNQ and DCV derivatives and their anion radicals

Molecule	E^a	E_{LUMO}^b	E_{ea}^c	λ_i^d
24	-822.484 11	-86.8		
24⁻	-822.570 47		226.7	
24^{-e}	-822.548 61			57.4
25	-898.913 67	-90.7		
25⁻	-899.000 30		227.4	
25^{-e}	-898.981 25			50.0
4	-1014.252 36	-60.8		
4⁻	-1014.328 83		200.7	
4^{-e}	-1014.308 77			52.7
6	-1053.086 26	-28.0		
6⁻	-1053.151 62		171.6	
6^{-e}	-1053.130 32			55.9
26	-670.689 98	-149.1		
26⁻	-670.791 52		266.5	
26^{-e}	-670.778 57			34.0
27	-490.632 56	208.7		
27⁻	-490.622 54		-26.30	
27^{-e}	-490.602 88			51.6

^a Energies in Hartrees (1 Hartree = 2625 kJ mol⁻¹). ^b Energy of the LUMO (kJ mol⁻¹). ^c Adiabatic electron affinity (kJ mol⁻¹): $E(\text{neutral}) - E(\text{anion radical})$. ^d Internal reorganization energy (kJ mol⁻¹). ^e Energy of anion radical at relaxed geometry of the respective neutral precursor.

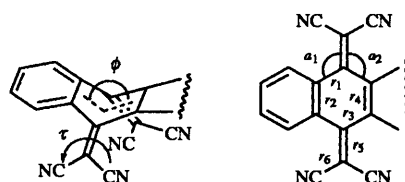


Fig. 1 Definition of the geometrical parameters used in Tables 2–4. A planar quinonoid ring corresponds to $\phi = 180^\circ$. A value of $\tau = 0^\circ$ corresponds to a planar double bond, that is, the double bond carbon atoms, together with the four carbon atoms directly bonded to the double bond lie in a plane.

geometry optimizations using a basis set containing polarization functions on all carbon atoms, e.g. 6-31G(d).²⁴ Unfortunately, this was not possible, given current computing resources at our disposal. Nevertheless, the similarity between the HF/3-21G optimized structure for **24** and the X-ray structure for this molecule²⁵ suggests that the 3-21G basis set probably gives a qualitatively reliable description of the molecular geometries for all of the benzo-TCNQ derivatives studies herein. For example, the optimized values of a_1 , a_2 , and ϕ for **24** (Table 2) are reasonably close to the X-ray values of 125.3, 117.4 and 164.7°, respectively.²⁵

Geometries. X-Ray structure determination of simple non-annulated TCNQ derivatives reveals the TCNQ quinonoid ring to be completely planar.²⁶ This is to be expected since planarity

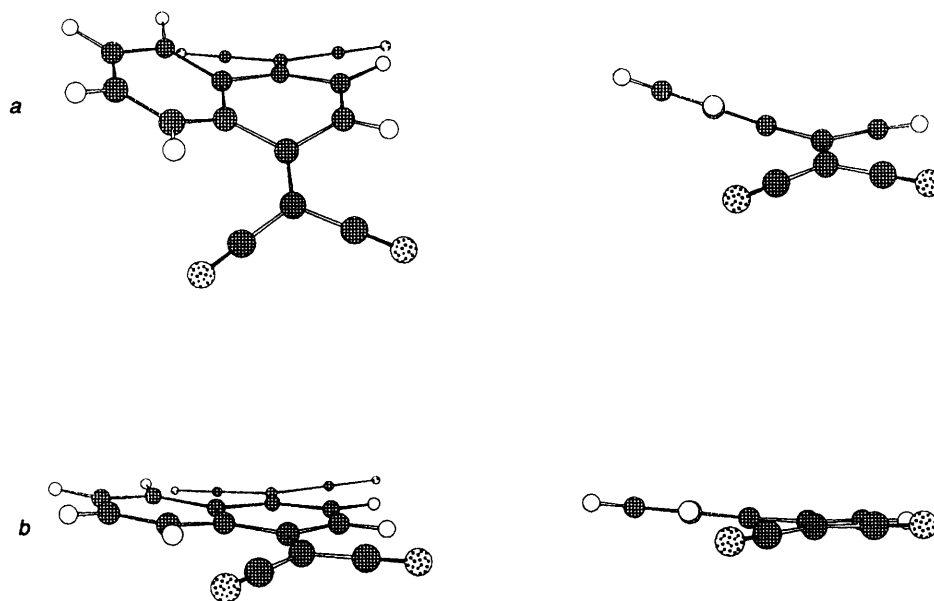


Fig. 2 (a) HF/3-21G optimized structure of **24**; (b) UHF/3-21G optimized structure of the anion radical **24**⁻

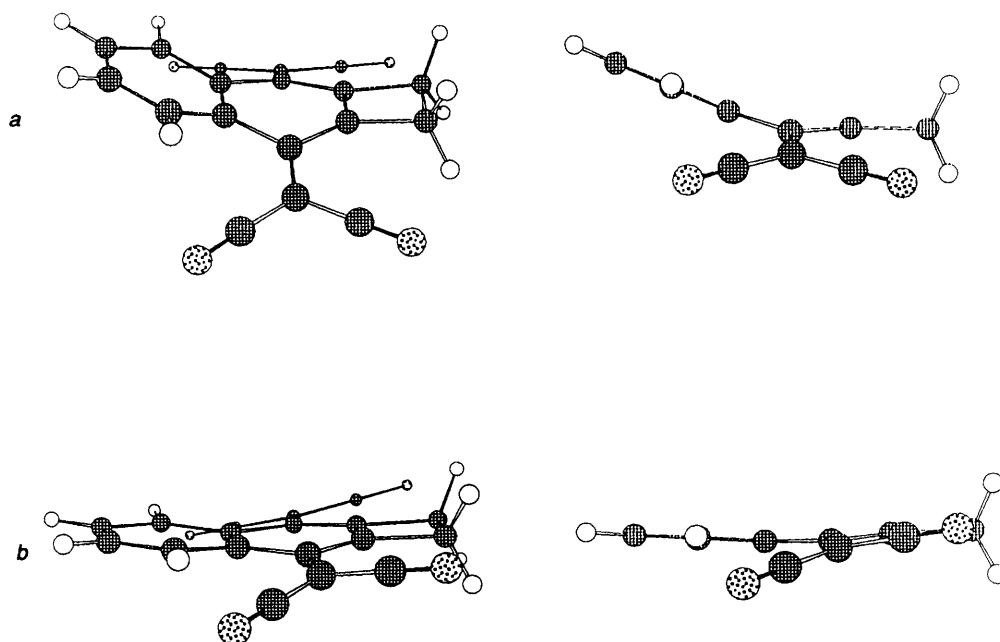


Fig. 3 (a) HF/3-21G optimized structure of **25**; (b) UHF/3-21G optimized structure of the anion radical **25**⁻

maximizes electron delocalization throughout the quinonoid ring and both =C(CN)₂ groups. Indeed, we find that TCNQ, **26**, adopts a planar minimum energy structure (*D*_{2h}) at the HF/3-21G level of theory.

However, fusion of benzene ring(s) to the TCNQ quinonoid ring causes severe steric congestion between the cyano groups and the *peri* C–H atoms of the benzene ring(s). This steric congestion can be relieved by modifying the geometry of the quinonoid ring in three distinct ways: (i) decreasing the magnitude of the flap angle, ϕ from 180°, thereby converting the planar quinonoid ring into a boat conformation (see Fig. 1); (ii) increasing the magnitude of the angle a_1 ; (iii) twisting each =C(CN)₂ group about its respective double bond axis (increasing the value of τ , see Fig. 1).

X-Ray data for tetracyanoanthraquinodimethane[bis(dicyanomethylidene)anthracene] (TCNAQ) illustrate the importance of reducing the flap angle ϕ in alleviating steric congestion.²⁷ This molecule possesses two aromatic rings fused to the quinonoid moiety; the large steric congestion in this

molecule is reflected by a flap angle of only 145°. Steric congestion in the parent benzo-TCNQ molecule **24** which has only one fused benzene ring, is less than that in TCNAQ. Consequently, the flap angle for **24** is more obtuse (165°)²⁵ than for TCNAQ. Steric strain in **24** is further relieved by increasing the magnitude of the angle, a_1 to 125° (*cf.* 120° for TCNQ.²⁵)

The trends in the values of a_1 , ϕ and τ along the series of neutral benzo-TCNQ derivatives, **4**, **6**, **24** and **25** are informative (Table 2). These molecules alleviate strain mainly by changing the magnitude of both ϕ and a_1 ; the deviation of the twisting angle τ from 0° is minor. The steadily diminishing value of the flap angle ϕ along the series **25** > **4** > **6** reflects increasing strain caused by progressive increase in the bulk of the fused alicyclic ring.

Both the magnitude and direction of the changes in the bond lengths, Δr (Table 4), accompanying formation of the anion radicals from the neutral precursors, are fully consistent with substantial spin delocalization in these species.

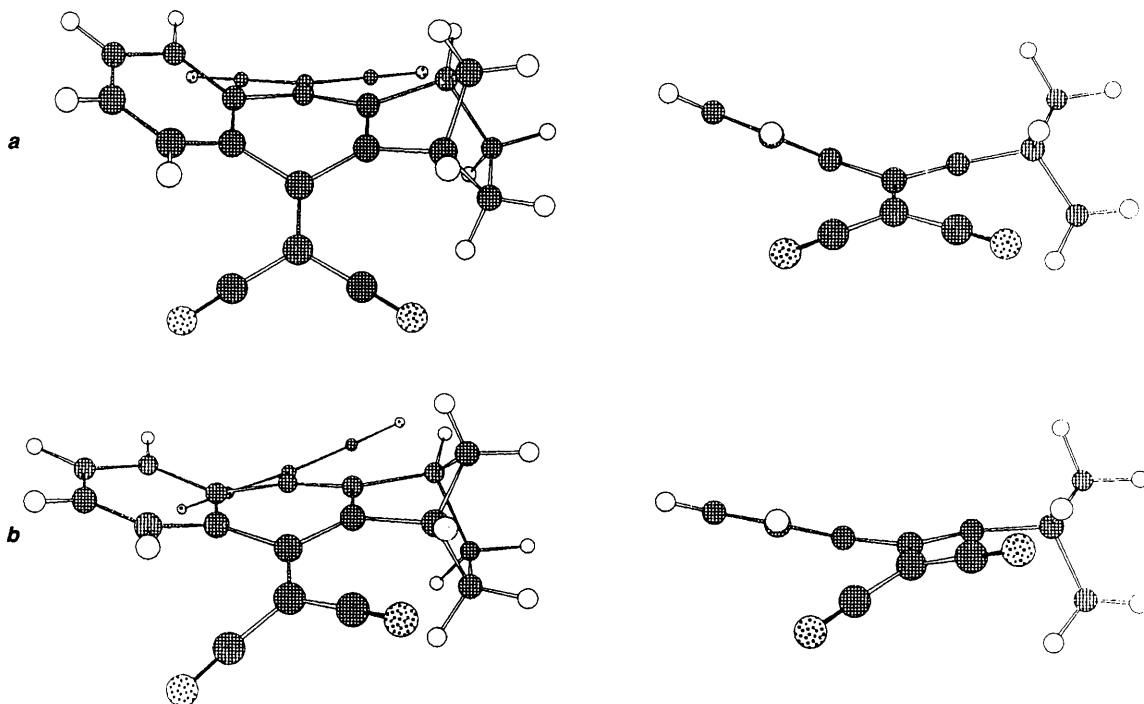


Fig. 4 (a) HF/3-21G optimized structure of 4; (b) UHF/3-21G optimized structure of the anion radical 4^-

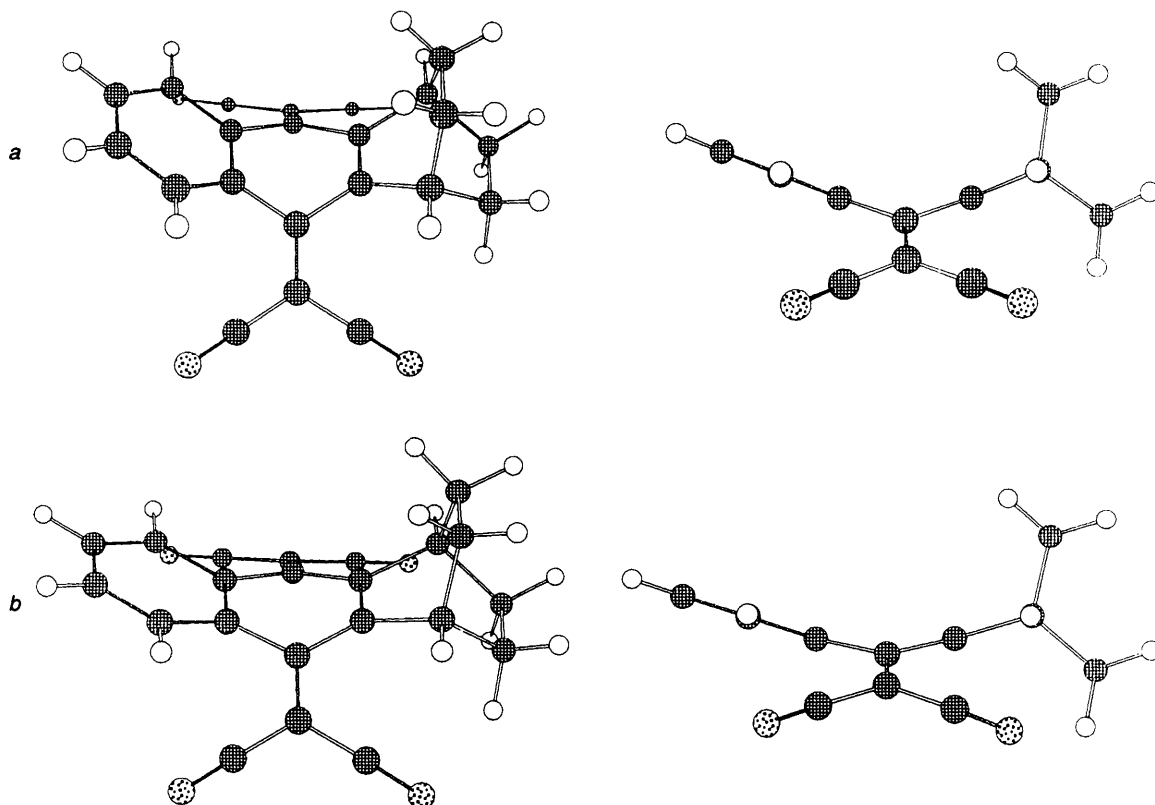


Fig. 5 (a) HF/3-21G optimized structure of 6; (b) UHF/3-21G optimized structure of the anion radical 6^-

The quinonoid ring in the benzo-TCNQ anion radicals is expected to display a tendency towards planarity because planarization of the quinonoid ring would enhance π electron delocalization, thereby resulting in a reduction in π - π electron repulsion. Not unexpectedly, we find that the sterically unencumbered TCNQ anion radical 26^- adopts the planar (D_{2h}) geometry at the UHF/3-21G level.

The anion radicals, 24^- and 25^- are able to achieve near planarity of the quinonoid ring ($\varphi > 172^\circ$): for 25^- this comes

at the expense of increased twisting about the $C=C(CN)_2$ double bonds ($\Delta\tau \approx 5^\circ$, Table 4) in order to reduce steric strain between the cyclobutane ring and the nearest neighbour cyano groups.

The bulky norbornane and bicyclo[2.2.2]octane groups, however, prevent the achievement of planarity of the quinonoid ring in the anion radicals 4^- and 6^- respectively; the flap angle, φ in these species is significantly smaller than that in 24^- and 25^- (Table 3). Although φ is moderately larger for 4^- and 6^- ,

compared with their respective neutral precursors **4** and **6** ($\Delta\phi \approx 13$ and 11° for **4**⁻ and **6**⁻, respectively; Table 4), this increased planarity of the quinonoid ring comes at the cost of an increase in the absolute magnitude of the twisting angle, τ ($\Delta\tau \approx 15$ and -8° for **4**⁻ and **6**⁻, respectively; Table 4), which alleviates steric interactions between the nearest neighbour cyano groups and the alicyclic C–H bridgeheads. This twisting reduces electron delocalization and thereby invokes an energy cost, although this is expected to be less for the anion radical than for the respective neutral precursor. For example, at the (U)HF/3-21G level, we find that out-of-plane twisting of both C(CN)₂ groups, in the same direction, by an amount $\Delta\tau = 15^\circ$ in TCNQ **26** requires 22 kJ mol⁻¹, as opposed to only 11.5 kJ mol⁻¹ for the corresponding anion radical, **26**⁻. The flap angle, ϕ , is smaller for **6**⁻ than for **4**⁻ because the bridgehead C–H bonds of the bicyclo[2.2.2]octane group in **6**⁻ lie in the plane of the fused benzene ring, thereby making planarity of the quinonoid ring even more difficult to achieve (the corresponding bridgehead C–H bonds of the norbornane ring in **4**⁻ make a dihedral angle of about 18° with respect to the plane of the benzene ring).

Electron affinities. The gas phase (U)HF/3-21G electron affinities, E_{ea} s, for the benzo-TCNQ systems fall within the range 172–227 kJ mol⁻¹ (Table 5).[†] There is a trend in these values in that E_{ea} decreases along the series **24**⁻ \approx **25**⁻ > **4**⁻ > **6**⁻. This trend can be explained in terms of geometric arguments. A (relative) measure of benzo-TCNQ anion radical stability is the magnitude of both the change in the flap angle, $\Delta\phi$ and the change in the twisting angle $\Delta\tau$ incurred upon adding an electron to the neutral precursor, and this stability is expected to increase with increasing $\Delta\phi$ and with decreasing $\Delta\tau$ (these directions of change lead to increasing conjugation in the anion radical, relative to the neutral precursor). Indeed, the trends in the $\Delta\phi$ and $\Delta\tau$ values (Table 4) for the benzo-TCNQ derivatives are largely consistent with the above sequence of E_{ea} s for these molecules.

Interestingly, both calculated E_{ea} and experimental $E_{1/2}^1$ values for these systems agree that the electron acceptor strength of the benzo-TCNQ derivatives decreases in the order: **8** \approx **24** > **4** > **6**. (System **8** is an acceptable experimental representative for **25**.) However, this agreement may be fortuitous, given the relatively low level of theory employed and the neglect of solvation in the calculations.

Two recent MO studies on various substituted (and annulated) TCNQ derivatives have revealed the existence of a reasonable correlation between the lowest unoccupied MO (LUMO) energies of the neutral species and their E_{ea} s (reduction potentials).^{16,28} In agreement with those studies, we also find that the LUMO energies for our neutral systems **24**, **25**, **4** and **6** follow the same trend as the E_{ea} s (Table 5). Thus, the negative of the LUMO energy and the E_{ea} both decrease along the series **24** \approx **25** > **4** > **6**. These findings, together with those reported by other research groups^{16,28} show that LUMO energies reliably predict trends in the electron affinities for series of TCNQ derivatives. This is most useful since it is computationally much quicker to calculate LUMO energies than it is to calculate E_{ea} s.

Our calculations predict that the gas phase E_{ea} for TCNQ, **26**, is 39–95 kJ mol⁻¹ larger than the benzo-TCNQ systems. This prediction is consistent with CV data for TCNQ, **26**, and benzo-TCNQ, **24**, which reveal that the E_{ea} for **26** is ca. 26 kJ mol⁻¹ larger than that for the **24** (in acetonitrile solution),¹⁷ and this

compares favourably with the calculated value of 40 kJ mol⁻¹. Note also that, in accordance with expectation based on the findings above, the LUMO energy for **26** is much lower than that for the benzo-TCNQ systems.

The DCV system, **27**, is calculated to be a substantially weaker electron acceptor than the benzo-TCNQ derivatives, by at least 200 kJ mol⁻¹. This finding is in qualitative agreement with the experimental value of ca. 180 kJ mol⁻¹, obtained from CV data for **8** (Table 1) and for an analogue of **27** ($E_{1/2}^1 = -1.7$ V²⁹). The LUMO energy for **27** is now a positive quantity, again indicating the poor electron affinity for this molecule.

Reorganization energies. Within the context of the Marcus–Hush theory,^{30,31} the free energy of activation for an ET process is given by eqn. (1), where ΔG° is the free energy change

$$\Delta G^\ddagger = \lambda/4(1 + \Delta G^\circ/\lambda)^2 \quad (1)$$

associated with the ET process (this is usually a negative quantity), and λ is the reorganization energy (a positive quantity) and is a sum of solvent and internal contributions. The internal contribution, λ_i is the energy associated with geometric changes in the system undergoing ET, and may be defined as the energy of the product state possessing the relaxed (*i.e.* optimized) geometry of the reactant state minus the energy of the product state in its relaxed geometry.

Guided by eqn. (1), an important strategy in the design of molecular systems capable of mediating efficient ET processes is to tune the system such that the ET process is barrierless, that is $\Delta G^\circ = -\lambda$. Thus, attention must be paid to both ΔG° and λ when attempting to optimize an ET process. Ideally, this entails designing a system which satisfies the dual requirements of a large driving force and a small reorganization energy.

It is therefore of interest to estimate the internal reorganization energies, λ_i associated with the benzo-TCNQ chromophores studied herein. These are equal to the energy difference between the anion radical at the relaxed geometry of the neutral precursor and the anion radical at its relaxed geometry. These values, computed at the (U)HF/3-21G level of theory, are given in Table 5. It can be seen from these data that the λ_i values for all benzo-TCNQ systems studied fall within a narrow range of 5 kJ mol⁻¹, the average value being ca. 54 kJ mol⁻¹.

The reorganization energy for TCNQ **26** (34 kJ mol⁻¹) is about one half of that for the benzo-TCNQ systems. This is probably due, in part, to the fact that, because TCNQ and its anion radical are both planar species, geometrical distortions following the addition of an electron to TCNQ are not as energetically demanding as those following the addition of an electron to the non-planar benzo-systems.

Interestingly, the calculated reorganization energy for the DCV molecule, **27**, is comparable to that for the benzo-TCNQ series of molecules. How much of the reorganization energy for **27** is due to the conversion of a planar C7 atom in the neutral molecule to a pyramidal C7 atom in the anion radical? This question may be addressed by carrying out the geometry optimization of **27**⁻ under C_{2v} symmetry constraint, thereby enforcing (among other things) planarity about C7. The (U)HF/3-21G λ_i value for the conversion of **27** into the C_{2v} anion radical is 36.7 kJ mol⁻¹. Thus, pyramidalization accounts for ca. 15 kJ mol⁻¹ of the total reorganization energy for the conversion of **27** into the fully relaxed C_s anion radical **27**⁻.

Conclusions

A series of norbornane- and bicyclo[2.2.2]octane-fused benzo-TCNQ derivatives, **4**, **6**, **8**, **10** and **12**, has been synthesized. Cyclic voltammetry measurements revealed two one-electron reduction waves for the benzo-TCNQ systems possessing either a cyclobutane or a norbornane moiety fused to the quinonoid

[†] These values are probably much too large, on account of the neglect of electron correlation in the calculations and because the UHF wavefunctions for the anion radicals are contaminated by higher spin multiplicities, as reflected by the $\langle S^2 \rangle$ value of ca. 1.0. Notwithstanding this problem, the calculations should reliably predict trends in the E_{ea} values along a series of structurally related molecules, which is the case for this study.

ring, but a single (presumably two-electron) reduction wave for systems possessing a bicyclo[2.2.2]octane group fused to the quinonoid ring.

The benzo-TCNQ systems are excellent electron acceptors and are more potent than the corresponding quinones (by *ca.* 0.65 V).

The results of (U)HF/3-21G calculations carried out on representative benzo-TCNQ derivatives suggest that steric interactions between the quinonoid ring and its adjacent fused alicyclic group are largely responsible for the observed decrease in the electron affinities along the series: **8** > **4** > **6**. The calculations further suggest that LUMO energies for neutral TCNQ derivatives are qualitatively reliable predictors of electron affinities.

The calculated (gas phase) internal reorganization energies, λ_i , for the benzo-TCNQ systems are *ca.* 54 kJ mol⁻¹ and are comparable to that calculated for the DCV system **27**. The similarity between the λ_i values for the benzo-TCNQ systems and **27**, together with the experimental finding that benzo-TCNQ systems are reduced at *ca.* 1.7 V less negative potentials than **27**, should make the norbornane- and bicyclo[2.2.2]octane-benzo-TCNQ systems superior to the DCV moiety as acceptor chromophores in giant multichromophoric systems. Synthesis of multichromophoric systems containing the benzo-TCNQ chromophore is currently underway.

The *ab initio* MO calculations reported herein have provided some useful qualitative insights into the structure and energetics of the benzo-TCNQ chromophore. However, these calculations used a fairly low level of theory and ignored solvent effects. These deficiencies will be addressed in future work.

Experimental

Melting points were determined with a Melt-Temp (II) apparatus and are uncorrected. Elemental microanalyses were performed by Dr H. P. Pham of the University of New South Wales. IR spectra (Nujol mull) were recorded on a Perkin-Elmer Model 298 spectrometer. ¹H NMR spectra were obtained on a Bruker AC300F (300MHz) spectrometer. ¹H data is reported as follows: Chemical shift (δ) measured in parts per million (ppm) down field from TMS; proton count, multiplicity; observed coupling constant (*J*) in Hertz (Hz), proton assignment. Multiplicities are reported as singlet (s), broad singlet (br s), doublet (d), triplet (t), multiplet (m). ¹³C NMR spectra were obtained on a Bruker AC300F (75.47 MHz) spectrometer. ¹³C chemical shifts (δ) are reported in parts per million (ppm) downfield from TMS and identifiable signals are given. Assignment was determined with the aid of 90 °C DEPT and 135 °C DEPT experiments. Chromatography was performed using gravity columns packed with Merck silica gel 7724 60 (70–230 mesh). Cyclic voltammetry measurements were performed on a BAS 100 Electrochemical Analyser. Experiments were conducted at room temperature in a one-compartment cell containing a glassy carbon working electrode, platinum wire auxiliary electrode and a Ag/AgCl quasireference electrode. As internal reference redox system the Fc/Fc⁺ couple was used with a redox potential measured to 0.45 V (*vs.* Ag/AgCl). Solutions were made using acetonitrile solvent (Aldrich) containing Bu₄NBF₄ (0.1 mol dm⁻³, Aldrich) as supporting electrolyte with a scan rate of 100 mV s⁻¹.

1,2,3,4-Tetrahydro-1,4-methano-9,10-anthraquinone 3

A solution of cerium ammonium nitrate (3.03 g, 5.52 mmol) in water (6.0 cm³), was added to **13**¹² (562.0 mg, 2.21 mmol) in THF–MeCN (25.0 cm³, 1:2) and after 5 min quinone **3** was collected by filtration. The filtrate was extracted with CH₂Cl₂ (2 × 30 cm³), the combined organic extracts washed with water (2 × 20 cm³) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the solid residue

recrystallised from methanol to give a further crop of quinone **3** (combined, 482.0 mg, 98%), mp 136–138 °C (lit.,¹² mp 138 °C) ν_{\max} (Nujol)/cm⁻¹ 1660vs (CO) and 1595; δ_{H} (300 MHz, CDCl₃) 1.23 (2 H, dd, *J* 2.2 and 7.7, 2_{endo}-, 3_{endo}-H), 1.44 (1 H, d, *J* 9.0, 11-H), 1.68 (1 H, dt, *J* 1.8 and 9.0, 11-H), 1.96 (2 H, d, *J* 7.7, 2_{exo}-, 3_{exo}-H), 3.63 (2 H, s, 1-, 4-H), 7.65 (2 H, dd, *J* 3.3 and 5.6, aromatic), 8.02 (2 H, dd, *J* 3.3 and 5.6, aromatic).

9,10-Bis(dicyanomethylidene)-1,2,3,4,9,10-hexahydro-1,4-methanoanthracene 4

To quinone **3** (61.4 mg, 0.27 mmol) in dry CH₂Cl₂ (5.0 cm³) at 0 °C under an inert atmosphere was added TiCl₄ (0.08 cm³, 0.68 mmol) and the resulting suspension slowly warmed to reflux. A solution of CH₂(CN)₂ (90.4 mg, 1.37 mmol) in CH₂Cl₂ (3.0 cm³) was then added at reflux and after 10 min pyridine (0.11 cm³, 1.37 mmol) in CH₂Cl₂ (3.0 cm³) was added dropwise. After 10 min of refluxing the reaction mixture was cooled to room temperature, quenched with water (4.0 cm³) and extracted with CH₂Cl₂ (5 × 25 cm³). The combined organic extracts were washed successively with 1 mol dm⁻³ HCl (2 × 20 cm³), aq. NaHCO₃ (2 × 20 cm³), water (1 × 20 cm³) and then dried over anhydrous Na₂SO₄. Removal of the solvent under reduced pressure gave a solid which was purified by column chromatography (silica, CH₂Cl₂–hexane, 3:1) to give the title compound **4** as an orange yellow solid (60.0 mg, 98%), mp 249–250 °C (Found: C, 78.9; H, 4.0; N, 17.0. C₂₁H₁₂N₄ requires C, 78.7; H, 3.8; N, 17.5%); ν_{\max} (Nujol)/cm⁻¹ 2230 (CN) and 1545; δ_{H} (300 MHz, CDCl₃) 1.59–1.64 (2 H, dm, 2_{endo}-, 3_{endo}-H), 1.60 (2 H, br s, 11-H₂), 2.21–2.25 (2 H, dm, 2_{exo}-, 3_{exo}-H), 4.16 (2 H, t, *J* 1.8, 1, 4-H), 7.71–7.74 (2 H, m, aromatic) and 8.42–8.45 (2 H, m, aromatic); δ_{C} (75 MHz, CDCl₃) 25.29 (CH₂), 45.31 (CH), 47.02 (CH₂), 79.73 [C,C–(CN)₂], 113.75 (CN), 114.22 (CN), 128.53 (CH, aromatic), 129.14 (C, aromatic), 132.45 (CH, aromatic), 151.34 (C, aromatic) and 153.52 [C, C–C–(CN)₂].

1,2,3,4-Tetrahydro-1,4-ethano-9,10-anthraquinone 5

A mixture of **14**¹² (700.0 mg, 2.63 mmol), EtOAc (100 cm³) and 5% palladium on charcoal (50 mg) was hydrogenated at atmospheric pressure until the uptake of hydrogen had ceased and the ¹H NMR showed the absence of the vinylic protons at δ 6.4. Filtration through Celite and evaporation of the filtrate under reduced pressure gave the hydrogenated compound **15** in quantitative yield (705.0 mg, 100%).

Without any further purification, a solution of **15** in THF–MeCN (30.0 cm³, 1:2) was treated with cerium ammonium nitrate (4.3 g, 7.9 mmol) in water (8.0 cm³) as described for the oxidation of **13** above, to give the quinone **5** as a yellow crystalline solid (614.0 mg, 98%), mp 148–150 °C (Found: C, 80.5; H, 6.0. C₁₆H₁₄O₂ requires C, 80.7; H, 5.9); ν_{\max} (Nujol)/cm⁻¹ 1660vs (CO), 1625 and 1590; δ_{H} (300 MHz, CDCl₃) 1.34 (4 H, d, *J* 7.2, 2-, 3-, 11-, 12-H), 1.77 (4 H, d, *J* 7.2, 2-, 3-, 11-, 12-H), 3.54 (2 H, s, 1-, 4-H), 7.68 (2 H, dd, *J* 3.6 and 5.6, aromatic) and 8.09 (2 H, dd, *J* 3.6 and 5.6, aromatic); δ_{C} (75 MHz, CDCl₃) 25.27 (CH₂), 26.81 (CH), 126.31 (CH, aromatic), 132.58 (C, aromatic), 133.27 (CH, aromatic), 150.56 (C, aromatic) and 181.84 (C=O).

9,10-Bis(dicyanomethylidene)-1,2,3,4,9,10-hexahydro-1,4-ethanoanthracene 6

To a solution of quinone **5** (100.0 mg, 0.42 mmol) in dry CH₂Cl₂ (10.0 cm³) at 0 °C under an inert atmosphere was added TiCl₄ (0.11 cm³, 1.05 mmol), and the resulting suspension heated to reflux. After 30 min a solution of CH₂(CN)₂ (139.0 mg, 2.1 mmol) in CH₂Cl₂ (2.0 cm³) was added and the mixture was refluxed for a further 5 min, after which time pyridine (0.17 cm³, 2.1 mmol) in CH₂Cl₂ (3.0 cm³) was added dropwise. After 10 min the reaction mixture was cooled to room temperature, quenched with water (5.0 cm³) and extracted with CH₂Cl₂ (5 × 30 cm³). The combined organic extracts were successively washed with 1.0 mol dm⁻³

HCl (2 × 30 cm³), aq. NaHCO₃ (2 × 30 cm³), water (1 × 30 cm³) and then dried over anhydrous Na₂SO₄. Removal of the solvent under reduced pressure gave the title compound **6** as a yellow solid (from CH₂Cl₂-hexane, 3:1 (129.1 mg, 92%), mp > 300 °C (Found: C, 79.1; H, 4.2; N, 17.0. C₂₂H₁₄N₄ requires C, 79.0; H, 4.2; N, 16.8%); ν_{max}(Nujol)/cm⁻¹ 2230 (CN) and 1540; δ_H(300 MHz, CDCl₃) 1.52 (4 H, d, *J* 7.95, 2-, 3-, 11-, 12-H), 1.87 (4 H, d, *J* 7.95, 2-, 3-, 11-, 12-H), 3.82 (2 H, br s, 1-, 4-H), 7.67–7.70 (2 H, m, aromatic) and 8.27–8.30 (2 H, m, aromatic); δ_C(75 MHz, CDCl₃) 25.07 (CH₂), 32.70 (CH), 81.46 [C, C-(CN)₂], 113.25 (CN), 113.75 (CN), 127.55 (CH, aromatic), 129.52 (C, aromatic), 131.81 (CH, aromatic), 146.45 (C, aromatic) and 156.83 [C, C-C-(CN)₂].

rel-(1R,4S,4aR,10bS)-1,2,3,4,4a,5,10,10b-Octahydro-1,4-methanobenzo[3,4]cyclobuta[1,2-b]alene-5,10-dione 7

The catalytic hydrogenation using 5% Pd/C of **16**³² (2.0 g, 7.2 mmol) and subsequent oxidation of the hydrogenated product **17** using cerium ammonium nitrate (11.8 g, 21.5 mmol) was carried out as described for quinone **3** to give the quinone **7** (1.6 g, 90%) as a yellow crystalline solid, mp 162–163 °C (Found: C, 81.5; H, 5.7. C₁₇H₁₄O₂ requires C, 81.6; H, 5.6%); ν_{max}(Nujol)/cm⁻¹ 1665 vs (CO), 1620 and 1590; δ_H(300 MHz, CDCl₃) 1.16–1.24 (3 H, m, 2_{endo}-, 3_{endo}-, 11-H), 1.29 (1 H, d, *J* 11.3, 11-H), 1.65 (2 H, dm, 2_{exo}-, 3_{exo}-H), 2.39 (2 H, s, 1-, 4-H), 3.15 (2 H, s, 4a-, 10b-H), 7.66 (2 H, dd, *J* 3.6 and 5.6, aromatic) and 8.00 (2 H, dd, *J* 3.6 and 5.6, aromatic); δ_C(75 MHz, CDCl₃) 27.78 (CH₂ × 2), 31.46 (CH₂), 33.94 (CH), 49.13 (CH), 126.42 (CH, aromatic), 133.26 (CH, aromatic), 133.63 (C), 153.88 (C) and 180.64 (C=O).

rel-(1R,4S,4aR,10bS)-5,10-Bis(dicyanomethylidene)-1,2,3,4,4a,5,10,10b-octahydro-1,4-methanobenzo[3,4]cyclobuta[1,2-b]-naphthalene 8

TiCl₄ (0.11 cm³, 1.0 mmol) was added to a solution of quinone **7** (100.0 mg, 0.40 mmol) in dry CH₂Cl₂ (5.0 cm³) at 0 °C under an inert atmosphere and the resulting suspension was warmed to 30 °C. After 10 min a solution of CH₂(CN)₂ (132.0 mg, 2.00 mmol) in CH₂Cl₂ (3.0 cm³) was added and after a further 10 min pyridine (0.16 cm³, 2.0 mmol) in CH₂Cl₂ (3.0 cm³) was added dropwise and the resulting reaction mixture heated at 30 °C for 15 min. After cooling to room temperature, the mixture was quenched with water (4.0 cm³) and extracted with CH₂Cl₂ (5 × 20 cm³). The combined organic extracts were successively washed with 1 mol dm⁻³ HCl (2 × 20 cm³), aq. NaHCO₃ (2 × 20 cm³) and dried over anhydrous Na₂SO₄. Removal of the solvent under reduced pressure gave an orange residue which was further purified by column chromatography (silica, CH₂Cl₂-hexane, 75:25) to give the compound **8** as a yellow solid (132.0 mg, 96%), mp 216–218 °C (Found: C, 79.6; H, 4.2; N, 16.1. C₂₃H₁₄N₄ requires C, 79.7; H, 4.2; N, 16.2%); ν_{max}(Nujol)/cm⁻¹ 2225 (CN) and 1535; δ_H(300 MHz, CDCl₃) 1.19 (2 H, br s, 13-H₂), 1.32 (2 H, dd, *J* 1.7 and 7.7, 2_{endo}-, 3_{endo}-H), 1.71–1.74 (2 H, dm, 2_{exo}-, 3_{exo}-H), 2.65 (2 H, br s, 1-, 4-H), 3.55 (2 H, s, 4a-, 10b-H), 7.77–7.81 (2 H, m, aromatic) and 8.83–8.86 (2 H, m, aromatic); δ_C(75 MHz, CDCl₃) 27.47 (CH₂), 31.03 (CH), 36.37 (CH), 51.22 (CH), 79.92 [C, C-(CN)₂], 113.56 (CN), 114.24 (CN), 128.69 (CH, aromatic), 128.91 (C, aromatic), 133.19 (CH, aromatic), 147.99 (C, aromatic) and 149.76 (C, C-C-(CN)₂).

rel-(1R,4S)-1,2,3,4,5,7,8,9,10,12-Decahydro-7,10-ethano-1,4-methanonaphthalene-5,12-dione 9

A solution of **18**³³ (500.0 mg, 2.90 mmol), **19**³⁴ (500.0 mg, 3.70 mmol) and PbO₂ (3.0 g) in dry benzene (20.0 cm³) was heated for 16 h at 90 °C in a reaction tube. The solution was filtered through Celite, the solvent removed under reduced pressure and the solid residue purified by column chromatography (silica, EtOAc-hexane, 3:7) to give the title compound **9** as an orange-yellow solid (520.0 mg, 61.2%), mp 210–211 °C (Found: C, 82.7;

H, 6.8. C₂₁H₂₀O₂ requires C, 82.8; H, 6.6%); ν_{max}(Nujol)/cm⁻¹ 1655 vs (CO) and 1605; δ_H(300 MHz, CDCl₃) 1.19 (2 H, dd, *J* 2.1 and 7.2, 8_{endo}-, 9_{endo}-H), 1.34 (4 H, br d, *J* 7.7, 2-, 3-, 11-, 12-H), 1.41 (1 H, d, *J* 7.9, 13-H), 1.66 (1 H, dt, *J* 1.9 and 9.2, 13-H), 1.82 (4 H, br d, *J* 7.7, 2-, 3-, 11-, 12-H), 1.93 (1 H, dt, *J* 1.8 and 7.5, 8_{exo}-, 9_{exo}-H), 3.15 (2 H, s, 1-, 4-H), 3.61 (2 H, s, 7-, 10-H) and 7.81 (2 H, s, aromatic); δ_C(75 MHz, CDCl₃) 25.20 (CH₂), 25.66 (CH₂), 34.45 (CH), 40.92 (CH), 47.49 (CH₂), 121.41 (CH, aromatic), 131.57 (C), 150.34 (C), 153.74 (C) and 182.80 (C=O).

rel-(1R,4S)-5,12-Bis(dicyanomethylidene)-1,2,3,4,5,7,8,9,10,12-decahydro-7,10-ethano-1,4-methanonaphthalene 10

TiCl₄ (0.05 cm³, 0.49 mmol) was carefully added to a solution of quinone **9** (50.0 mg, 0.16 mmol) in dry CH₂Cl₂ (10.0 cm³) at 0 °C under an inert atmosphere and the resulting suspension was heated to reflux. After 10 min a solution of CH₂(CN)₂ (54.0 mg, 0.82 mmol) in CH₂Cl₂ (3.0 cm³) was added and the mixture refluxed for a further 10 min after which time pyridine (0.12 cm³, 1.51 mmol) in CH₂Cl₂ (3.0 cm³) was added dropwise. The reaction mixture was then refluxed for 1 h, cooled to room temperature, quenched with water (10.0 cm³) and extracted with CH₂Cl₂ (5 × 30 cm³). The combined organic extracts were successively washed with 1 mol dm⁻³ HCl (3 × 20 cm³), aq. NaHCO₃ (3 × 20 cm³) and dried over anhydrous Na₂SO₄. Solvent removal under reduced pressure gave a solid residue which was purified by column chromatography (silica, CH₂Cl₂-hexane, 3:1) to give the title compound **10** as an orange-yellow solid (60.0 mg, 91%), mp (decomp.) > 260 °C (Found: C, 80.6; H, 5.4; N, 13.9. C₂₃H₁₄N₄ requires C, 80.9; H, 5.0; N, 14.0%); ν_{max}(Nujol)/cm⁻¹ 2220 (CN) and 1540; δ_H(300 MHz, CDCl₃) 1.29 (1 H, d, *J* 7.7, 17-H), 1.50 (1 H, d, *J* 7.9, 17-H), 1.55 (4 H, br d, *J* 7.4, 2-, 3-, 15-, 16-H), 1.59 (2 H, d, *J* 8.2, 8_{endo}-, 9_{endo}-H), 1.87 (4 H, br d, *J* 7.4, 2-, 3-, 15-, 16-H), 2.18 (2 H, dt, *J* 2.0 and 7.9, 8_{exo}-, 9_{exo}-H), 3.17 (2 H, s, 1-, 4-H), 4.14 (2 H, s, 7-, 10-H) and 8.18 (2 H, s, aromatic); δ_C(75 MHz, CDCl₃) 25.30 (CH₂), 25.39 (CH₂), 25.69 (CH₂), 34.43 (CH), 45.18 (CH), 46.93 (CH₂), 78.42 [C, C-(CN)₂], 114.07 (CN), 114.59 (CN), 123.89 (CH, aromatic), 149.93 (C), 151.09 (C) and 154.30 [C, C-C-(CN)₂].

rel-(1R,4S,4aR,12bS)-1,2,3,4,4a,5,5a,6,7,8,9,10,11,11a,12,12b-hexadecahydro-7,10-ethano-1,4-methano-benzo[3,4]cyclobuta[1,2-b]anthracene-6,11-dione 23

CH₃AlCl₂ (0.5 cm³, 2.5 mmol) was carefully added to a solution of quinone **21**³⁵ (1.54 g, 8.2 mmol) in dry CH₂Cl₂ (22 cm³) at 0 °C under an inert atmosphere. After 10 min, diene **22**³⁶ (1.2 g, 8.2 mmol) in CH₂Cl₂ (4 cm³) was added dropwise over a period of 3 min and the resulting reaction mixture maintained at 0 °C for 1.25 h, whereupon it was quenched with water (15 cm³) and extracted with CH₂Cl₂ (3 × 50 cm³). The combined organic extracts were washed successively with aq. NaHCO₃ (2 × 50 cm³), water (2 × 50 cm³) and dried over anhydrous Na₂SO₄. Solvent removal under reduced pressure gave the adduct **23** (2.7 g, 95%) as a solid residue that was not further purified; δ_H(300 MHz, CDCl₃) 0.96–1.03 (3 H, m, 2_{endo}-, 3_{endo}-, 13-H), 1.18–1.27 (5 H, m, 8-, 9-, 13-, 14-, 15-H), 1.49 (2 H, dt, *J* 2.8 and 7.4, 2_{exo}-, 3_{exo}-H), 1.69 (4 H, d, *J* 8.5, 8-, 9-, 14-, 15-H), 1.97 (2 H, s, 1-, 4-H), 2.05 (2 H, dd, *J* 4.9 and 15.1, 5_{gem}-, 12_{gem}-H), 2.28 (2 H, dd, *J* 4.9 and 15.1, 5_{gem}-, 12_{gem}-H), 2.46 (2 H, s, 4a-, 12b-H) and 3.21 (4 H, m, 5a-, 7-, 10-, 11a-H).

rel-(1R,4S,4aR,12bS)-1,2,3,4,4a,6,7,8,9,10,11,12b-dodecahydro-7,10-ethano-1,4-methanobenzo[3,4]cyclobuta[1,2-b]-anthracene-6,11-dione 11

A suspension of adduct **23** (2.0 g, 5.8 mmol), DDQ (2.8 g, 12.2 mmol) and trifluoroacetic acid (1.0 cm³) in dry dioxane (25 cm³) was refluxed for 24 h under an argon atmosphere. The reaction mixture was cooled to room temperature, filtered and the solvent removed under reduced pressure to give a solid residue which was purified by column chromatography (silica,

CH₂Cl₂-hexane, 70:30) to give the quinone **11** as a bright yellow solid (1.8 g, 91%), mp 224–225 °C (Found: C, 83.1; H, 6.7. C₂₃H₂₂O₂ requires C, 83.6; H, 6.7%); ν_{\max} (Nujol)/cm⁻¹ 1655vs (CO), 1630 and 1590; δ_{H} (300 MHz, CDCl₃) 0.81 (1 H, d, *J* 10.5, 13-H), 1.00 (1 H, d, *J* 10.5, 13-H), 1.18 (2 H, dd, *J* 2.3 and 7.2, 2_{endo}-, 3_{endo}-H), 1.32 (4 H, br d, *J* 7.2, 8-, 9-, 14-, 15-H), 1.60 (2 H, dd, *J* 2.3 and 7.2, 2_{exo}-, 3_{exo}-H), 1.75 (4 H, br d, *J* 7.4, 8-, 9-, 14-, 15-H), 2.36 (2 H, s, 1-, 4-H), 3.20 (2 H, s, 4a-, 12b-H), 3.51 (2 H, s, 7-, 10-H) and 7.74 (2 H, s, aromatic); δ_{C} (75 MHz, CDCl₃) 25.33 (CH₂), 26.82 (CH), 27.63 (CH₂), 2.00 (CH₂), 36.38 (CH), 51.04 (CH), 119.82 (CH, aromatic), 133.07 (C), 150.01 (C), 152.74 (C) and 182.41 (C=O).

rel-(1R,4S,4aR,12bS)-6,11-Bis(dicyanomethylidene)-1,2,3,4,4a,6,7,8,9,10,11,12b-dodecahydro-7,10-ethano-1,4-methanobenzo-[3,4]cyclobuta[1,2-b]anthracene **12**

TiCl₄ (0.08 cm³, 0.76 mmol) was carefully added to a solution of quinone **11** (100.0 mg, 0.30 mmol) in dry CH₂Cl₂ (10.0 cm³) at 0 °C under an inert atmosphere and the resulting suspension was heated to reflux. After 5 min a solution of CH₂(CN)₂ (100.0 mg, 1.51 mmol) in CH₂Cl₂ (3.0 cm³) was added and the mixture refluxed for a further 5 min, after which time pyridine (0.12 cm³, 1.51 mmol) in CH₂Cl₂ (3.0 cm³) was added dropwise. The reaction mixture was then refluxed for a further 45 min, cooled to room temperature, quenched with water (10.0 cm³) and extracted with CH₂Cl₂ (5 × 30 cm³). The combined organic extracts were successively washed with 1 mol dm⁻³ HCl (3 × 20 cm³), aq. NaHCO₃ (3 × 20 cm³) and dried over anhydrous Na₂SO₄. Removal of the solvent under reduced pressure gave a solid residue which was purified by column chromatography (silica, CH₂Cl₂-hexane, 3:1) to give the title compound **12** as an orange-yellow solid (122.0 mg, 95%), mp (decomp.) > 240 °C (Found: C, 81.4; H, 5.5; N, 12.9. C₂₉H₂₂N₄ requires C, 81.6; H, 5.2; N, 13.1%); ν_{\max} (Nujol)/cm⁻¹ 2220 (CN) and 1560; δ_{H} (300 MHz, CDCl₃) 0.80 (1 H, d, *J* 10.5, 15-H), 1.05 (1 H, d, *J* 10.5, 15-H), 1.23 (2 H, dd, *J* 2.0 and 7.4, 2_{endo}-, 3_{endo}-H), 1.44 (2 H, br d, *J* 7.4, 8-, 9-H), 1.55–1.68 (4 H, m, 2_{exo}-, 3_{exo}-, 8-, 9-H), 1.81 (4 H, dd, *J* 6.4 and 12.1, 16-, 17-H₂), 2.39 (2 H, s, 1-, 4-H), 3.36 (2 H, s, 4a-, 12b-H), 3.78 (2 H, s, 7-, 10-H) and 7.87 (2 H, s, aromatic); δ_{C} (75 MHz, CDCl₃) 24.96 (CH₂), 25.17 (CH₂), 27.51 (CH₂), 32.23 (CH₂), 32.57 (CH), 36.58 (CH), 51.16 (CH), 80.68 [C, C-(CN)₂], 113.47 (CN), 114.01 (CN), 121.30 (CH, aromatic), 129.16 (C), 145.99 (C), 151.35 (C) and 158.28 [C, C-(CN)₂].

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