Benzoquinones and Related Compounds. Part I. Crystal and Molecular Structure of 1,4,4a,5,8,8a,9a,10a-Octahydro-1,4:5,8-dimethano-9,10-anthraquinone, a Diels–Alder Adduct from 1,4-Benzoquinone and Cyclopentadiene

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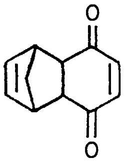
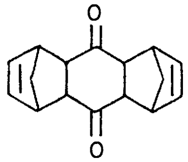
X-Ray crystallography of the Diels–Alder adduct from 1,4-benzoquinone and two equivalents of cyclopentadiene confirms that its stereochemistry is *endo,cis,anti,cis,endo*. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 11{\cdot}992(8)$, $b = 6{\cdot}236(4)$, $c = 16{\cdot}977(9)$ Å, $\beta = 110{\cdot}63(9)^\circ$. The structure was solved from diffractometer data by symbolic addition methods and refined by least-squares techniques to R 6·6 for 1294 independent reflexions.

THE Diels–Alder reaction between equimolar quantities of 1,4-benzoquinone and cyclopentadiene gives[1] the adduct (1), which with further cyclopentadiene affords[2] 1,4,4a,5,8,8a,9a,10a-octahydro-1,4:5,8-dimethano-9,10-anthraquinone (2). Support for the structure of the mono-adduct (1) has been obtained[3] from the identity of its reduction product with the hydrocarbon (3) prepared by other routes. The *endo,cis*-stereochemistry[4] of compound (1) is indicated by the ^{1}H n.m.r. spectra of its 2,3-epoxide and related compounds,[5] and by formation of the cage-like isomer (4) when a solution in ethyl acetate is irradiated[6] with u.v. light; *exo* to *endo* isomerisation during irradiation is unlikely, but its possibility has not been excluded.


(1)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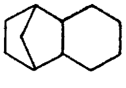
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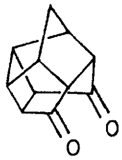
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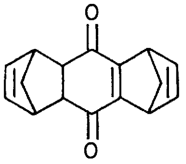
The structure of part of the bis-adduct (2) follows from this, but the *endo*- or *exo*-stereochemistry of the newly added bridged ring system, and its *syn* or *anti* relation to the one previously present, does not. Evidence that the stereochemistry of (2) is *endo,cis,anti,cis,endo* has been obtained[7] by photocyclisation of the derived conjugated enedione (5) to a cage-like molecule analogous to (4), and by optical resolution[8] of a number of compounds prepared from the 2,3,6,7-tetrahydro-derivative of (2), which establishes the *endo,cis,anti,cis,endo* structure (6), subsequently confirmed[9] by *X*-ray crystallography for an unspecified member of the series of isomeric tetrahydro-compounds derived from (2), but presumably that obtained directly from the hydrogenation.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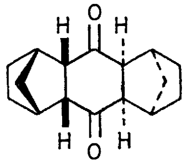

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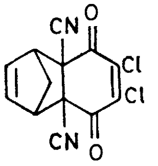

(7)

An *X*-ray analysis[10] of a mono-adduct obtained from 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and cyclopentadiene has shown that it has the *exo*-configuration † (7), but since this adduct is known[12] to result from thermal isomerisation of the *endo*-isomer formed initially, it follows that configurations assigned to adducts such as (1) and (2) on the basis of chemical transformations, particularly those involving relatively drastic conditions,

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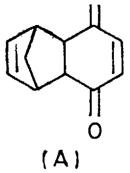
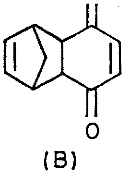
† There is no generally accepted convention for representation of *endo*- and *exo*-adducts in the 1,4-quinone–cyclopentadiene series, and it has been suggested[11] that *endo*- and *exo*-adducts should be represented as (A) and (B) respectively. This notation is used in this paper, and will be used in subsequent papers in the series; formula (2) therefore denotes an *endo,endo*-system, each 'methylene bridge' pointing away from the quinone residue.


(A)


(B)

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[11] J. M. Bruce, in 'Rodd's Chemistry of Carbon Compounds,' 2nd edn., vol. IIIB, ed. S. Coffey, ch 8, in the press, and refs. therein.

[12] R. Al-Hamdany, J. M. Bruce, M. W. Coville, F. Heatley, and R. F. Warren, unpublished work.

must be treated with caution.* In view of this, and to provide bond-length and -angle data required for other studies [15] of Diels–Alder reactions of 1,4-quinones, an *X*-ray crystallographic examination of the bis-adduct (2) was undertaken. The results of this are now described.

EXPERIMENTAL

1,4,4a,5,8,8a,9a,10a-*Octahydro*-1,4:5,8-*dimethano*-9,10-*anthraquinone*.—A mixture of 1,4-benzoquinone (1·0 g; sublimed) and cyclopentadiene (5 ml; freshly prepared) was kept in the dark at room temperature for 24 h. Volatile materials were removed at 20°, finally at 0·1 mmHg, and the residue was crystallised from ethanol to give the bis-adduct (2·0 g, 90%), m.p. 159—160 °C (lit.,[16] 157—158 °C). It had $\nu_{max.}$ (CCl_4) 3060w, 2990m, 2940m, 2860m, 1690s, 1455w, 1338m, and 1302m cm^{-1}; τ (15% $CDCl_3$, 100 MHz) 3·88 (m, H-2 + H-3 + H-6 + H-7), 6·72 (m, H-1 + H-4 + H-5 + H-8), 7·72 (m, H-4a + H-8a + H-9a + H-10a), and 8·7 (m, 2 × H-11 + 2 × H-12), these assignments being confirmed by spin decoupling; *m/e* 240 (M^+, 15%), 212 (25), 174 (100), 146 (40), 117 (32), 108 (40), 91 (100), 82 (40), and 80 (20). Monitoring of the addition, in $CDCl_3$, in the cavity of a ^1H n.m.r. spectrometer showed that the only detectable intermediate was the mono-adduct, and that the sole final product was the octahydrodimethanoanthraquinone, further shown to be homogeneous by t.l.c. on silica gel using 9 : 1 benzene–ethanol, 2 : 1 ether–cyclohexane, and methanol as eluants.

Crystal Data.—1,4,4a,5,8,8a,9a,10a-Octahydro-1,4:5,8-dimethano-9,10-anthraquinone, $C_{16}H_{16}O_2$, $M = 240·3$. Monoclinic, $a = 11·992(8)$, $b = 6·236(4)$, $c = 16·977(9)$ Å, $\beta = 110·63(9)°$, $U = 1188$ Å^3, $D_m = ca.$ 1·31, $Z = 4$, $D_c = 1·34$, $F(000) = 512$. Space group $P2_1/c$ (C^5_{2h}, No. 14) by systematic absences. Mo-K_α radiation, $\lambda = 0·7107$ Å; μ(Mo-K_α) = 0·94 cm^{-1}.

X-Ray intensities from a crystal with dimensions 0·6 × 0·4 × 0·2 mm were collected on a Hilger and Watts computer-controlled four-circle diffractometer [17] as far as θ 24° with zirconium-filtered Mo-K_α radiation by the ω—2θ scan method with background measurements at both ends of a one-degree scan. Of the 2172 independent reflexions so measured, 1294 had $F^2 > 3\sigma(F^2)$ and were used in the analysis. Corrections were applied for Lorentz and polarisation factors.

Solution and Refinement.—The structure was solved by a symbolic addition procedure based on the direct phase-determination approach.[18] 335 Reflexions had values of $E > 1·4$ and the three reflexions (*a*) $31\bar{6}$, $|E|$ 3·38, (*b*) $6,2,\overline{13}$, $|E|$ 2·91, and (*c*) $12\bar{3}$, $|E|$ 2·89 were given positive signs and a further three (*d*) $7,3,\overline{12}$, $|E|$ 3·09, (*e*) $6,2,\overline{11}$, $|E|$ 3·07, and (*f*) $10,0,\bar{2}$, $|E|$ 2·63 assigned symbols. A reiterative procedure [19] resulted in 178 signs determined in terms of the three symbols with an internally consistent set of (*d*) negative, (*e*) negative, and (*f*) positive. An *E* map computed with these 178 signed reflexions revealed probable sites for 12 of the 18 non-hydrogen atoms. The complete structure was revealed by a Fourier synthesis of electron density with phases based on the 12 positions.† The initial structure (*R* 44%) was refined by least-squares methods in which the function minimised was $\Sigma w(|F_o| - k|F_c|)^2$. The 164 parameters were partitioned into three large blocks each of 54 and one of 2 parameters. At *R* 13·4, a difference-Fourier synthesis indicated somewhat diffuse maxima (*ca.* 0·3—0·6 eÅ^{-3}) at likely hydrogen atom positions. The parameters for the final structure yielded *R* 6·6%. The hydrogen atoms were placed 1·06 Å from, and given isotropic temperature factors equal to, the appropriate carbon atoms and their parameters were not refined. The final weighting scheme was $w^{-1} = 2·29 - 0·2215\,F_o + 0·00583\,F_o^2$ if $F_o < 64$, else $w^{-1} = 0·8\,F_o$. The scattering factors of ref. 20 were used throughout. All programmes used in this analysis were written by members of our laboratory.

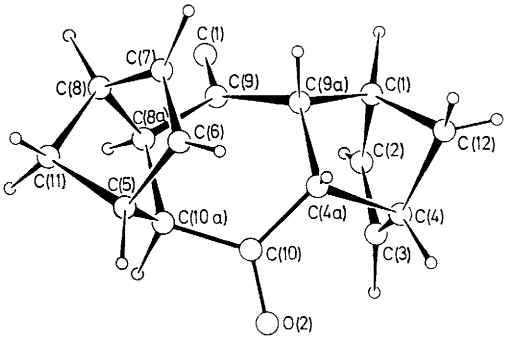

FIGURE 1 View of (2), showing the atom numbering scheme used in the analysis

RESULTS

Table 1 contains the final atomic parameters and a view of the molecule is given in Figure 1. Details of the molecular geometry are given in Tables 2—4. There were no intermolecular contacts <3 Å (hydrogen atoms excluded) (Figure 2). Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20869 (13 pp., 1 microfiche).‡

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* Irradiation of an ethyl acetate solution of the *endo*-mono-adduct of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and cyclopentadiene with either visible or u.v. (Pyrex filter) light gives the corresponding cage-compound [as (4)]; the *exo*-adduct is unchanged by visible light, but affords unidentified non-olefinic material with u.v. (Pyrex filter) light.[13] The most definitive photochemical test of configuration in this series is therefore that using visible light (tungsten filament lamp); the adduct (1) and all its derivatives which have been examined are smoothly cyclised to the corresponding cage-compounds under these conditions.[14]

† It is interesting that a solution was obtained in spite of a sign contradiction introduced at a very early stage in sign development which corresponded to the sign of $31\bar{6}$ being sometimes positive and sometimes negative. The *E*-map revealed only twelve atoms, and phases calculated from these twelve led to poor agreement between F_o and F_c for the reflexions whose signs were directly related to the ambiguously defined initial reflexion. The phases were accepted for a Fourier synthesis of electron density and the structure which corresponded to the negative sign emerged. Although a satisfactory conclusion was arrived at, this procedure is not to be recommended.

‡ See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[13] R. Al-Hamdany, J. M. Bruce, and M. W. Coville, unpublished work.

[14] R. Al-Hamdany, R. Brown, and J. M. Bruce, unpublished work.

[15] R. Al-Hamdany, R. Brown, J. M. Bruce, M. W. Coville, F. Heatley, L. M. J. Heelam, R. F. Warren, and J. G. Watkinson, unpublished work.

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TABLE 1

Atomic and thermal * parameters (all $\times 10^4$ except B), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	7723(3)	−1087(6)	8036(2)	59(3)	269(11)	39(1)	−11(5)	11(2)	26(4)
C(2)	7526(3)	−2897(6)	7408(2)	91(3)	176(11)	56(2)	16(5)	32(2)	32(4)
C(3)	6399(3)	−2815(6)	6891(2)	89(4)	186(10)	45(2)	−34(5)	23(2)	−1(4)
C(4)	5830(3)	−952(6)	7167(2)	53(3)	267(11)	36(1)	−10(5)	12(2)	0(4)
C(5)	7143(3)	1676(6)	4908(2)	76(3)	296(13)	28(1)	−2(5)	9(2)	−3(3)
C(6)	7540(3)	3933(6)	5201(2)	106(4)	258(12)	34(1)	0(6)	26(2)	20(4)
C(7)	8662(3)	3832(6)	5715(2)	99(4)	266(12)	38(2)	−42(6)	22(2)	8(4)
C(8)	9045(3)	1508(6)	5776(2)	64(3)	332(14)	38(2)	0(5)	18(2)	0(4)
C(9)	8615(3)	1283(5)	7155(2)	53(3)	160(9)	32(1)	−4(4)	3(2)	0(3)
C(10)	6165(3)	1438(5)	6025(2)	51(3)	145(9)	36(2)	−15(4)	6(2)	−5(3)
C(11)	8315(3)	722(7)	4886(2)	97(4)	343(14)	37(2)	−11(6)	28(2)	−19(4)
C(12)	6494(3)	−998(6)	8120(2)	77(3)	294(12)	35(2)	−7(6)	15(2)	12(4)
C(4a)	6363(3)	1179(5)	6948(2)	55(3)	189(10)	33(1)	12(5)	13(2)	−2(3)
C(8a)	8368(3)	358(5)	6284(2)	51(3)	182(10)	34(1)	−4(4)	11(2)	1(3)
C(9a)	7679(3)	1073(5)	7554(2)	61(3)	194(10)	29(1)	−21(5)	11(2)	−14(3)
C(10a)	7042(3)	463(5)	5677(2)	55(3)	190(10)	27(1)	−11(4)	5(2)	−9(3)
O(1)	9564(2)	2129(4)	7538(1)	64(2)	350(9)	41(1)	−50(4)	7(1)	−6(3)
O(2)	5280(2)	2364(4)	5568(1)	64(2)	313(9)	43(1)	40(4)	4(1)	22(3)

Atom	x/a	y/b	z/c	$B/Å^2$	Atom	x/a	y/b	z/c	$B/Å^2$
H(1)	8499	−1279	8574	4·79	H(8)	9980	1281	6010	5·07
H(2)	8171	−4028	7385	5·21	H(8a)	8651	−1239	6646	4·04
H(3)	5981	−3862	6383	4·99	H(9a)	7908	2423	7955	4·09
H(4)	4888	−1019	6924	4·57	H(10a)	6666	−1086	5536	3·97
H(4a)	5935	2589	7039	4·05	H(11)	8591	1408	4414	5·57
H(5)	6369	1600	4362	4·87	Hx(11)	8295	−967	4830	5·57
H(6)	7016	5337	5026	5·18	H(12)	6361	395	8428	5·06
H(7)	9196	5140	6027	5·32	Hx(12)	6300	−2377	8412	5·06

* Anisotropic temperature coefficients: $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$.

TABLE 2

(*a*) Intramolecular distances (Å) with estimated standard deviations in parentheses

C(1)–C(2)	1·513(5)	C(5)–C(11)	1·538(5)
C(1)–C(9a)	1·568(4)	C(6)–C(7)	1·323(5)
C(1)–C(12)	1·530(5)	C(7)–C(8)	1·513(5)
C(2)–C(3)	1·328(5)	C(8)–C(8a)	1·554(5)
C(3)–C(4)	1·504(5)	C(8)–C(11)	1·536(5)
C(4)–C(4a)	1·576(5)	C(8a)–C(9)	1·516(4)
C(4)–C(12)	1·531(4)	C(8a)–C(10a)	1·562(4)
C(4a)–C(9a)	1·552(4)	C(9)–C(9a)	1·507(4)
C(4a)–C(10)	1·508(4)	C(9)–O(1)	1·215(4)
C(5)–C(6)	1·514(5)	C(10)–C(10a)	1·505(4)
C(5)–C(10a)	1·551(5)	C(10)–O(2)	1·217(3)

(*b*) Intramolecular angles (deg.) with estimated standard deviations in parentheses

C(2)–C(1)–C(9a)	107·8(2)	C(8a)–C(8)–C(11)	99·9(3)
C(2)–C(1)–C(12)	100·2(3)	C(8)–C(8a)–C(9)	113·9(3)
C(9a)–C(1)–C(12)	99·3(3)	C(8)–C(8a)–C(10a)	102·9(3)
C(1)–C(2)–C(3)	107·9(3)	C(9)–C(8a)–C(10a)	115·6(3)
C(2)–C(3)–C(4)	107·0(3)	C(8a)–C(9)–C(9a)	119·0(3)
C(3)–C(4)–C(4a)	108·2(2)	C(8a)–C(9)–O(1)	120·8(3)
C(3)–C(4)–C(12)	101·0(3)	C(9a)–C(9)–O(1)	120·2(3)
C(4a)–C(4)–C(12)	99·4(3)	C(1)–C(9a)–C(4a)	102·8(3)
C(4)–C(4a)–C(9a)	102·1(3)	C(1)–C(9a)–C(9)	114·6(3)
C(4)–C(4a)–C(10)	114·1(3)	C(4a)–C(9a)–C(9)	116·3(3)
C(9a)–C(4a)–C(10)	116·5(3)	C(4a)–C(10)–C(10a)	119·2(3)
C(6)–C(5)–C(10a)	106·6(3)	C(4a)–C(10)–O(2)	119·8(3)
C(6)–C(5)–C(11)	100·6(3)	C(10a)–C(10)–O(2)	120·9(3)
C(10a)–C(5)–C(11)	100·1(3)	C(5)–C(10a)–C(8a)	102·3(3)
C(5)–C(6)–C(7)	107·6(3)	C(5)–C(10a)–C(10)	114·0(3)
C(6)–C(7)–C(8)	107·7(3)	C(8a)–C(10a)–C(10)	116·6(3)
C(7)–C(8)–C(8a)	106·0(3)	C(5)–C(11)–C(8)	93·5(3)
C(7)–C(8)–C(11)	100·7(3)	C(1)–C(12)–C(4)	93·5(2)

DISCUSSION

The analysis confirms that the bis-adduct has the *endo,cis,anti,cis,endo* structure (2) and provides therefore the first structural information on such compounds.

Our analysis shows that the central cyclohexanedione ring is non-planar in the solid and that the distortion is towards the boat conformer. A similar, but smaller, distortion from planarity has been reported [21] in the case of *anti*-1-bromotricyclo[5.1.0.0^{3,5}]octane-2,6-dione (8). Thus whereas the recorded deviations of the atoms corresponding to C(9) and C(10) from the mean plane of C(4a), C(8a), C(9a), and C(10a) is 0·06 Å, in the present analysis we find 0·37 Å. This latter is, even so, less than that to be expected in an idealised boat structure. *X*-Ray analyses of both (7) and *endo*-2,3-dichloro-4a,8a-dicyano-4a,5,8,8a-tetrahydro-5,7-dimethyl-5,8-(2,2-dimethylethano)-1,4-naphthoquinone (9) [10] likewise show distortions towards boat conformers but in these cases the carbonyl groups are unsymmetrically arranged and the displacements are less than in (2); a contributory factor here may well be the conjugation in the enedione system.

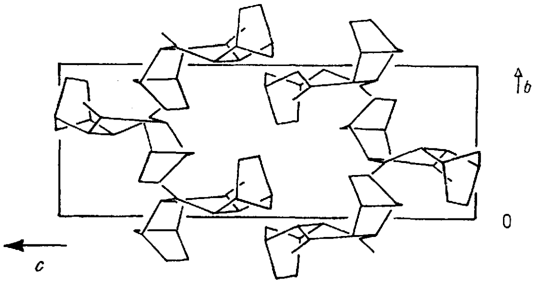

FIGURE 2 Packing diagram as viewed along the *a* axis

It is debatable whether the non-planarity of (2) persists in solution or not. On the one hand it is recorded [22] that in CCl_4 ' the central ring is quite flat

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[21] J. Heller, A. S. Dreiding, R. Grieb, and A. Niggli, *Angew. Chem.*, 1972, **84**, 170; *Angew. Chem. Internat. Edn.*, 1972, **11**, 366.

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and the bond angle associated with the principal dipole moment is 25° ' whilst elsewhere,[23] when considering the unchanged ^{1}H n.m.r. spectrum of (2) in CH_2Cl_2 at room temperature and at −100°, ' the cyclohexanedione ring could therefore be planar. . . . However the evidence would also be consistent with a boat-shaped cyclohexanedione ring which was undergoing a degenerate conformational change still rapid at −100°.'

TABLE 3

Equations of least-squares planes in terms of X, Y, Z which refer to orthogonal co-ordinates obtained by the transformation:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

Distances (Å) of some relevant atoms from the plane are given in square brackets

Plane (1): C(1)—(4)

$$-0{\cdot}5115X - 0{\cdot}6034Y + 0{\cdot}6118Z - 5{\cdot}9430 = 0$$

[C(1) 0·000, C(2) 0·000, C(3) 0·000, C(4) 0·000, C(4a) −1·410, C(9a) −1·402, C(12) 0·827]

Plane (2): C(5)—(8)

$$-0{\cdot}6169X - 0{\cdot}1273Y + 0{\cdot}7767Z - 2{\cdot}4496 = 0$$

[C(5) 0·001, C(6) −0·001, C(7) 0·001, C(8) −0·001, C(8a) 1·406, C(10a) 1·406, C(11) −0·825]

Plane (3): C(1), C(4), C(12)

$$0{\cdot}0376X + 0{\cdot}9992Y + 0{\cdot}0134Z + 0{\cdot}3392 = 0$$

Plane (4): C(5), C(8), C(11)

$$-0{\cdot}3496X - 0{\cdot}8557Y + 0{\cdot}3816Z - 1{\cdot}1264 = 0$$

Plane (5): C(1), C(4), C(4a), C(9a)

$$-0{\cdot}5259X + 0{\cdot}4877Y + 0{\cdot}6968Z - 6{\cdot}2240 = 0$$

[C(1) 0·000, C(4) 0·000, C(4a) 0·000, C(9a) 0·000]

Plane 6: C(5), C(8), C(8a), C(10a)

$$0{\cdot}2699X - 0{\cdot}8723Y - 0{\cdot}4077Z + 2{\cdot}5699 = 0$$

[C(5) −0·002, C(8) 0·002, C(8a) −0·003, C(10a) 0·003]

Plane (7): C(4a), C(8a), C(9), C(9a), C(10), C(10a)

$$-0{\cdot}1352X - 0{\cdot}9844Y + 0{\cdot}1123Z + 0{\cdot}0751 = 0$$

[C(4a) 0·121, C(8a) 0·128, C(9) −0·254, C(9a) 0·130, C(10) −0·246, C(10a) 0·121, O(1) −0·829, O(2) −0·789]

Plane (8): C(8a), C(9), C(9a), O(1)

$$0{\cdot}2602X - 0{\cdot}8794Y + 0{\cdot}3987Z - 5{\cdot}4164 = 0$$

[C(8a) 0·003, C(9) −0·011, C(9a) 0·003, O(1) 0·004]

Plane (9): C(4a), C(10), C(10a), O(2)

$$-0{\cdot}4813X - 0{\cdot}8567Y - 0{\cdot}1855Z + 4{\cdot}3569 = 0$$

[C(4a) 0·004, C(10) −0·014, C(10a) 0·004, O(2) 0·005]

Plane (10): C(4a), C(8a), C(9a), C(10a)

$$0{\cdot}1390X + 0{\cdot}9842Y - 0{\cdot}1090Z - 0{\cdot}0032 = 0$$

[C(4a) 0·001, C(8a) 0·001, C(9a) −0·001, C(10a) −0·001]

Angles between planes (deg.)

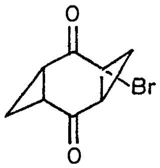
(1)–(2)	29·8	(3)–(5)	61·5
(1)–(3)	127·9	(3)–(10)	9·2
(1)–(5)	66·4	(4)–(6)	60·2
(1)–(10)	137·0	(4)–(10)	158·8
(2)–(4)	51·6	(8)–(9)	56·3
(2)–(6)	111·9	(8)–(10)	150·8
(2)–(10)	107·2	(9)–(10)	152·9

In the analyses of (7) and (9), comment is made on the usually long bond-lengths which correspond to C(4a)–C(9a) and recorded as 1·59(1) and 1·63(2) Å. Our values [1·552(4) and 1·562(4) Å], though shorter are nevertheless longer than the standard value (1·54 Å), which suggests that influences additional to those of the cyano-groups in (7) and (9) are operative. Similarly, the bonds C(1)–C(9a), C(4)–C(4a), C(5)–C(10a), and C(8)–C(8a), formed by the addition reactions, of length 1·55—1·58 Å are somewhat long and reflect, with greater precision, the findings in structures (7) and (9) (range 1·54—1·61 Å). The angles at the bridging methylene groups C(11) and C(12) are both 93·5(3)°, in close agreement with the value (94°) reported[10] for (7) and somewhat less than the 96·5° reported[9] for the tetrahydro-compound (6), perhaps reflecting the constraining influence of the olefinic double bond.

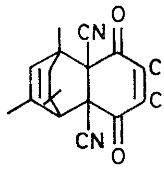
TABLE 4

Torsion angles (deg.)

C(10a)–C(8a)–C(9)–C(9a)	33·9
C(8a)–C(9)–C(9a)–C(4a)	−28·5
C(9)–C(9a)–C(4a)–C(10)	1·1
C(9a)–C(4a)–C(10)–C(10a)	32·1
C(4a)–C(10)–C(10a)–C(8a)	−32·3
C(10)–C(10a)–C(8a)–C(9)	−0·7
C(10a)–C(8a)–C(9)–O(1)	−148·1
C(4a)–C(9a)–C(9)–O(1)	147·8
C(9a)–C(4a)–C(4)–C(12)	37·6
C(4a)–C(4)–C(12)–C(1)	−60·5
C(4)–C(12)–C(1)–C(9a)	60·4
C(12)–C(1)–C(9a)–C(4a)	−37·6
O(1)–C(9a)–C(4a)–C(4)	0·0
C(1)–C(12)–C(4)–C(3)	50·3
C(12)–C(4)–C(3)–C(2)	−33·4
C(4)–C(3)–C(2)–C(1)	0·0
C(3)–C(2)–C(1)–C(12)	33·3
C(2)–C(1)–C(12)–C(4)	−49·7
C(8a)–C(10a)–C(10)–O(2)	150·3
C(9a)–C(4a)–C(10)–O(2)	−150·4
C(5)–C(6)–C(7)–C(8)	0·2
C(6)–C(7)–C(8)–C(11)	32·9
C(7)–C(8)–C(11)–C(5)	−49·4
C(8)–C(11)–C(5)–C(6)	49·6
C(11)–C(5)–C(6)–C(7)	−33·3
C(10a)–C(5)–C(11)–C(8)	−59·6
C(5)–C(11)–C(8)–C(8a)	59·1
C(11)–C(8)–C(8a)–C(10a)	−36·8
C(8)–C(8a)–C(10a)–C(5)	−0·4
C(8a)–C(10a)–C(5)–C(11)	37·5
C(6)–C(7)–C(8)–C(8a)	−70·7
C(7)–C(8)–C(8a)–C(10a)	67·4
C(8a)–C(10a)–C(5)–C(6)	−66·9
C(10a)–C(5)–C(6)–C(7)	70·7



(8)



(9)

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[23] D. M. Bratby and G. I. Fray, *J.C.S. Perkin I*, 1972, 195.