Crystal Structure of Tricyclo[4,4,0,$0^{2,8}$]dec-3-ene-7,10-dione

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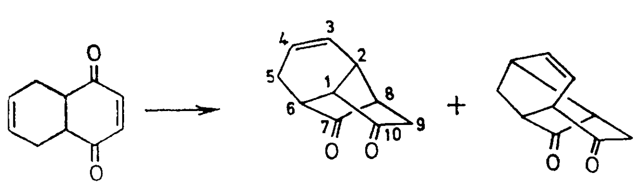
Crystals of the title compound are monoclinic, $a = 6\cdot806(1)$, $b = 15\cdot171(1)$, $c = 7\cdot667(1)$ Å, $\beta = 92\cdot18(9)°$, $Z = 4$, space group $P2_1/n$. The structure was determined from counter data by direct methods, and refined by full-matrix least-squares techniques to R 0·046 for 984 observed reflexions. Bond lengths and angles generally are normal, with slight deviations which may be related to the bridging.

A REINVESTIGATION of the photochemistry of the butadiene-*p*-benzoquinone Diels–Alder adduct (I) has been reported.[1] Selective $n \rightarrow \pi^*$ excitation of (I) resulted in two new photoproducts, (II) and (III). A single-crystal X-ray structure analysis of (II) was undertaken to provide direct evidence for the novel tricyclic structure in support of the spectroscopic data.



(I) (II) (III)

(II) Shows systematic numbering

EXPERIMENTAL

Crystals of tricyclo[4,4,0,$0^{2,8}$]dec-3-ene-7,10-dione (II) are colourless prisms elongated along a. Unit-cell and space group data were determined from rotation, Weissenberg, and precession photographs, the unit-cell parameters being refined by a least-squares procedure applied to the $\sin^2\theta$ values of 30 reflexions measured on a spectrogoniometer with Cu-K_α radiation.

Crystal Data.—$C_{10}H_{10}O_2$, $M = 162\cdot19$, Monoclinic, $a = 6\cdot806(1)$, $b = 15\cdot171(1)$, $c = 7\cdot667(1)$ Å, $\beta = 92\cdot18(9)°$ $U = 791\cdot1$ Å^3, D_m (by flotation) $= 1\cdot32$, $Z = 4$, $D_c = 1\cdot362$, $F(000) = 344$. Space group $P2_1/n$ (C^5_{2h}) from systematic absences: $h0l$, $h + l$ odd; $0k0$, k odd. Cu-K_α radiation, $\lambda = 1\cdot5418$ Å, μ(Cu-K_α) $= 7\cdot8$ cm^{-1}.

The intensities of all reflexions with 2θ(Cu-K_α) $\leq 120°$ (minimum interplanar spacing, 0·89 Å) were measured on a Datex-automated General Electric XRD 6 spectrogoniometer with a scintillation counter, approximately monochromatic Cu-K_α radiation (Ni filter and pulse-height analyser), and a θ—2θ scan of 2° min^{-1} in 2θ. Background counts were made at the beginning and end of each scan. The crystal used was a prism with dimensions $0\cdot5 \times 0\cdot2 \times 0\cdot2$ mm, and was mounted with a^* parallel to the ϕ axis of the goniostat. No absorption correction was made. Lorentz and polarization factors were applied and the structure amplitudes derived. Of the 1173 reflexions, 986 (84%) had intensities greater than $3\sigma(I)$ above background, where σ(I) is defined by $\sigma^2(I) = S + B + (0\cdot03\ S)^2$, where S = scan count, and B = background count. The remaining 187 reflexions were classified as unobserved.

Structure Analysis.—The structure was solved by a direct sign-determining procedure,[2] which used a reiterative application of Sayre relationships.[3] The carbon and oxygen positions were determined from an E-map, and a structure-factor calculation based on these preliminary co-ordinates, with scattering factors from ref. 4 and isotropic temperature factors B 4·0 Å^2, gave R 0·33. After five cycles of full-matrix least-squares refinement with $\sqrt{w} = |F_o|/3\cdot0$ when $|F_o| < 3\cdot0$, $\sqrt{w} = 3\cdot0/|F_o|$ when $|F_o| \geq 3\cdot0$, $\sqrt{w}$ (unobs) $= 0\cdot35$, R was 0·14, and a difference electron-density map revealed the positions of the hydrogen atoms. These were included in the refinement and, after three cycles, were fixed in their new locations, while the non-hydrogen atoms were assigned anisotropic thermal parameters. After two cycles of anisotropic refinement for carbon and oxygen (hydrogen atoms fixed), two final cycles varying all parameters (carbon and oxygen anisotropic; hydrogen isotropic) gave a final R value of 0·046 for 984 observed reflexions. The 021 and $10\bar{1}$ reflexions were given zero weight in the final cycles because of suspected extinction errors. The maximum parameter shift in the final cycle was 1σ for non-hydrogen atoms and 2σ for hydrogen atoms, and a final difference map showed maximum fluctuations of $\pm 0\cdot2$ eÅ^{-3}.

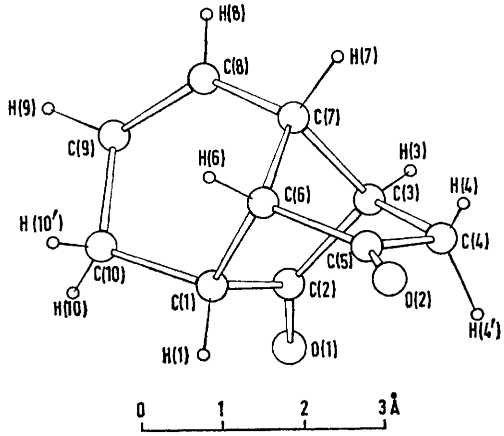


FIGURE 1 Molecular diagram showing the alternative chemical numbering system used in the analysis

Final positional and thermal parameters are listed in Table 1, and interatomic distances and angles are in Table 2. Figure 1 shows a general view of the molecule together with the crystallographic numbering system used, and Figure 2 shows the packing of the molecules in the cell.

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TABLE 1

Final positional (fractional $\times 10^4$) and thermal (Å^2 for isotropic; Å^2 $\times 10^2$ for anisotropic) parameters, with standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Mean $\sigma(U)$
C(1)	5079(3)	3903(1)	2769(3)	4·59	4·27	4·37	−0·75	0·24	−0·22	0·10
C(2)	3871(3)	3934(1)	4413(3)	5·88	3·38	3·70	0·05	−0·13	−0·23	0·10
C(3)	1759(3)	3827(2)	3815(3)	5·17	5·25	3·70	−0·26	0·84	0·40	0·11
C(4)	1152(4)	4718(2)	2985(3)	5·36	6·15	4·54	0·89	0·67	0·62	0·12
C(5)	2343(3)	4728(1)	1344(3)	5·07	5·33	3·84	−0·51	0·00	0·66	0·11
C(6)	3447(3)	3872(1)	1317(3)	5·04	5·12	3·19	−0·47	0·63	−0·16	0·11
C(7)	2025(3)	3232(1)	2192(3)	5·07	5·31	3·75	−1·04	0·04	−0·21	0·11
C(8)	2963(4)	2356(2)	2605(3)	7·47	4·38	4·38	−1·65	0·22	−0·70	0·12
C(9)	4881(4)	2267(2)	2832(3)	7·69	4·57	4·51	0·55	−0·08	−0·71	0·12
C(10)	6247(4)	3037(2)	2776(3)	5·47	6·31	4·79	0·82	0·25	−0·42	0·13
O(1)	4513(3)	4021(1)	5891(2)	8·25	5·68	3·87	0·32	−1·12	−0·58	0·09
O(2)	2343(3)	5315(1)	0280(2)	7·52	6·44	5·29	0·20	0·60	2·04	0·10
				B						
H(1)	5898(34)	4430(17)	2677(28)	3·07(45)						
H(3)	0869(41)	3595(18)	4721(36)	4·62(56)						
H(4)	0226(52)	4728(19)	2645(39)	5·48(71)						
H(4′)	1491(48)	5258(21)	3736(41)	5·83(75)						
H(6)	3900(40)	3695(18)	0167(36)	4·21(54)						
H(7)	0714(41)	3178(16)	1488(39)	5·17(63)						
H(8)	2167(50)	1863(24)	2777(48)	6·06(76)						
H(9)	5537(42)	1697(20)	3102(37)	5·25(63)						
H(10)	7144(36)	3015(15)	3791(35)	3·99(50)						
H(10′)	6950(41)	3031(17)	1709(44)	4·97(60)						

Measured and calculated structure factors are given in Supplementary Publication No. SUP 20331 (4 pp., 1 microfiche).*

TABLE 2

Interatomic distances (Å) and angles (deg.), with standard deviations in parentheses

(*a*) Distances

C(1)–C(2)	1·532(3)	C(2)–O(1)	1·206(3)
C(1)–C(6)	1·543(3)	C(5)–O(2)	1·208(3)
C(1)–C(10)	1·536(3)	C(1)–H(1)	0·98(2)
C(2)–C(3)	1·501(3)	C(3)–H(3)	1·00(3)
C(3)–C(4)	1·544(3)	C(4)–H(4)	0·96(4)
C(3)–C(7)	1·554(3)	C(4)–H(4′)	1·02(3)
C(4)–C(5)	1·523(3)	C(6)–H(6)	0·98(3)
C(5)–C(6)	1·501(3)	C(7)–H(7)	1·03(3)
C(6)–C(7)	1·542(3)	C(8)–H(8)	0·94(4)
C(7)–C(8)	1·502(3)	C(9)–H(9)	0·99(3)
C(8)–C(9)	1·317(4)	C(10)–H(10)	0·97(3)
C(9)–C(10)	1·495(4)	C(10)–H(10′)	0·96(3)

(*b*) Angles

C(6)–C(1)–C(2)	101·6(2)	C(4)–C(3)–C(7)	102·5(2)
C(6)–C(1)–C(10)	109·5(2)	H(3)–C(3)–C(2)	115(2)
C(2)–C(1)–C(10)	108·5(2)	H(3)–C(3)–C(4)	116(2)
H(1)–C(1)–C(2)	111(1)	H(3)–C(3)–C(7)	116(2)
H(1)–C(1)–C(6)	112(1)	C(3)–C(4)–C(5)	101·9(2)
H(1)–C(1)–C(10)	114(1)	H(4)–C(4)–C(3)	112(2)
C(1)–C(2)–C(3)	106·4(2)	H(4)–C(4)–C(5)	109(2)
C(1)–C(2)–O(1)	126·1(2)	H(4)–C(4)–H(4′)	110(2)
C(3)–C(2)–O(1)	127·4(2)	H(4′)–C(4)–C(3)	115(2)
C(2)–C(3)–C(4)	105·6(2)	H(4′)–C(4)–C(5)	110(2)
C(2)–C(3)–C(7)	99·7(2)	C(4)–C(5)–C(6)	106·6(2)
C(4)–C(5)–O(2)	125·4(2)	H(7)–C(7)–C(8)	113(1)
C(6)–C(5)–O(2)	128·0(2)	C(7)–C(8)–C(9)	122·0(2)
C(5)–C(6)–C(1)	108·1(2)	H(8)–C(8)–C(7)	120(2)
C(5)–C(6)–C(7)	102·5(2)	H(8)–C(8)–C(9)	118(2)
C(1)–C(6)–C(7)	98·7(2)	C(8)–C(9)–C(10)	122·0(2)
H(6)–C(6)–C(5)	115(2)	H(9)–C(9)–C(8)	124(2)
H(6)–C(6)–C(7)	116(2)	H(9)–C(9)–C(10)	114(2)
H(6)–C(6)–C(1)	114(2)	C(9)–C(10)–C(1)	110·2(2)
C(6)–C(7)–C(3)	94·4(2)	H(10)–C(10)–C(9)	109(1)
C(6)–C(7)–C(8)	112·3(2)	H(10)–C(10)–C(1)	110(1)
C(3)–C(7)–C(8)	114·0(2)	H(10)–C(10)–H(10′)	111(2)
H(7)–C(7)–C(3)	110(2)	H(10′)–C(10)–C(1)	106(2)
H(7)–C(7)–C(6)	112(2)	H(10′)–C(10)–C(9)	110(2)

DISCUSSION

The crystal analysis has shown that photoproduct (II) is obtained from the Diels–Alder adduct (I) by the formation of the bond C(3)–C(7) [numbering of Figure 1; C(2)–C(8) in numbering of (II)], and has provided details of the geometry of the tricyclic system.

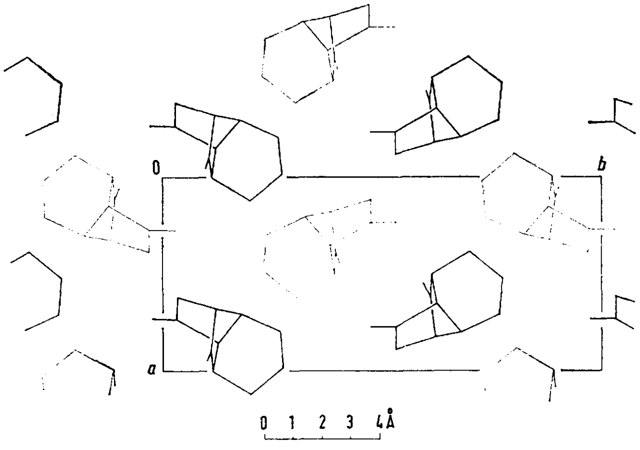

FIGURE 2 Packing of the molecules in the unit cell (heavy lines indicate molecules in the top part of the cell)

The six-membered ring containing the carbonyl groups is in the boat conformation, with the C(3) ··· C(6) distance decreased significantly by the single carbon bridge [2·57 calculated for an ideal boat form decreased to 2·27 Å for (II)]. The angle at the apex of the bridge, C(3)–C(7)–C(6), is 94·4°. These features are common to

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

several compounds of the norbornyl type.[5-10] All other angles at C(7) are in the range 110—114° (Table 2) in contrast to the large values of H–C–H (126°) obtained in ref. 9. The n.m.r. value of 113—114° or the semi-empirical value of 112° quoted in ref. 9 are more reasonable, and in agreement with the values found here, although in the present compound the angles involve a carbon atom leading to the C(8), C(9), C(10) bridge, so the comparison may not be valid.

The six-membered ring containing the double bond is in a half-chair conformation, having atoms C(7)—(10) in a plane, with C(1) and C(6) on opposite sides of the plane, displaced from it by 0·31 and 0·64 Å respectively. The carbonyl groups are planar, and Table 3 lists details of planes relevant to the ring geometry.

The bond lengths agree well with expected values,[11] the mean values being C(sp^3)–C(sp^3) 1·544, C(sp^2)–C(sp^3) 1·509, C(sp^2)=C(sp^2) 1·317, C=O 1·207, and C–H 0·98 Å. Bonds C(1)–C(2) and C(4)–C(5) (1·532 and 1·523 Å) are significantly longer than normal, and the C(2)–C(3)–C(7) and C(1)–C(6)–C(7) angles (99·7 and 98·7°) are smaller than others in the ring; these features may be attributed to the strain caused by the bridging. Other angles are generally less than the tetrahedral value, in agreement with the values reported for the structures referred to previously.

TABLE 3

Equations of mean planes, in the form $lX' + mY + nZ' = p$, where X', Y, and Z' are co-ordinates in Å referred to orthogonal axes a, b, and c^*, with deviations from the planes (Å) in square brackets

Plane (A): C(1)—(3), C(6) $-0{\cdot}0647X' + 0{\cdot}9975Y - 0{\cdot}0293Z' = 5{\cdot}6589$

[C(1) −0·033, C(2) 0·034, C(3) −0·023, C(6) 0·022, O(1) 0·106]

Plane (B): C(3)—(6) $0{\cdot}7474X' + 0{\cdot}4380Y + 0{\cdot}4995Z' = 4{\cdot}8085$

[C(3) −0·007, C(4) 0·010, C(5) −0·010, C(6) 0·007, O(2) −0·016]

Plane (C): C(3), C(6), C(7) $-0{\cdot}7588X' + 0{\cdot}4528Y - 0{\cdot}4682Z' = 0{\cdot}4364$

Plane (D): C(7)—(10) $-0{\cdot}1333X' + 0{\cdot}1573Y + 0{\cdot}9785Z' = 2{\cdot}2446$

[C(7) 0·005, C(8) −0·012, C(9) 0·012, C(10) −0·005, C(1) −0·313, C(6) 0·641]

Angles between plane normals:

(A)–(B)	112·0°
(A)–(C)	121·0
(B)–(C)	127·1

Intermolecular distances correspond to van der Waals interactions, the shortest C · · · C, C · · · O, and O · · · O distances being 3·620, 3·203, and 3·341 Å.

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