Table 2. *Bond angles* (°) *and lengths* (Å) *with e.s.d.'s in parentheses*

Accepted values are enclosed in brackets.

C(sp^3)—C(sp^3)—C(sp^3)	[109·5]	C(8)—C(7)—C(6)	106·1 (2)
C(21)—C(2)—C(7)	114·7 (3)	C(4a)—C(8a)—C(1)	107·4 (2)
C(4a1)—C(4a)—C(5)	108·9 (3)	C(8)—C(8a)—C(1)	94·3 (2)
C(4a1)—C(4a)—C(8a)	110·6 (3)	C(8a1)—C(8a)—C(1)	112·5 (3)
C(5)—C(4a)—C(8a)	109·5 (2)	C(sp^2)—C(sp^3)—C(sp^2)	[109·5]
C(2)—C(7)—C(71)	113·8 (3)	C(1)—C(2)—C(3)	98·4 (2)
C(2)—C(7)—C(8)	101·4 (2)	X(sp^2)—C(sp^2)—C(sp^3)	[120·0]
C(71)—C(7)—C(8)	112·0 (3)	O—C(1)—C(2)	126·5 (3)
C(7)—C(8)—C(8a)	102·8 (2)	O—C(1)—C(8a)	128·0 (3)
C(4a)—C(8a)—C(8)	109·4 (2)	C(4)—C(3)—C(2)	117·1 (2)
C(4a)—C(8a)—C(8a1)	116·9 (3)	C(4)—C(3)—C(31)	123·9 (3)
C(8)—C(8a)—C(8a1)	113·9 (3)	C(3)—C(4)—C(41)	122·5 (3)
C(sp^3)—C(sp^3)—C(sp^2)	[109·5]	C(3)—C(4)—C(4a)	118·7 (2)
C(21)—C(2)—C(1)	111·8 (3)	C(5)—C(6)—C(61)	122·2 (3)
C(21)—C(2)—C(3)	113·8 (3)	C(61)—C(6)—C(7)	124·8 (3)
C(7)—C(2)—C(1)	102·2 (2)	C(sp^3)—C(sp^2)—C(sp^3)	[120·0]
C(7)—C(2)—C(3)	114·0 (2)	C(2)—C(1)—C(8a)	105·3 (2)
C(4a1)—C(4a)—C(4)	112·9 (3)	C(2)—C(3)—C(31)	118·9 (3)
C(5)—C(4a)—C(4)	103·3 (2)	C(41)—C(4)—C(4a)	118·2 (3)
C(8a)—C(4a)—C(4)	111·3 (2)	C(5)—C(6)—C(7)	113·0 (2)
C(4a)—C(5)—C(6)	110·4 (2)		
C(2)—C(7)—C(6)	110·3 (2)		
C(71)—C(7)—C(6)	112·4 (3)		

C(sp^3)—C(sp^3)	[1·537 (5)]*	C(2)—C(3)	1·535 (4)
C(2)—C(21)	1·530 (4)	C(31)—C(3)	1·504 (4)
C(2)—C(7)	1·602 (4)	C(41)—C(4)	1·511 (4)
C(4a)—C(4a1)	1·541 (5)	C(4a)—C(4)	1·532 (4)
C(4a)—C(5)	1·544 (4)	C(5)—C(6)	1·500 (5)
C(4a)—C(8a)	1·604 (4)	C(7)—C(6)	1·519 (4)
C(7)—C(71)	1·524 (5)	C(sp^2)—C(sp^2)	[1·335 (5)]
C(7)—C(8)	1·537 (4)	C(3)—C(4)	1·333 (4)
C(8)—C(8a)	1·536 (6)	C(6)—C(61)	1·316 (6)
C(8a)—C(8a1)	1·525 (5)	C(sp^2)—O	[1·215 (5)]
C(sp^3)—C(sp^2)	[1·510 (5)]	C(1)—O	1·212 (3)
C(2)—C(1)	1·507 (4)		
C(8a)—C(1)	1·500 (4)		

* Accepted values from Sutton (1965).

The strain induced in the cyclohexenone ring on bonding C(2) to C(7) is compensated somewhat by the stretching of the bridge C(4a)—C(8a); in addition, bonds C(2)—C(3) and C(4a)—C(4) show increases as well, averaging 0·024 Å greater than the accepted value of 1·510 Å for C(sp^3)—C(sp^2). Other bonds within the structure (Table 2) do not deviate significantly from accepted values. Intermolecular contacts generally correspond to van der Waals distances (shortest C···C = 3·61, C···O = 3·45, O···O > 4·2 Å).

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Tricyclo[4.4.0.$0^{3,8}$]dec-9-ene-2,5-dione (a Twistenone), $C_{10}H_{10}O_2$

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Abstract. $M_r = 162{\cdot}19$, monoclinic, $P2_1/n$, $a = 6{\cdot}381\,(2)$, $b = 19{\cdot}454\,(2)$, $c = 6{\cdot}708\,(2)$ Å, $\beta = 106{\cdot}24\,(1)°$, $V = 799{\cdot}5\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}347$ g cm^{-3}, μ(Mo $K\alpha$) = 0·87 cm^{-1}, $\lambda = 0{\cdot}71073$ Å. Final $R = 0{\cdot}037$ for 930 observed reflections. All six-membered rings of the twistane skeleton have

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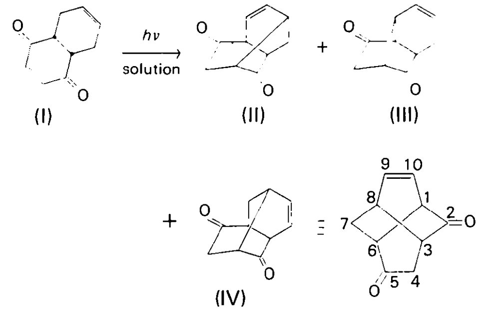
twisted-boat conformations, with ring strain resulting in bridging C—C bonds of 1·559 (3) and 1·573 (3) Å and bond angles deviating by up to 12° from normal values.

Introduction. Irradiation of a solution of tetrahydronaphthoquinone (I) results in the formation of the photoproducts (II) and (III) (Scheffer, Bhandari, Gayler & Wostradowski, 1975; Scheffer, Jennings & Louwerens, 1976). In a recent extension of this study (Scheffer & Walsh, 1982, unpublished work) a modified procedure (irradiation from within the reacting vessel) resulted in the formation of a third photoproduct, whose structure could not be deduced from chemical and spectroscopic evidence. The present X-ray crystal analysis indicates that this additional photoproduct is the twistane derivative (IV).



Experimental. Thin crystals obtained by slow evaporation of a hexane/acetone solution, 0·2 × 0·3 × 0·3 mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, θ range 0·0 to 27·5°, ω-scan angle $(0{\cdot}80 + 0{\cdot}35\ \tan\theta)^\circ$ (extended by 25% on each side for background counts), variable horizontal aperture width $(2{\cdot}00 + \tan\theta)$ mm, ω–$(\frac{4}{3})\theta$ scan type, scan speeds in range 1·34–10·06 deg min^{-1}, intensity and orientation controls regularly throughout data collection, cell parameters by least-squares fit to observed $\sin\theta$ values for 21 centred reflections, intensities corrected for Lorentz and polarization effects but not for absorption; decay of three standard intensities [$2\bar{5}\bar{3}$ (1·9%), $\bar{1}3\bar{1}$ (5·8%), $\bar{1}6\bar{2}$ (4·1%)] necessitated application of a decay correction; 1828 unique reflections, 930 (50·9%) had $I \geq 3\sigma(I)$ where $\sigma^2(I) = S + 2B + [0{\cdot}04(S-B)]^2$, S being the scan count and B the time-averaged background; direct methods with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); full-matrix least squares with anisotropic thermal parameters, H atoms identified on a difference map and included in refinement with isotropic temperature factors, convergence at $R_w = 0{\cdot}043$ for the observed reflections, mean and maximum parameter shifts in the final cycle 0·019 and 0·170σ respectively, standard deviation in an observation of unit weight 1·844, $w = 1/\sigma^2(F)$, random fluctuations of ±0·17 e Å^{-3} on final difference map; $F(000) = 344$, scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965).

Discussion. Atomic coordinates and equivalent isotropic temperature factors are given in Table 1.*

The crystal structure analysis has shown that the additional photoproduct is a derivative of twistane (Whitlock, 1962), unsaturated at C(9)—C(10), and having carbonyl substituents at positions 2 and 5 [(IV) and Fig. 1]. A plausible mechanism for its formation from the tetrahydronaphthoquinone involves abstraction of a C_5 H atom by C_2 (γ-H abstraction by C), followed by C_3—C_7 bonding (naphthoquinone numbering system), a process which is topochemically forbidden in the solid state, but feasible in solution (Scheffer & Dzakpasu, 1978).

Table 1. *Final positional (fractional,* ×10^5, H ×10^4) *and isotropic thermal parameters* (U ×10^3 Å^2) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}/U_{iso}
C(1)	43183 (30)	9198 (11)	73230 (32)	42
C(2)	46946 (32)	16445 (10)	81296 (30)	43
C(3)	68270 (35)	18800 (11)	78540 (33)	50
C(4)	84231 (40)	15878 (13)	98328 (40)	55
C(5)	79127 (29)	8327 (11)	99726 (31)	43
C(6)	66087 (30)	5539 (10)	79168 (29)	40
C(7)	78841 (39)	7886 (12)	64120 (37)	51
C(8)	71086 (37)	15293 (13)	58557 (36)	55
C(9)	49048 (43)	14393 (14)	43397 (36)	62
C(10)	35198 (41)	10864 (12)	50506 (36)	56
O(2)	34914 (28)	19664 (9)	89031 (27)	70
O(5)	85239 (26)	5020 (9)	115598 (24)	67
H(1)	3304 (37)	696 (11)	7830 (32)	53 (6)
H(3)	6943 (38)	2367 (14)	7803 (36)	68 (7)
H1(4)	8257 (47)	1812 (14)	11038 (47)	84 (9)
H2(4)	9855 (43)	1611 (11)	9740 (34)	59 (6)
H(6)	6439 (32)	82 (13)	7943 (31)	52 (6)
H1(7)	7583 (39)	488 (13)	5098 (41)	75 (7)
H2(7)	9442 (38)	766 (10)	7115 (34)	58 (6)
H(8)	8141 (38)	1794 (13)	5341 (35)	67 (7)
H(9)	4646 (47)	1596 (15)	3003 (48)	91 (9)
H(10)	2038 (40)	995 (12)	4290 (37)	68 (7)

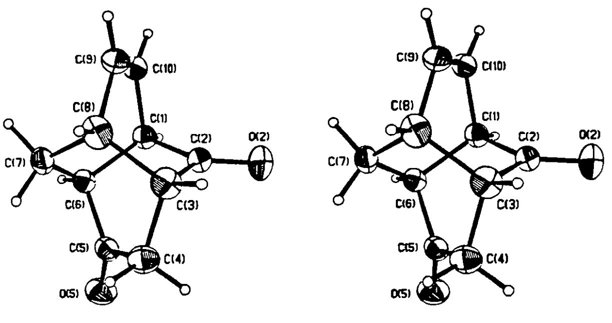


Fig. 1. Stereo diagram of the twistenone (IV).

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* Lists of structure factors, anisotropic temperature factors, bond lengths and angles involving H atoms, mean planes of carbonyl groups and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38201 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

This appears to be the first example of an X-ray crystal structure determination of an unsaturated twistane derivative, and structural comparisons are limited to the relatively few twistanes whose crystal structures are known (Barnett & Yordy, 1975; Ramakumar, Venkatesan & Weber, 1977; Greenhough & Trotter, 1980).

The carbonyl groups are essentially planar,* but the alkene moiety is distorted noticeably from a planar configuration, with a C(8)—C(9)—C(10)—C(1) torsion angle of 7·4 (3)°. Other torsion angles in the five unique six-membered rings are shown in Fig. 2. As expected, the presence of the double bond within the tricyclic skeleton introduces marked deviations from the twistane geometry, where the five rings approach twist-boat conformations. Ideal torsion angles for twist-boat conformers are four of +33° and two of −71° (Bucourt & Hainaut, 1965); empirical force-field calculations for twistane (Engler, Androse & Schleyer, 1973) give values of +20 to +50° and −66 and −82°. The torsion angles in twistenone (IV) show even larger deviations from the ideal values, but the ring conformations are still best described as twisted boats.

The D_2 symmetry of the twistane skeleton is drastically reduced to C_1, with the addition of O(2) and O(5). Notwithstanding the change in hybridization at C atoms 2 and 5, the tricyclic skeleton of (IV) has symmetry closely approximating C_2 (Fig. 1). The pseudo-rotation axis passes through the centre of, and is perpendicular to, bonds C(9)=C(10) and C(4)—C(5), similar to the pseudo C_2 axis in 4-azatricyclo[4.4.0.0^{3,8}]decan-5-one ('aza-twistanone') (Ramakumar *et al.*, 1977).

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·505 (3)	C(5)—C(6)	1·499 (3)
C(1)—C(10)	1·501 (3)	C(5)—O(5)	1·211 (2)
C(2)—C(3)	1·495 (3)	C(6)—C(7)	1·533 (3)
C(2)—O(2)	1·214 (2)	C(6)—C(1)	1·573 (3)
C(3)—C(4)	1·538 (3)	C(7)—C(8)	1·535 (3)
C(3)—C(8)	1·559 (3)	C(8)—C(9)	1·497 (4)
C(4)—C(5)	1·513 (3)	C(9)—C(10)	1·310 (4)

C(2)—C(1)—C(6)	106·8 (2)	C(4)—C(5)—O(5)	123·2 (2)
C(2)—C(1)—C(10)	97·9 (2)	C(6)—C(5)—O(5)	125·2 (2)
C(6)—C(1)—C(10)	112·5 (2)	C(5)—C(6)—C(7)	103·8 (2)
C(3)—C(2)—C(1)	107·6 (2)	C(5)—C(6)—C(1)	107·8 (2)
C(3)—C(2)—O(2)	126·9 (2)	C(7)—C(6)—C(1)	109·0 (2)
C(1)—C(2)—O(2)	125·5 (2)	C(6)—C(7)—C(8)	104·2 (2)
C(2)—C(3)—C(4)	100·7 (2)	C(3)—C(8)—C(7)	108·0 (2)
C(2)—C(3)—C(8)	107·5 (2)	C(3)—C(8)—C(9)	108·8 (2)
C(4)—C(3)—C(8)	111·9 (2)	C(7)—C(8)—C(9)	103·5 (2)
C(3)—C(4)—C(5)	108·1 (2)	C(8)—C(9)—C(10)	114·5 (2)
C(4)—C(5)—C(6)	111·6 (2)	C(9)—C(10)—C(1)	114·3 (2)

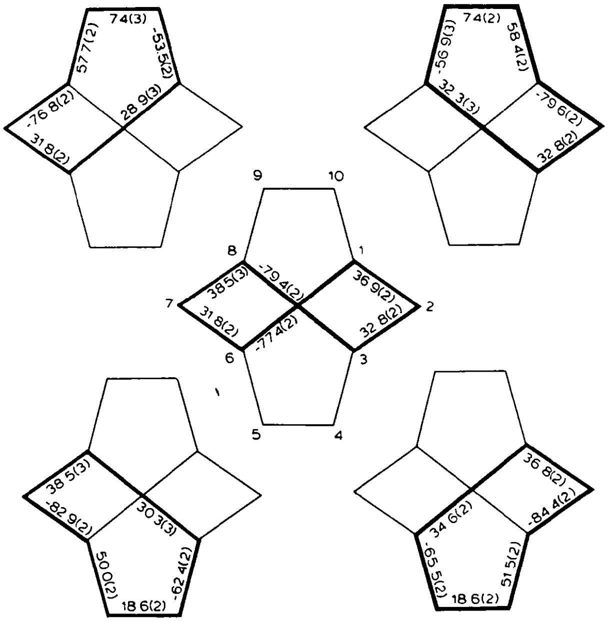

Fig. 2. Torsion angles for the twistenone (IV) (°).

Generally, bond lengths are comparable to normal values, with the exception of C(9)=C(10) [1·310 (4) Å] and the bridging bonds, C(1)—C(6) [1·573 (3) Å] and C(3)—C(8) [1·559 (3) Å] (Table 2). However, the lengthening of the latter two bonds is not unusual for this type of system; similar lengthening of C(sp^3)—C(sp^3) bonds has been reported for bridged-ring hydrocarbons (see, for example, Greenhough & Trotter, 1980; Acton, Roth, Katz, Frank, Maier & Paul, 1972).

In addition to torsional strain, twistenone (IV) suffers from considerable angular strain. Compared with normal values, endocyclic angles are observed to deviate up to 12·4°, with the most noticeable divergence from accepted values occurring for angles involving the O-bearing C atoms as vertices, C(1)—C(2)—C(3), 107·6 (2)°, and C(4)—C(5)—C(6), 111·6 (2)° (Table 2). Of similar magnitude is the difference between the C(2)—C(1)—C(10) angle of 97·9 (2)° and the normal tetrahedral value of 109·5°, suggesting marked deviation from sp^3 hybridization at C(1). Other angles which include one bridging C atom, flanked on either side by C atoms not involved in a bridge [*e.g.* C(2)—C(3)—C(4)], show a mean compression of 6·8° from the ideal tetrahedral value.

Intermolecular packing involves normal van der Waals interactions.*

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* See deposition footnote.

* See deposition footnote.

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The Structure of the Hydrated Salt of 3,5-Dichlorosalicylaldehyde and 4-Aminopyridine, $C_5H_7N_2^+.C_7H_3Cl_2O_2^-.H_2O$

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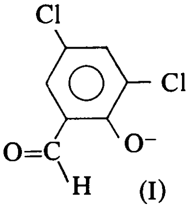
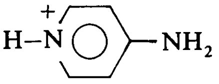
Abstract. $M_r = 303\cdot15$, orthorhombic, $Pna2_1$, $a = 22\cdot897$ (5), $b = 3\cdot9476$ (6), $c = 30\cdot398$ (6) Å, $V = 2747$ (4) Å^3, $Z = 8$, $D_x = 1\cdot466$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54184$ Å, $\mu = 43\cdot9$ cm^{-1}, $F(000) = 1248$. Final $R = 0\cdot049$, $R_w = 0\cdot045$ for 963 observed reflections. There are two crystallographically independent groups of cations and anions in the asymmetric unit arranged separately in chains along **a** and held together by H bonds. Two neighboring chains are also linked by H bonds *via* water molecules. The aldehyde and aminopyridine ions are in an appropriate relative geometry to react and form a Schiff base.

Introduction. In continuation of our studies on the molecular structure and behavior of 2-(pyridyliminomethyl)phenols (Moustakali-Mavridis, Hadjoudis & Mavridis, 1978, 1980), the crystallization of a number of derivatives of 2-(4-pyridyliminomethyl)phenol was attempted. This proved to be not an easy task because, when left in solution, the compounds either polymerized or hydrolyzed yielding crystals of 4-aminopyridine (Chao & Schempp, 1977). Finally the derivative 4,6-dichloro-2-(4-pyridyliminomethyl)phenol gave good quality yellow crystals from a mixture of ethanol and chlorobenzene. To our surprise the X-ray study showed that the crystals are formed from a co-crystallization of the hydrolysis products of the above derivative, namely the phenolic anion (I) and the pyridinium cation (II) with a water molecule.



(I)



(II)

Single crystals of the above salt (m.p.=357 K) are destroyed when heated above 318 K yielding an orange powder (m.p.=447 K) that exhibits photochromic behavior, a fact indicating that the molecules react in the solid state to form the Schiff base. The latter is again easily hydrolyzed.

Experimental. $0\cdot4 \times 0\cdot1 \times 0\cdot1$ mm, mounted along **b**, systematic absences $0kl$:$k + l = 2n$, $h0l$:$h = 2n$, $Pnam$ or $Pna2_1$, unit-cell parameters by least-squares from setting angles of 12 reflections, $45 < 2\theta < 60°$; room temperature, Cu $K\alpha$, Picker 4-circle diffractometer (Vandlen & Tulinsky, 1971), $1 < 2\theta < 110°$, 'wandering' ω step scan, balanced Ni/Co filters, alignment and decay of the crystal monitored every 100 reflections and automatically corrected for, no radiation damage; 1936 reflections measured (including 356 systematically absent), 963 observed $[I \geq 2\sigma(I)]$, correc-