

Intermolecular distances mainly correspond to van der Waals interactions, except for a close N...H contact. There is a hydrogen bond between the N atom of one cyano group and the hydroxyl H of a neighbouring molecule such that HO...N(1) [$\frac{1}{2} - x, -1 - y, \frac{1}{2} + z$] is 2.05 (3) Å. The corresponding O—H and O...N distances are 0.89 (3) and 2.902 (3) Å respectively and the O—H...N angle is 156 (2)°. The hydrogen bonds link chains of molecules related by the screw axis in the *c* direction. A stereo diagram of the crystal packing is shown in Fig. 2.

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11-Oxa-5,10-dicyano-6,9-dimethyltetracyclo[6.2.1.0^{1,7}.0^{5,10}]undec-2-en-4-one

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Abstract. C₁₄H₁₂N₂O₂, orthorhombic, *P*2₁2₁2₁, *a* = 18.701 (6), *b* = 7.274 (2), *c* = 9.005 (2) Å, *d*_m = 1.29 (floatation), *Z* = 4, *d*_x = 1.303 g cm⁻³, μ(Cu Kα) = 7.4 cm⁻¹. The geometry of the molecule is closely related to that of the 1,4-naphthoquinone derivative from which it is formed. Bond lengths and angles are normal, but the four-membered CCCO ring is very distorted with all internal torsion angles greater than 30°.

Introduction. Large, well formed, colourless crystals were obtained by crystallization from petroleum spirit. Unit-cell and intensity data were measured on a Datex-automated GE XRD 6 diffractometer with Cu Kα radiation and the θ–2θ scan technique. Unit-cell parameters were refined by least squares from the observed 2θ values of 15 reflexions. Of the 1433 independent reflexions with 2θ < 146°, 1320 had intensities greater than 3σ(*I*) above background [$\sigma^2(I) = S + B + (0.06S)^2$, where *S* = scan and *B* = background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. Crystal dimensions were approximately 0.07 × 0.05 × 0.02 cm and no absorption correction was applied.

The structure was solved by direct methods with symbolic-addition and tangent-refinement techniques.

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Origin-defining reflexions and starting symbols for this procedure were chosen manually. The set of phases with the highest consistency gave an *E* map showing all non-hydrogen atoms. Several cycles of full-matrix least-squares refinement were carried out where the function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights defined as follows: $\sqrt{w} = 1.0$ for $|F_o| \leq 6.4$ and $\sqrt{w} = 6.4/|F_o|$ for $|F_o| > 6.4$. A difference Fourier map showed ten H atoms, the remaining two being placed in calculated positions. All non-hydrogen atoms were included with anisotropic temperature factors, the hydrogens being refined isotropically. Atomic scattering factors for O, N and C atoms are those of Cromer & Mann (1968) and for H atoms those of Stewart, Davidson & Simpson (1965). The real and imaginary parts of the anomalous-scattering factors for O, N and C atoms were taken from Cromer & Liberman (1970). Poor agreement among the low-angle planes suggested that extinction effects were present, but application of a correction as for 1,6-dicyano-2-hydroxy-8,9-dimethyltricyclo[4.4.0.0^{2,8}]dec-3,9-dien-5-one (III) (Phillips & Trotter, 1977) resulted in an unrealistic refined value for the parameter *E*. The ten planes showing the worst agreement, all in the *hk0* zone, were zero weighted in the final cycles of refinement. The final *R* and *R'*

$\{ = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \}$ for the 1320 reflexions with $I > 3\sigma(I)$ are 0.048 and 0.062 respectively. For all 1433 data R is 0.052 and R' is 0.068. The absolute configuration for the crystal studied has not been determined, as the R values for the two enantiomorphs do not differ significantly (Hamilton, 1965). Final positional parameters are listed in Table 1.*

Thermal-motion analysis and correction of bond lengths for libration were carried out as for (III), with C(1)–C(10), C(11), C(14) and O(1) as the rigid-body core, outer bonds being corrected for independent motion as before. R.m.s. ΔU_{ij} for the rigid body is 0.0019 Å², compared to an r.m.s. $\sigma(U_{ij})$ from the least squares of 0.0015 Å², and the rigid body was assumed to give a good approximation to the thermal motion. Corrected bond lengths are given in Table 2. Bond angles are not significantly affected and corrected values are not reported.

Discussion. The crystal structure of 11-oxa-5,10-dicyano-6,9-dimethyltetracyclo[6.2.1.0^{1,7}.0^{5,10}]undec-2-en-4-one (II) was determined as part of a study of the photochemistry of various substituted 1,4-naphthoquinone systems with *cis* bridgehead substituents. Irradiation of 5 α ,8 α -dimethyl-4 $\alpha\beta$,8 $\alpha\beta$ -dicyano-4 α ,5,8,8 α -tetrahydro-1,4-naphthoquinone (I) in solution or the solid state gives rise to (II), through addition of one C=O bond to the C=C bond in the other ring (Scheffer, Jennings & Louwerens, 1976; Scheffer & Dzakpasu, 1975).

A stereo diagram of the molecule, with the crystallographic numbering scheme, is shown in Fig. 1, together with a view of the initial molecule of (I), whose crystal structure has already been reported (Phillips & Trotter, 1976). Comparison of the two molecules shows that the C(1)=O(1) and C(7)=C(8) bonds are oriented such that

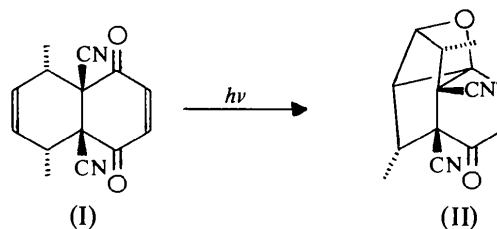


Table 1. Final positional parameters (fractional, $\times 10^4$, H $\times 10^3$) with estimated standard deviations in parentheses

	x	y	z
O(1)	4715 (1)	1663 (3)	7110 (2)
O(2)	2460 (1)	3594 (4)	3718 (3)
C(1)	4061 (2)	2121 (4)	6353 (3)
C(2)	3497 (2)	3232 (5)	7015 (3)
C(3)	2969 (2)	3751 (5)	6112 (4)
C(4)	2961 (1)	3232 (4)	4523 (3)
C(5)	3620 (1)	2161 (4)	3915 (3)
C(6)	3568 (2)	63 (4)	4377 (3)
C(7)	3972 (2)	104 (4)	5861 (3)
C(8)	4788 (2)	293 (4)	5882 (3)
C(9)	4954 (1)	1511 (4)	4559 (3)
C(10)	4292 (1)	2798 (3)	4760 (3)
C(11)	3659 (1)	2438 (4)	2299 (3)
C(12)	2819 (2)	-708 (6)	4449 (6)
C(13)	5679 (2)	2457 (6)	4656 (5)
C(14)	4426 (2)	4766 (4)	4575 (3)
N(1)	3698 (2)	2677 (5)	1062 (3)
N(2)	4507 (2)	6278 (4)	4336 (4)
H(2)	358 (2)	355 (6)	799 (5)
H(3)	258 (2)	455 (6)	634 (5)
H(6)	391 (2)	-60 (4)	374 (4)
H(7)	379 (2)	-80 (5)	654 (4)
H(8)	503 (3)	-90 (7)	609 (6)
H(9)	493 (2)	76 (4)	366 (3)
H(12a)	283 (2)	-187 (7)	461 (5)
H(12b)	260 (2)	-8 (7)	530 (5)
H(12c)	261 (3)	-60 (7)	350 (6)
H(13a)	585 (3)	333 (9)	384 (7)
H(13b)	576 (2)	326 (6)	560 (5)
H(13c)	609 (3)	166 (8)	479 (6)

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32402 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond lengths (Å) for non-hydrogen atoms with estimated standard deviations in parentheses

	Uncorrected	Corrected		Uncorrected	Corrected
O(1)–C(1)	1.439 (3)	1.443	O(2)–C(4)	1.214 (4)	1.215
O(1)–C(8)	1.495 (4)	1.500	C(1)–C(2)	1.455 (5)	1.461
C(1)–C(7)	1.542 (4)	1.548	C(1)–C(10)	1.577 (4)	1.583
C(2)–C(3)	1.333 (5)	1.337	C(3)–C(4)	1.480 (4)	1.484
C(4)–C(5)	1.557 (4)	1.563	C(5)–C(6)	1.585 (4)	1.591
C(5)–C(10)	1.542 (4)	1.547	C(5)–C(11)	1.471 (4)	1.475
C(6)–C(7)	1.535 (4)	1.540	C(6)–C(12)	1.511 (5)	1.514
C(7)–C(8)	1.532 (5)	1.537	C(8)–C(9)	1.517 (4)	1.522
C(9)–C(10)	1.563 (4)	1.567	C(9)–C(13)	1.524 (4)	1.525
C(10)–C(14)	1.463 (4)	1.468	C(11)–N(1)	1.130 (4)	1.130
C(14)–N(2)	1.130 (4)	1.131			

cycloaddition is possible with relatively small changes in conformation. The major change in the C skeleton is the large shift of both C(7) and C(8). The C(7)···C(1) and C(8)···O(1) separations in the starting material are 3.365 and 3.199 Å respectively, reducing to σ -bonded distances of 1.542 and 1.495 Å in the product. The largest change of torsion angle within the skeleton is 82.8° for C(5)–C(6)–C(7)–C(8). The change in the C(5)–C(10) ring may be regarded as a conversion from the half-chair to twisted-boat conformation.

The bond lengths and angles in (II) (see Tables 2 and 3) are mostly normal for this type of condensed ring system, except for the rather long C(5)–C(6) and O(1)–C(8) bonds. The bridgehead torsion angle C(11)–C(5)–C(10)–C(14) is 61.1(2)° compared to 57.1(2)° in (I). The four-membered CCCO ring is severely twisted, the O(1)–C(1)–C(7)–C(8) torsion angle being –32.2(2)°. Trimethylene oxide itself has an essentially planar four-membered ring (Chan, Borgers, Russell, Strauss & Gwinn, 1966) so the distortion must be imposed by the fused norbornane skeleton.

Intermolecular distances correspond to van der Waals interactions. There is, however, one close

O···H contact: O(1)···H(8) [$1 - x, \frac{1}{2} + y, \frac{3}{2} - z$] is 2.45(5) Å and the angle O(1)···H(8)–C(8) is 147°, but this only qualifies as a weak C–H···O interaction.

Table 3. Bond angles (°) for non-hydrogen atoms the estimated standard deviations in parentheses

C(1)–O(1)–C(8)	83.2(2)	O(1)–C(1)–C(2)	123.4(2)
O(1)–C(1)–C(7)	90.4(2)	O(1)–C(1)–C(10)	105.6(2)
C(2)–C(1)–C(7)	124.6(3)	C(2)–C(1)–C(10)	113.4(3)
C(7)–C(1)–C(10)	93.7(2)	C(1)–C(2)–C(3)	116.4(3)
C(2)–C(3)–C(4)	121.7(3)	O(2)–C(4)–C(3)	122.1(3)
O(2)–C(4)–C(5)	120.6(3)	C(3)–C(4)–C(5)	117.4(3)
C(4)–C(5)–C(6)	110.0(2)	C(4)–C(5)–C(10)	108.7(2)
C(4)–C(5)–C(11)	108.6(2)	C(6)–C(5)–C(10)	102.1(2)
C(6)–C(5)–C(11)	113.3(2)	C(10)–C(5)–C(11)	114.0(2)
C(5)–C(6)–C(7)	100.4(2)	C(5)–C(6)–C(12)	115.2(3)
C(7)–C(6)–C(12)	115.2(3)	C(1)–C(7)–C(6)	108.8(2)
C(1)–C(7)–C(8)	78.7(2)	C(6)–C(7)–C(8)	120.2(3)
O(1)–C(8)–C(7)	88.7(2)	O(1)–C(8)–C(9)	102.1(2)
C(7)–C(8)–C(9)	104.3(2)	C(8)–C(9)–C(10)	95.5(5)
C(8)–C(9)–C(13)	113.6(3)	C(10)–C(9)–C(13)	115.3(3)
C(1)–C(10)–C(5)	97.5(2)	C(1)–C(10)–C(9)	97.8(2)
C(1)–C(10)–C(14)	117.1(2)	C(5)–C(10)–C(9)	114.1(2)
C(5)–C(10)–C(14)	112.2(2)	C(9)–C(10)–C(14)	115.9(2)
C(5)–C(11)–N(1)	178.8(4)	C(10)–C(14)–N(2)	175.1(3)

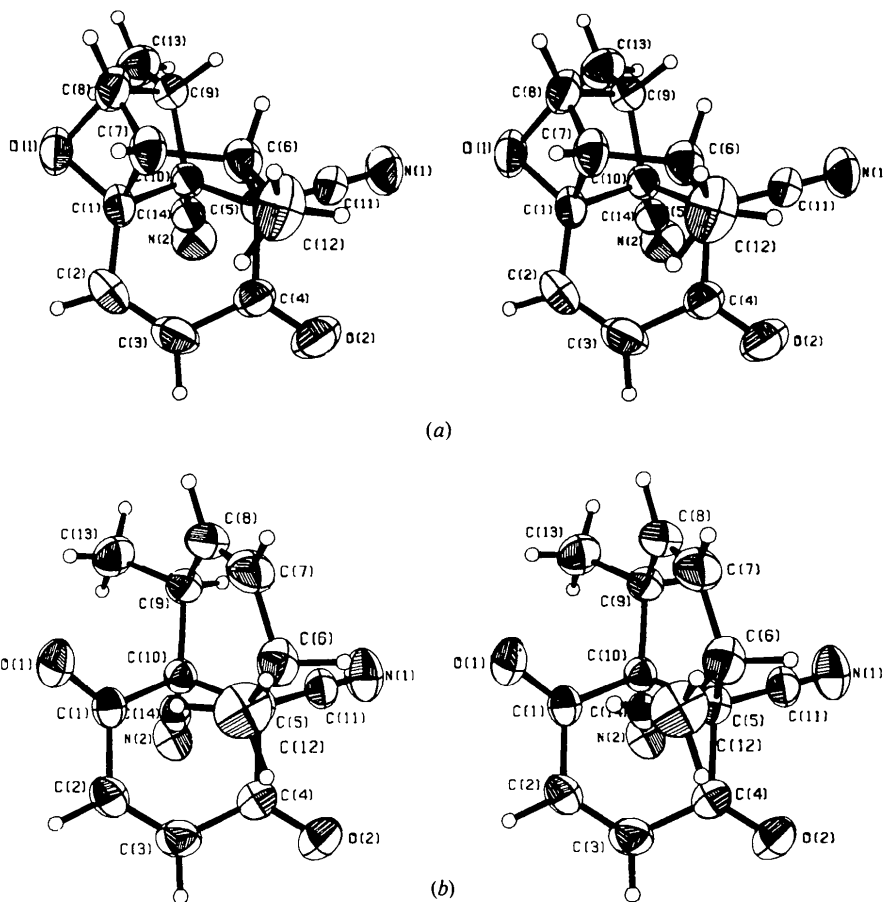


Fig. 1. Stereo diagrams of (a) 11-oxa-5,10-dicyano-6,9-dimethyltetracyclo[6.2.1.0^{1,7}.0^{5,10}]undec-2-en-4-one and (b) a corresponding view of the original 1,4-naphthoquinone molecule (I).

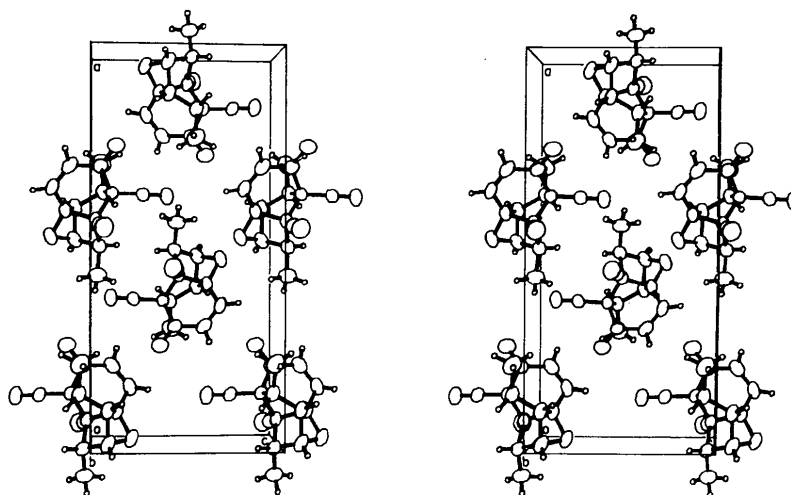


Fig. 2. Stereo diagram of the contents of the unit cell projected down *b*.

A stereo diagram of the crystal packing is shown in Fig. 2.

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2,3-Dimethyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone

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Abstract. C₁₆H₁₆O₂, orthorhombic, *Pna*2₁, *a* = 15.643 (2), *b* = 5.160 (1), *c* = 15.568 (2) Å, *d_m* = 1.26, *d_x* = 1.270 g cm⁻³, *Z* = 4, μ(Cu Kα) = 6.6 cm⁻¹. The conformation of the molecule is twisted such that the bridgehead H atoms are staggered with a torsion angle of 57°. Bond lengths and angles are close to normal values.

Introduction. A small piece, dimensions ca 0.10 × 0.08 × 0.03 cm, was cut from a large, colourless, rod-shaped crystal and used for data collection. Unit-cell and intensity data were measured on a Datex-automated GE XRD 6 diffractometer with Cu Kα radiation and the θ–2θ scan technique. Unit-cell parameters were refined by least squares from the ob-