1,6-Dicyano-2-hydroxy-8,9-dimethyltricyclo[4.4.0.0^{2,8}]dec-3,9-dien-5-one

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Abstract. $C_{14}H_{12}N_2O_2$, orthorhombic, $P2_12_12_1$, $a = 13.135$ (2), $b = 6.875$ (2), $c = 13.529$ (2) Å, $d_m = 1.30$ (flotation), $Z = 4$, $d_x = 1.306$ g cm^{-3}, μ(Cu $K\alpha$) $= 7.4$ 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 and the crystal structure is held together by O—H···N hydrogen bonds.

Introduction. Well formed colourless crystals were ob-
tained by crystallization from petroleum spirit. Unit-cell and intensity data were measured on a Datex-automated GE XRD 6 diffractometer with Cu $K\alpha$ radiation and the θ–2θ scan technique. Unit-cell parameters were refined by least squares from the observed 2θ values of 13 reflexions. Of the 1432 independent reflexions with $2\theta < 146°$, 1272 had intensities greater than $3\sigma(I)$ above background [$\sigma^2(I) = S + B + (0.05S)^2$, where $S = $ scan and $B = $ background count]. Lorentz and polarization corrections were applied and
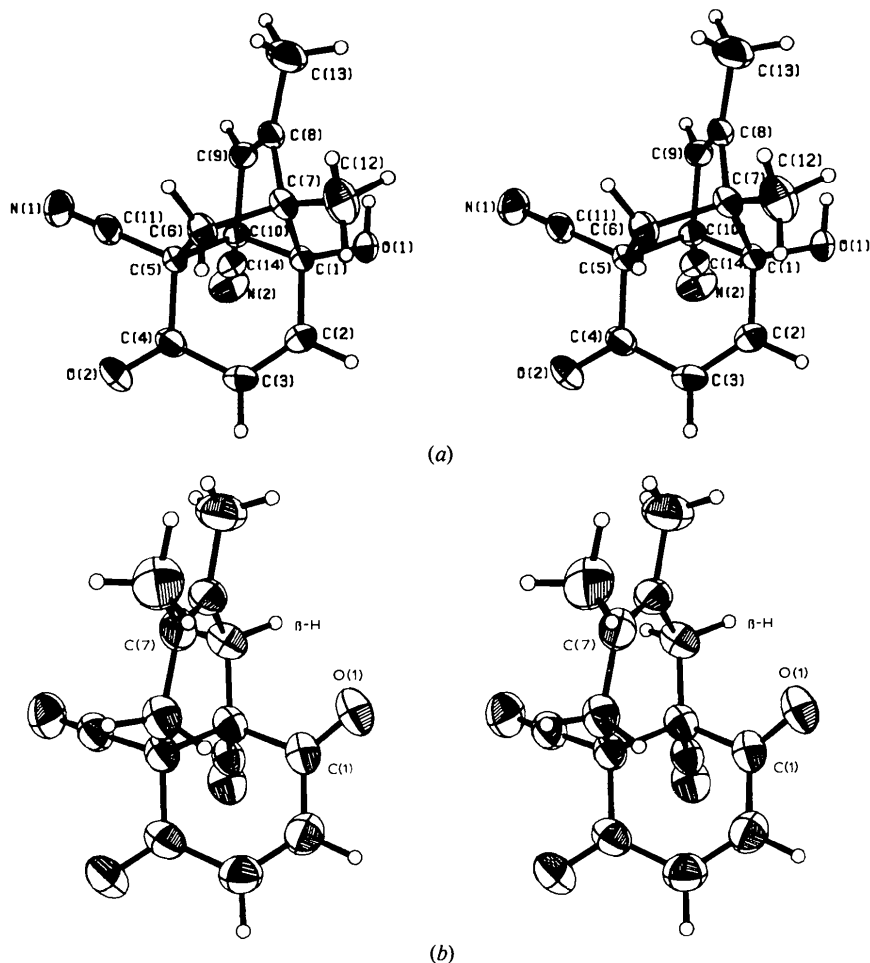

Fig. 1. Stereo diagrams of (*a*) 1,6-dicyano-2-hydroxy-8,9-dimethyltricyclo[4.4.0.0^{2,8}]dec-3,9-dien-5-one, and (*b*) a corresponding view of the original 1,4-naphthoquinone molecule (I).

the structure amplitudes derived. Crystal dimensions were 0·020 × 0·024 × 0·020 cm and no absorption correction was applied.

The structure was solved by direct methods with symbolic-addition and tangent-refinement techniques. Origin-defining reflexions and starting symbols for this procedure were chosen manually. The set of phases with the highest consistency gave an E map clearly showing all 18 non-hydrogen atoms. Several cycles of full-matrix least-squares refinement were carried out

Table 1. *Final positional parameters (fractional, ×10⁴, H ×10³) with estimated standard deviations in parentheses*

	x	y	z
O(1)	4184 (1)	−2927 (3)	1300 (1)
O(2)	4710 (2)	−4091 (4)	−2556 (1)
N(1)	2497 (2)	−6565 (4)	−2332 (2)
N(2)	2669 (2)	−823 (4)	−859 (2)
C(1)	4334 (2)	−4040 (4)	444 (2)
C(2)	5251 (2)	−3189 (5)	−43 (2)
C(3)	5414 (2)	−3218 (5)	−1011 (2)
C(4)	4689 (2)	−4186 (4)	−1666 (2)
C(5)	3895 (2)	−5414 (4)	−1107 (2)
C(6)	4451 (2)	−7018 (4)	−491 (2)
C(7)	4346 (2)	−6296 (4)	594 (2)
C(8)	3230 (2)	−6644 (4)	845 (2)
C(9)	2676 (2)	−5405 (4)	331 (2)
C(10)	3398 (2)	−4132 (4)	−259 (2)
C(11)	3116 (2)	−6119 (4)	−1797 (2)
C(12)	5147 (3)	−7068 (6)	1296 (2)
C(13)	2867 (3)	−8245 (6)	1508 (3)
C(14)	2998 (2)	−2270 (4)	−600 (2)
H(2)	574 (2)	−253 (5)	43 (2)
H(3)	599 (2)	−266 (5)	−129 (2)
H(6a)	411 (2)	−832 (5)	−60 (2)
H(6b)	517 (2)	−721 (5)	−66 (2)
H(9)	193 (2)	−536 (4)	28 (2)
H(12a)	585 (3)	−674 (5)	105 (2)
H(12b)	497 (2)	−666 (5)	195 (2)
H(12c)	510 (3)	−847 (8)	143 (3)
H(13a)	207 (3)	−837 (7)	147 (3)
H(13b)	314 (3)	−811 (7)	219 (3)
H(13c)	304 (3)	−945 (7)	125 (3)
HO	363 (2)	−337 (6)	162 (2)

where the function minimized was $\Sigma \, w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F)$, $\sigma(F)$ values being derived from the previously calculated $\sigma(I)$ values. A difference Fourier map showed nine H atoms, the remaining three 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). In the final stages of refinement extinction effects were apparent in the data and a correction was applied. A parameter E was introduced such that F_c was replaced in the calculations by F_{corr}, where $F_{corr} = F_c/(1 + EI_o)$, I_o being the uncorrected intensity (Stout & Jensen, 1968). The final refined value of E was 1·9 (1) × 10⁻⁶. Three low-angle reflexions were still in poor agreement and these were zero weighted in the final cycles of refinement. The final R and $R'\{= [\Sigma \, w(|F_o| - |F_c|)^2/\Sigma \, w|F_c|^2]^{1/2}\}$ for the 1272 reflexions with $I > 3\sigma(I)$ are 0·042 and 0·055 respectively. For all 1432 data R is 0·048 and R' 0·055. The correct absolute configuration has been determined, for the particular crystal chosen, from comparison of the R values of the two enantiomorphs. The ratios for R and R' showed it to be that in Fig. 1 with better than 95% and 99·5% significance respectively (Hamilton, 1965). The error in an observation of unit weight $\{[\Sigma \, w(|F_o| - |F_c|)^2/(m - n)]^{1/2}\}$ is 1·63. Final positional parameters are listed in Table 1.*

Thermal-motion analysis and correction of bond lengths for libration were carried out as for 6,7-dimethyl-*cis*-4a,8a-dicyano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (I) (Phillips & Trotter, 1976) with C(1)—C(10), C(11) and C(14) as the rigid-body core.

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

	Uncorrected	Corrected		Uncorrected	Corrected
O(1)—C(1)	1·402 (3)	1·403	O(2)—C(4)	1·207 (3)	1·208
N(1)—C(11)	1·131 (3)	1·131	N(2)—C(14)	1·140 (4)	1·140
C(1)—C(2)	1·492 (3)	1·496	C(1)—C(7)	1·565 (4)	1·568
C(1)—C(10)	1·556 (3)	1·561	C(2)—C(3)	1·327 (4)	1·330
C(3)—C(4)	1·461 (4)	1·464	C(4)—C(5)	1·541 (3)	1·545
C(5)—C(6)	1·563 (3)	1·568	C(5)—C(10)	1·587 (3)	1·591
C(5)—C(11)	1·467 (3)	1·470	C(6)—C(7)	1·556 (3)	1·560
C(7)—C(8)	1·523 (3)	1·528	C(7)—C(12)	1·514 (4)	1·514
C(8)—C(9)	1·319 (4)	1·322	C(8)—C(13)	1·498 (4)	1·497
C(9)—C(10)	1·517 (3)	1·521	C(10)—C(14)	1·459 (4)	1·462

Outer bonds were corrected for independent motion as before. R.m.s. ΔU_{ij} for the rigid body is 0.0018 Å^2, compared to an r.m.s. $\sigma(U_{ij})$ from the least squares of 0.0013 Å^2 and the rigid body was assumed to provide a good approxiation 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 1,6-dicyano-2-hydroxy-8,9-dimethyltricyclo[4.4.0.0²,⁸]dec-3,9-dien-5-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 (I) in solution or the solid state gives rise to (II) *via* an intramolecular β-H abstraction reaction (Scheffer, Jennings & Louwerens, 1976; Scheffer & Dzakpasu, 1975).

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

O(1)—C(1)—C(2)	105·4 (2)	O(1)—C(1)—C(7)	115·8 (2)
O(1)—C(1)—C(10)	114·5 (2)	C(2)—C(1)—C(7)	116·0 (2)
C(2)—C(1)—C(10)	112·6 (2)	C(7)—C(1)—C(10)	92·7 (2)
C(1)—C(2)—C(3)	124·0 (3)	C(2)—C(3)—C(4)	120·0 (3)
O(2)—C(4)—C(3)	124·5 (3)	O(2)—C(4)—C(5)	122·3 (2)
C(3)—C(4)—C(5)	113·1 (2)	C(4)—C(5)—C(6)	109·4 (2)
C(4)—C(5)—C(10)	109·2 (2)	C(4)—C(5)—C(11)	109·9 (2)
C(6)—C(5)—C(10)	101·5 (2)	C(6)—C(5)—C(11)	115·6 (2)
C(10)—C(5)—C(11)	110·9 (2)	C(5)—C(6)—C(7)	103·7 (2)
C(1)—C(7)—C(6)	101·2 (2)	C(1)—C(7)—C(8)	100·1 (2)
C(1)—C(7)—C(12)	115·8 (2)	C(6)—C(7)—C(8)	104·2 (2)
C(6)—C(7)—C(12)	114·7 (2)	C(8)—C(7)—C(12)	118·3 (2)
C(7)—C(8)—C(9)	108·2 (2)	C(7)—C(8)—C(13)	123·7 (3)
C(9)—C(8)—C(13)	128·0 (3)	C(8)—C(9)—C(10)	107·8 (2)
C(1)—C(10)—C(5)	98·0 (2)	C(1)—C(10)—C(9)	101·3 (2)
C(1)—C(10)—C(14)	116·2 (2)	C(5)—C(10)—C(9)	108·5 (2)
C(5)—C(10)—C(14)	114·0 (2)	C(9)—C(10)—C(14)	116·6 (2)
N(1)—C(11)—C(5)	176·4 (3)	N(2)—C(14)—C(10)	178·8 (3)

(I)   (II)
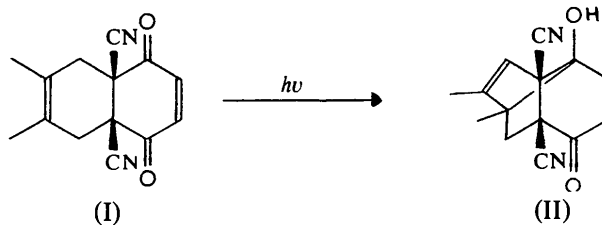
A stereo diagram of the molecule, with the crystallographic numbering scheme, is shown in Fig. 1, together with a view of the initial molecule of (I), whose crystal structure has already been reported (Phillips & Trotter, 1976). Comparison of the two structures shows that the abstraction of the β-H by O(1) and the ensuing collapse of the diradical formed can occur with relatively small changes in conformation. The major change in the C skeleton is the large shift of C(7), the distance C(1)···C(7) in the starting material of $3\cdot383$ Å reducing to the C—C bonded distance of $1\cdot565$ Å in the product. The largest change in torsion angle within the skeleton is for C(5)—C(6)—C(7)—C(8), which changes by $88\cdot3°$. The change in the C(5)—C(10) ring may be regarded as a conversion from the favourable half-chair (Bucourt & Hainaut, 1965) to the boat form.

The bond lengths and angles in (II) (see Tables 2 and 3) are normal except for a slight shortening of O(2)=C(4) and C(8)=C(9). The bridgehead torsion angle C(11)—C(5)—C(10)—C(14) is $-68\cdot9$ (2)°, compared to $-60\cdot9$ (2)° in (I). The bridgehead angle of the norbornene skeleton, C(7)—C(1)—C(10), is $92\cdot7$ (2)° and the angles between the two four-atom mean planes C(5), C(6), C(7), C(10) and C(7), C(8), C(9), C(10) and the three-atom plane C(1), C(7), C(10) are $118\cdot8$ and $128\cdot6°$ respectively. The mean-plane calculation for C(5), C(6), C(7), C(10) shows a slight deviation from planarity while C(7), C(8), C(9) and C(10) are more nearly coplanar.
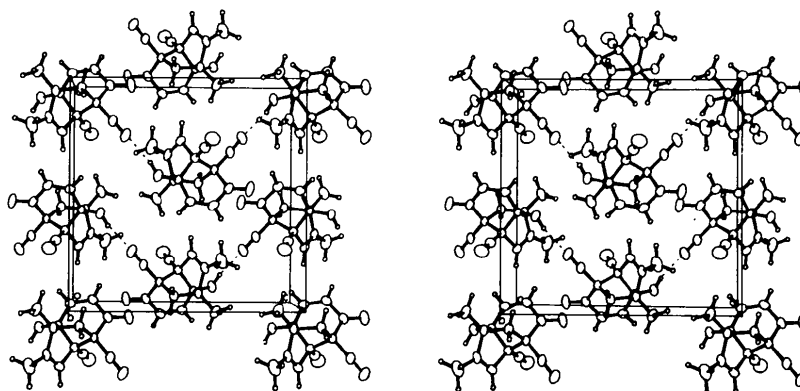

Fig. 2. Stereo diagram of the contents of the unit cell projected down b. Hydrogen bonds are shown by dotted lines.

Intermolecular distances mainly correspond to van der Waals interactions, except for a close N $\cdots$ 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 $\cdots$ N(1) [$\frac{1}{2} - x, -1 - y, \frac{1}{2} + z$] is 2·05 (3) Å. The corresponding O—H and O $\cdots$ N distances are 0·89 (3) and 2·902 (3) Å respectively and the O—H $\cdots$ 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. $C_{14}H_{12}N_2O_2$, orthorhombic, $P2_12_12_1$, $a = 18·701$ (6), $b = 7·274$ (2), $c = 9·005$ (2) Å, $d_m = 1·29$ (flotation), $Z = 4$, $d_x = 1·303$ g cm^{-3}, μ(Cu $K\alpha$) = 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 $K\alpha$ 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 $2\theta < 146°$, 1320 had intensities greater than $3\sigma(I)$ 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 $0·07 \times 0·05 \times 0·02$ cm and no absorption correction was applied.

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

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 $\Sigma w(|F_o| - |F_c|)^2$ 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'