6,7-Dimethyl-*cis*-4a,8a-dicyano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone

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Abstract. $C_{14}H_{12}N_2O_2$, monoclinic, $P2_1/c$; $a=8\cdot717$ (5), $b=12\cdot464$ (2), $c=12\cdot783$ (5) Å, $\beta=117\cdot87$ (3)°; $d_m=1\cdot31$ (flotation), $d_x=1\cdot300$ g cm^{-3}, $Z=4$; μ(Cu $K\alpha$)$=7\cdot3$ cm^{-1}. The conformation of the molecule is twisted such that the bridgehead cyano groups are staggered with a torsion angle of $60\cdot9$°. Bond lengths and angles are close to normal values.

Introduction. Well formed yellow crystals were obtained by crystallization from petroleum spirit. Unit-cell and intensity data were measured on a Datex-automated G.E. 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 23 reflexions. Of the 2445 independent reflexions with $2\theta<146$°, 2053 had intensities greather than $3\sigma(I)$ above background $[\sigma^2(I)=S+B+(0\cdot04S)^2$, where S=scan and B=background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. Crystal dimensions were $0\cdot05\times0\cdot04\times0\cdot04$ cm and no absorption correction was applied.

The structure was solved by direct methods with an automatic computer program (Long, 1965) to apply a multisolution procedure to the 312 E values $>1\cdot50$. The most consistent set of phases gave an E map in which all the non-hydrogen atoms were located. Several cycles of full-matrix least-squares refinement, where the function minimized was $\sum w(|F_o|-|F_c|)^2$ with weights $w=1/\sigma^2(F)$, $\sigma(F)$ values being derived from the previously calculated $\sigma(I)$ values, were carried out and a difference map was calculated. All 12 hydrogen atoms were found in this map and were used in subsequent refinement cycles. All non-hydrogen atoms were included with anisotropic temperature factors, the hydrogens being refined isotropically. 15 planes were zero weighted in the final cycles of refinement due to poor agreement revealed by the weighting statistics. The final R and R' $\{=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}\}$ for the 2053 reflexions with $I>3\sigma(I)$ are $0\cdot055$ and $0\cdot091$ respectively. For all 2445 data R is $0\cdot064$ and R' is $0\cdot091$. The error in an observation of unit weight, $[\sum w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, is $3\cdot30$. Atomic scattering factors for O, N and C are those of Cromer & Mann (1968) and for H those of Stewart, Davidson & Simpson (1965). Final positional and thermal parameters are listed in Tables 1 and 2.*

Thermal-motion analysis and correction of bond lengths for libration were carried out as for 2,3,4aβ,-5β,8β,8aβ-hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (Phillips & Trotter, 1976b) except that the rigid-body core model was extended to include C(11) and C(14) as well as C(1) to C(10). Peripheral bonds were corrected for independent motion as before. The r.m.s. ΔU_{ij} for the rigid body was $0\cdot0021$ Å^2 compared to an r.m.s. $\sigma(U_{ij})$ of $0\cdot0010$ Å^2 for the molecule. This suggests that the rigid-body model is a good approximation. Corrected bond lengths are reported in Table 3. Bond angles were not significantly affected and corrected values are not reported.

Discussion. The structural work on 6,7-dimethyl-*cis*-4a,8a-dicyano-4a,5,8,8a-tetrahydro-1,4-naphthoquin-

Table 1. *Final positional parameters (fractional $\times10^4$, H$\times10^3$) with estimated standard deviations in parentheses*

	x	y	z
O(1)	−3656 (2)	5723 (1)	996 (1)
O(2)	−407 (2)	2199 (1)	869 (2)
C(1)	−2634 (2)	5070 (1)	1012 (2)
C(2)	−2508 (3)	4729 (2)	−47 (2)
C(3)	−1789 (3)	3799 (2)	−93 (2)
C(4)	−1118 (2)	3026 (2)	891 (2)
C(5)	−1441 (2)	3288 (1)	1947 (2)
C(6)	−3292 (2)	2901 (2)	1649 (2)
C(7)	−3957 (2)	3329 (2)	2459 (2)
C(8)	−3227 (2)	4160 (2)	3179 (2)
C(9)	−1704 (3)	4762 (2)	3223 (2)
C(10)	−1335 (2)	4517 (1)	2187 (2)
C(11)	−130 (2)	2753 (2)	3012 (2)
C(12)	−5538 (2)	2738 (2)	2349 (3)
C(13)	−3789 (4)	4588 (3)	4051 (3)
C(14)	413 (2)	4897 (1)	2443 (2)
N(1)	905 (3)	2359 (2)	3848 (2)
N(2)	1756 (2)	5177 (1)	2614 (2)
H(2)	−305 (3)	521 (2)	−79 (2)
H(3)	−175 (3)	359 (2)	−82 (2)
H(6a)	−410 (3)	311 (2)	79 (2)
H(6b)	−322 (3)	212 (2)	173 (2)
H(9a)	−68 (3)	456 (2)	396 (2)
H(9b)	−192 (3)	556 (2)	327 (2)
H(12a)	−643 (4)	272 (3)	142 (3)
H(12b)	−602 (5)	307 (3)	282 (3)
H(12c)	−530 (4)	201 (3)	257 (3)
H(13a)	−295 (5)	455 (3)	474 (3)
H(13b)	−470 (5)	417 (3)	404 (3)
H(13c)	−431 (5)	523 (3)	381 (4)

Table 2. *Final thermal parameters and their estimated standard deviations*

Anisotropic thermal parameters in the expression:

$$f = f^0 \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\right].$$

(a) Anisotropic thermal parameters ($U_{ij} \times 10^3$ Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	44 (1)	46 (1)	78 (1)	7 (1)	23 (1)	0 (1)
O(2)	98 (1)	57 (1)	95 (1)	19 (1)	63 (1)	−2 (1)
C(1)	36 (1)	38 (1)	60 (1)	−2 (1)	20 (1)	2 (1)
C(2)	50 (1)	63 (1)	57 (1)	5 (1)	26 (1)	12 (1)
C(3)	59 (1)	67 (1)	57 (1)	3 (1)	34 (1)	1 (1)
C(4)	52 (1)	46 (1)	67 (1)	0 (1)	35 (1)	−7 (1)
C(5)	42 (1)	38 (1)	55 (1)	1 (1)	26 (1)	1 (1)
C(6)	44 (1)	40 (1)	64 (1)	−4 (1)	26 (1)	1 (1)
C(7)	41 (1)	50 (1)	62 (1)	5 (1)	27 (1)	12 (1)
C(8)	42 (1)	57 (1)	53 (1)	10 (1)	27 (1)	8 (1)
C(9)	46 (1)	52 (1)	58 (1)	0 (1)	27 (1)	−8 (1)
C(10)	36 (1)	38 (1)	54 (1)	−1 (1)	23 (1)	−2 (1)
C(11)	50 (1)	44 (1)	67 (1)	4 (1)	33 (1)	2 (1)
C(12)	57 (1)	73 (2)	106 (2)	−5 (1)	50 (1)	14 (1)
C(13)	64 (1)	95 (2)	66 (2)	13 (1)	42 (1)	0 (1)
C(14)	39 (1)	40 (1)	60 (1)	1 (1)	23 (1)	1 (1)
N(1)	66 (1)	71 (1)	76 (1)	22 (1)	32 (1)	18 (1)
N(2)	42 (1)	59 (1)	84 (1)	−4 (1)	28 (1)	1 (1)

(b) Isotropic thermal parameters ($U_{\text{iso}} \times 10^3$ Å^2)

	U		U		U
H(2)	92 (8)	H(9a)	47 (5)	H(12c)	120 (12)
H(3)	72 (7)	H(9b)	71 (7)	H(13a)	107 (11)
H(6a)	62 (6)	H(12a)	117 (11)	H(13b)	112 (10)
H(6b)	57 (6)	H(12b)	133 (13)	H(13c)	145 (15)

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

|		Cor-rected			Cor-rected
O(1)—C(1)	1·200 (2)	1·202	O(2)—C(4)	1·210 (2)	1·212
C(1)—C(2)	1·471 (3)	1·476	C(1)—C(10)	1·557 (3)	1·560
C(2)—C(3)	1·332 (3)	1·335	C(3)—C(4)	1·472 (3)	1·475
C(4)—C(5)	1·538 (3)	1·542	C(5)—C(6)	1·551 (2)	1·553
C(5)—C(10)	1·556 (2)	1·561	C(6)—C(7)	1·501 (3)	1·505
C(7)—C(8)	1·333 (3)	1·337	C(8)—C(9)	1·503 (3)	1·506
C(9)—C(10)	1·532 (5)	1·536	C(5)—C(11)	1·466 (3)	1·469
C(7)—C(12)	1·511 (3)	1·513	C(8)—C(13)	1·510 (3)	1·510
C(10)-C(14)	1·479 (2)	1·481	C(11)-N(1)	1·139 (3)	1·140
C(14)-N(2)	1·141 (2)	1·142			

one (I) was undertaken as part of a study of the photochemistry of various substituted 1,4-naphthoquinone systems with *cis* bridgehead substituents.

(I)   (II)
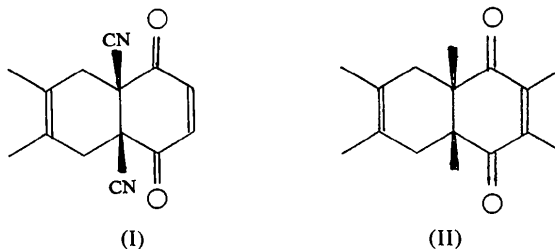
A stereo diagram of the molecule, with the crystallographic numbering scheme, is shown in Fig. 1. The conformation is staggered about the C(5)–C(10) bond as in *cis*-2,3,4a,6,7,8a-hexamethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (II) (Phillips & Trotter, 1976a). The torsion angles C(6)–C(5)–C(10)–C(1) and C(11)–C(5)–C(10)–C(14) are −64·0 (2) and 60·9 (2)° respectively, compared to corresponding values of −61·4 (5) and 60·0 (6)° in (II).

The bridgehead cyano groups have the effect of lengthening the C(1)–C(10), C(4)–C(5), C(5)–C(6) and C(5)–C(10) bonds compared with (II). C(1)–C(2), C(3)–C(4) and C(6)–C(7) are correspondingly shortened. The carbonyl C=O bonds are short with significantly different bond lengths, a departure from the trend shown by the related molecules studied which all had equal C=O bond lengths (Phillips & Trotter, 1976a, b, c, d). A mean-plane calculation showed the O(1) carbonyl group to be planar while the other is slightly, but significantly, non-planar.

The distance from the carbonyl oxygen O(1) to the β-hydrogen, H(9b), is 2·58 (3) Å, about 0·1 Å longer than in (II). H(6a)···C(2) and H(6a)···C(3) are 2·92 (3) and 2·86 (3) Å respectively, again slightly longer than in (II). Photolysis of (I) in solution or the solid
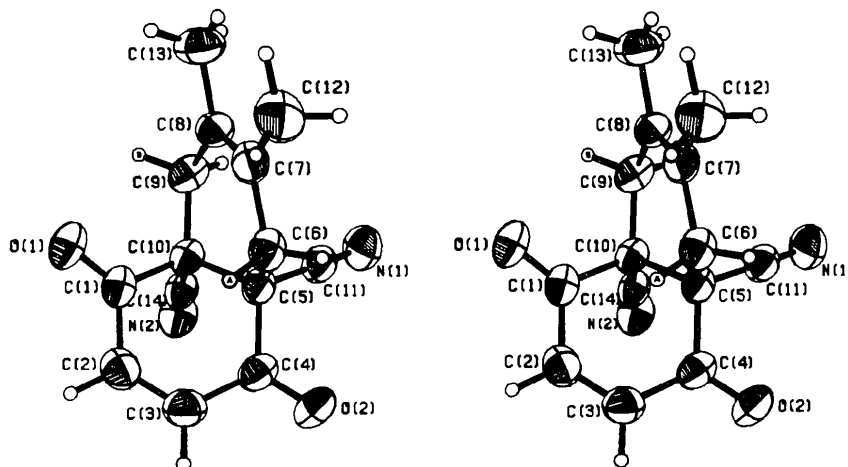
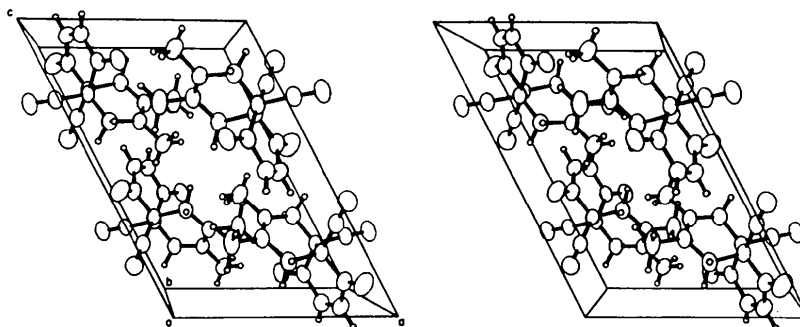Fig. 1. Stereo diagram of 6,7-dimethyl-cis-4a,8a-dicyano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone.

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

state gives only the alcohol product characteristic of β-hydrogen abstraction (Scheffer, Jennings & Louwerens, 1976; Scheffer & Dzakpasu, 1975).

Table 4. *Bond angles (°) for non-hydrogen atoms with estimated standard deviations in parentheses*

O(1)—C(1)—C(2)	123·6 (2)	O(1)—C(1)—C(10)	121·1 (2)
C(2)—C(1)—C(10)	115·3 (2)	C(1)—C(2)—C(3)	122·1 (2)
C(2)—C(3)—C(4)	122·6 (2)	O(2)—C(4)—C(3)	122·8 (2)
O(2)—C(4)—C(5)	120·5 (2)	C(3)—C(4)—C(5)	116·7 (2)
C(4)—C(5)—C(6)	108·3 (1)	C(4)—C(5)—C(10)	111·3 (1)
C(6)—C(5)—C(10)	108·3 (1)	C(5)—C(6)—C(7)	114·3 (2)
C(6)—C(7)—C(8)	122·6 (2)	C(7)—C(8)—C(9)	122·8 (2)
C(8)—C(9)—C(10)	114·0 (2)	C(1)—C(10)-C(5)	107·2 (1)
C(1)—C(10)-C(9)	113·2 (1)	C(5)—C(10)-C(9)	110·5 (1)
C(4)—C(5)—C(11)	109·6 (1)	C(6)—C(5)—C(11)	111·0 (2)
C(10)-C(5)—C(11)	108·4 (2)	C(6)—C(7)—C(12)	113·1 (2)
C(8)—C(7)—C(12)	124·3 (2)	C(7)—C(8)—C(13)	124·7 (2)
C(9)—C(8)—C(13)	112·4 (2)	C(1)—C(10)-C(14)	106·3 (1)
C(5)—C(10)-C(14)	108·7 (1)	C(9)—C(10)-C(14)	110·8 (1)
C(5)—C(11)-N(1)	178·5 (2)	C(10)-C(14)-N(2)	178·1 (2)

Intermolecular distances correspond mainly to van der Waals interactions. The nearest carbonyl group adjacent to C(1)=O(1) is related to it by a centre of symmetry such that O(1)···O(1) $[-1-x, 1-y, -z]$ is 3·105 and O(1)···C(1) $[-1-x, 1-y, -z]$ is 3·204 Å. The parallel planes of the two carbonyls lie 2·238 Å

apart but the groups do not overlap. A stereo diagram of the crystal packing is shown in Fig. 2. Bond lengths and angles are given in Tables 3 and 4.

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