

5 α ,8 α -Dimethyl-4 $\alpha\beta$,8 $\alpha\beta$ -dicyano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone

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Abstract. C₁₄H₁₂N₂O₂, orthorhombic, *Pbcn*; $a = 15.915$ (6), $b = 11.525$ (4), $c = 13.157$ (5) Å; $d_m = 1.32$ (floatation), $d_x = 1.322$ g cm⁻³, $Z = 8$; $\mu(\text{Cu } K\alpha) = 7.4$ cm⁻¹. The conformation of the molecule is twisted such that the bridgehead cyano groups are staggered with a torsion angle of 57.1°. Bond lengths and angles are close to normal values.

Introduction. Well formed colourless 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* α radiation and the θ - 2θ scan technique. Unit-cell parameters were refined by least squares from the observed 2θ values of 14 reflexions. Of the 2419 independent reflexions with $2\theta < 146^\circ$, 1767 had intensities greater than $3\sigma(I)$ above background [$\sigma^2(I) = S + B + (0.05S)^2$, where $S = \text{scan}$ and $B = \text{background count}$]. Lorentz and polarization corrections were applied and the structure amplitudes derived. Crystal dimensions were $0.05 \times 0.03 \times 0.03$ cm and no absorption correction was applied.

The structure was solved by direct methods with data for which $2\theta < 120^\circ$. An automatic computer program (Long, 1965) was used to apply a multisolution procedure to the 239 E values > 1.50 . The set of phases having the highest consistency was used to calculate 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. The 12 hydrogen atoms were found on this map and included in subsequent cycles of refinement. All data with $2\theta < 146^\circ$ were used in the final stages of refinement. All non-hydrogen atoms were included with anisotropic temperature factors, the hydrogens being refined isotropically. Three 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 1767 reflexions with $I > 3\sigma(I)$ are 0.046 and 0.066 respectively. For all 2419 data R is 0.069 and R' is 0.067. The error in an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, is 1.53. 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.*

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

| | <i>x</i> | <i>y</i> | <i>z</i> |
|--------|----------|-----------|-----------|
| O(1) | 6428 (1) | 5670 (1) | 663 (1) |
| O(2) | 6687 (1) | 10118 (1) | -12 (1) |
| C(1) | 6699 (1) | 6582 (2) | 364 (2) |
| C(2) | 7212 (2) | 7357 (2) | 1007 (2) |
| C(3) | 7208 (2) | 8497 (2) | 873 (2) |
| C(4) | 6705 (1) | 9075 (2) | 91 (2) |
| C(5) | 6145 (1) | 8300 (2) | -587 (2) |
| C(6) | 5232 (1) | 8245 (2) | -131 (2) |
| C(7) | 4766 (2) | 7214 (2) | -509 (2) |
| C(8) | 5084 (2) | 6353 (2) | -1044 (2) |
| C(9) | 5976 (2) | 6296 (2) | -1404 (2) |
| C(10) | 6538 (1) | 7057 (2) | -720 (1) |
| C(11) | 6113 (1) | 8839 (2) | -1607 (2) |
| C(12) | 5180 (2) | 8312 (3) | 1035 (2) |
| C(13) | 6309 (2) | 5058 (2) | -1550 (3) |
| C(14) | 7370 (1) | 7190 (2) | -1200 (1) |
| N(1) | 6113 (2) | 9222 (2) | -2405 (2) |
| N(2) | 8007 (1) | 7299 (2) | -1587 (2) |
| H(2) | 753 (2) | 697 (2) | 155 (2) |
| H(3) | 753 (2) | 901 (2) | 127 (2) |
| H(6) | 494 (2) | 897 (2) | -43 (2) |
| H(7) | 419 (2) | 721 (2) | -32 (2) |
| H(8) | 474 (2) | 568 (2) | -125 (2) |
| H(9) | 600 (1) | 665 (2) | -206 (2) |
| H(12a) | 463 (2) | 836 (2) | 120 (2) |
| H(12b) | 545 (2) | 905 (3) | 136 (3) |
| H(12c) | 541 (2) | 759 (3) | 133 (2) |
| H(13a) | 697 (2) | 507 (3) | -182 (3) |
| H(13b) | 596 (2) | 472 (3) | -209 (3) |
| H(13c) | 625 (2) | 463 (3) | -92 (3) |

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 (Phillips & Trotter, 1976e) with C(1) to C(10), C(11) and C(14) as the rigid-body core. Outer bonds were corrected for independent motion as before. The r.m.s. ΔU_{ij} for the rigid body is 0.0020 Å² compared to an r.m.s. $\sigma(U_{ij})$ of 0.0012 Å² for the molecule. Thus the rigid-body model was assumed to be a good approximation to the thermal motion. Cor-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31857 (22 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Final thermal parameters and their estimated standard deviations

Anisotropic thermal parameters in the expression:

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

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

| | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|-------|----------|----------|----------|----------|----------|----------|
| O(1) | 63 (1) | 49 (1) | 51 (1) | -3 (1) | 0 (1) | 16 (1) |
| O(2) | 68 (1) | 41 (1) | 69 (1) | -8 (1) | 0 (1) | 1 (1) |
| C(1) | 42 (1) | 41 (1) | 34 (1) | 5 (1) | 2 (1) | 5 (1) |
| C(2) | 61 (1) | 56 (1) | 32 (1) | -2 (1) | -8 (1) | 5 (1) |
| C(3) | 62 (2) | 56 (1) | 39 (1) | -9 (1) | -7 (1) | -5 (1) |
| C(4) | 45 (1) | 41 (1) | 41 (1) | -4 (1) | 6 (1) | 0 (1) |
| C(5) | 39 (1) | 37 (1) | 39 (1) | 1 (1) | 0 (1) | 5 (1) |
| C(6) | 39 (1) | 51 (1) | 59 (1) | 4 (1) | 6 (1) | 5 (1) |
| C(7) | 38 (1) | 69 (2) | 72 (2) | -8 (1) | -4 (1) | 11 (1) |
| C(8) | 54 (1) | 57 (1) | 63 (2) | -15 (1) | -17 (1) | 5 (1) |
| C(9) | 59 (1) | 43 (1) | 40 (1) | -6 (1) | -11 (1) | 0 (1) |
| C(10) | 39 (1) | 36 (1) | 32 (1) | 0 (1) | -1 (1) | 2 (1) |
| C(11) | 46 (1) | 43 (1) | 47 (1) | 6 (1) | -3 (1) | 7 (1) |
| C(12) | 54 (2) | 73 (2) | 65 (2) | 0 (1) | 23 (1) | -6 (1) |
| C(13) | 94 (2) | 45 (1) | 62 (2) | -1 (1) | -14 (2) | -11 (1) |
| C(14) | 44 (1) | 42 (1) | 32 (1) | 6 (1) | -1 (1) | 2 (1) |
| N(1) | 89 (2) | 72 (1) | 51 (1) | 12 (1) | -3 (1) | 22 (1) |
| N(2) | 49 (1) | 72 (1) | 49 (1) | 7 (1) | 6 (1) | 6 (1) |

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

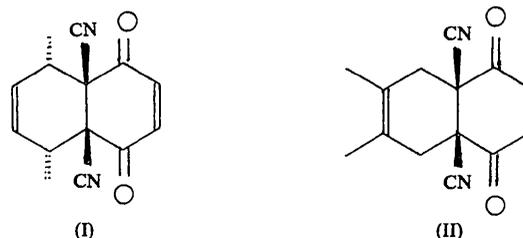
| | U | | U | | U |
|------|--------|--------|----------|--------|---------|
| H(2) | 55 (6) | H(8) | 77 (9) | H(12c) | 78 (9) |
| H(3) | 63 (7) | H(9) | 52 (6) | H(13a) | 95 (10) |
| H(6) | 68 (8) | H(12a) | 78 (9) | H(13b) | 97 (10) |
| H(7) | 62 (7) | H(12b) | 103 (11) | H(13c) | 82 (10) |

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

| | Corrected | | Corrected |
|-------------|-----------|------------|-----------|
| O(1)—C(1) | 1.202 (2) | O(2)—C(4) | 1.210 (2) |
| C(1)—C(2) | 1.477 (3) | C(1)—C(10) | 1.549 (3) |
| C(2)—C(3) | 1.326 (3) | C(3)—C(4) | 1.464 (3) |
| C(4)—C(5) | 1.546 (3) | C(5)—C(6) | 1.573 (3) |
| C(5)—C(10) | 1.573 (3) | C(6)—C(7) | 1.487 (4) |
| C(7)—C(8) | 1.317 (4) | C(8)—C(9) | 1.498 (4) |
| C(9)—C(10) | 1.543 (3) | C(5)—C(11) | 1.480 (3) |
| C(6)—C(12) | 1.538 (4) | C(9)—C(13) | 1.534 (3) |
| C(10)—C(14) | 1.474 (3) | C(11)—N(1) | 1.139 (3) |
| C(14)—N(2) | 1.142 (3) | | |

ected bond lengths are reported in Table 3. Bond angles were not significantly affected and corrected values are not reported.

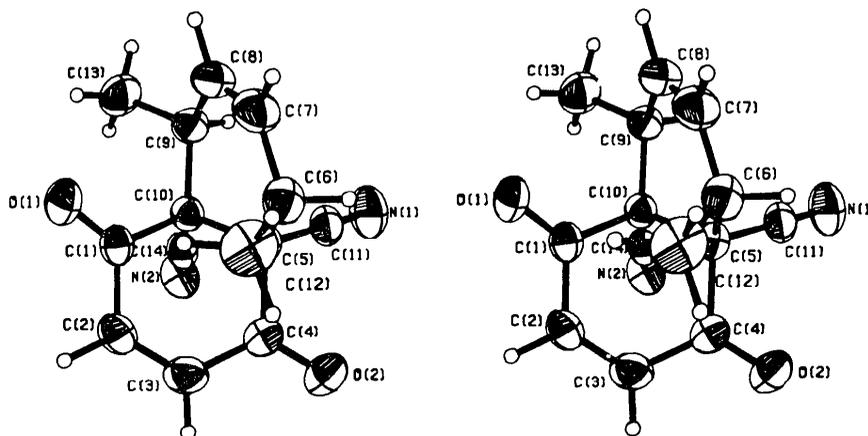
Discussion. The structural work on 5,8-dimethyl-4a,8a-dicyano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (I) was undertaken as part of a study of the photochemistry of various substituted 1,4-naphthoquinone systems with *cis* bridgehead substituents.



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 6,7-dimethyl-*cis*-4a,8a-dicyano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (II) (Phillips & Trotter, 1976e). The torsion angles C(6)—C(5)—C(10)—C(1) and C(11)—C(5)—C(10)—C(14) are $-69.0 (2)$ and $57.1 (2)^\circ$ respectively, compared to corresponding values of $-64.0 (2)$ and $60.9 (2)^\circ$ in (II).

The bond lengths in the molecule are very similar to the corresponding values in (II). The carbonyl C=O bonds again have significantly different bond lengths and both are shorter than in the other 1,4-naphthoquinones studied (Phillips & Trotter, 1976a, b, c, d). A mean-plane calculation showed that the O(1) carbonyl group is planar while the O(2) group is slightly, but significantly, non planar. Also C(1), C(2), C(3) and C(4) are accurately coplanar while C(6), C(7), C(8) and C(9) deviate slightly from planarity.

Due to the substitution at C(6) and C(9) the oxygen O(1) has no β -hydrogen but only a γ -hydrogen on the

Fig. 1. Stereo diagram of 5 α ,8 α -dimethyl-4a β ,8a β -dicyano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone.

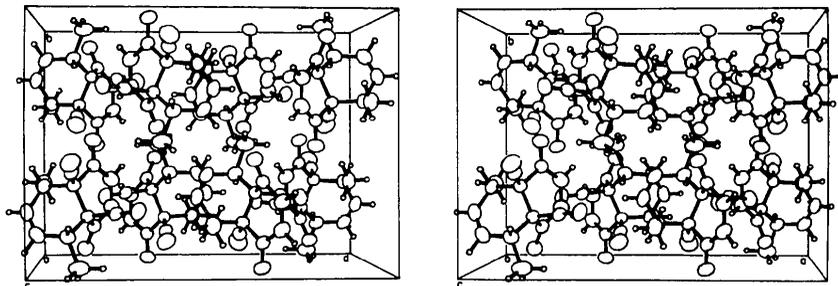


Fig. 2. Stereo diagram of the contents of the unit cell projected down the c axis.

C(13) methyl group. $O(1)\cdots H(13c)$ is 2.41 (3) Å, comparable to the $O\cdots\beta$ -hydrogen distances in the other 1,4-naphthoquinones. The other methyl group lies close to the $C(2)=C(3)$ bond such that $C(2)\cdots H(12c)$ is 2.91 (3) and $C(3)\cdots H(12b)$ is 2.94 (3) Å. Photolysis of (I) in solution or the solid state gives no γ -hydrogen abstraction and the molecule undergoes 2+2 cycloaddition between $C(1)=O(1)$ and $C(7)=C(8)$ to form an oxetane (Scheffer & Dzakpasu, 1976; Scheffer, Jennings & Louwerens, 1976).

Table 4. Bond angles ($^\circ$) for non-hydrogen atoms with estimated standard deviations in parentheses

| | | | |
|--------------------|-----------|--------------------|-----------|
| $O(1)-C(1)-C(2)$ | 122.6 (2) | $O(1)-C(1)-C(10)$ | 123.4 (2) |
| $C(2)-C(1)-C(10)$ | 113.9 (2) | $C(1)-C(2)-C(3)$ | 121.3 (2) |
| $C(2)-C(3)-C(4)$ | 123.2 (2) | $O(2)-C(4)-C(3)$ | 122.9 (2) |
| $O(2)-C(4)-C(5)$ | 119.7 (2) | $C(3)-C(4)-C(5)$ | 117.3 (2) |
| $C(4)-C(5)-C(6)$ | 109.6 (2) | $C(4)-C(5)-C(10)$ | 111.1 (2) |
| $C(6)-C(5)-C(10)$ | 111.9 (2) | $C(5)-C(6)-C(7)$ | 111.4 (2) |
| $C(6)-C(7)-C(8)$ | 126.1 (2) | $C(7)-C(8)-C(9)$ | 124.5 (2) |
| $C(8)-C(9)-C(10)$ | 109.9 (2) | $C(1)-C(10)-C(5)$ | 106.6 (1) |
| $C(1)-C(10)-C(9)$ | 115.6 (2) | $C(5)-C(10)-C(9)$ | 110.6 (2) |
| $C(4)-C(5)-C(11)$ | 107.5 (2) | $C(6)-C(5)-C(11)$ | 109.4 (2) |
| $C(10)-C(5)-C(11)$ | 107.1 (2) | $C(5)-C(6)-C(12)$ | 115.3 (2) |
| $C(7)-C(6)-C(12)$ | 110.4 (2) | $C(8)-C(9)-C(13)$ | 114.0 (2) |
| $C(10)-C(9)-C(13)$ | 113.6 (2) | $C(1)-C(10)-C(14)$ | 106.4 (2) |
| $C(5)-C(10)-C(14)$ | 108.1 (2) | $C(9)-C(10)-C(14)$ | 109.2 (2) |
| $N(1)-C(11)-C(5)$ | 177.2 (2) | $N(2)-C(14)-C(10)$ | 178.8 (2) |

Intermolecular distances correspond to van der Waals interactions. The nearest carbonyl group adjacent to $O(1)=C(1)$ is $O(2)=C(4)$ of a neighbouring

molecule such that $O(1)\cdots O(2)$ [$\frac{3}{2}-x, -\frac{1}{2}+y, z$] is 3.192 Å and $O(1)\cdots C(4)$ [$\frac{3}{2}-x, -\frac{1}{2}+y, z$] is 3.574 Å. The planes of the two carbonyls are not parallel. 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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