SHORT STRUCTURAL PAPERS

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1,4-Bis-(4′,4′-dimethyloxazolidine-*N*-oxyl)cyclohexane

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Abstract. Monoclinic, $P2_1/a$, $a=10\cdot539$ (11), $b=5\cdot662$ (6), $c=12\cdot766$ (13) Å, $\beta=99\cdot4$ (1), $C_{12}H_{24}N_2O_4$, $Z=2$, $D_{\text{meas}}=1\cdot23$, $D_{\text{calc}}=1\cdot25$ g cm^{-3}. The two *N*-oxyl groups in the molecule are *trans*-diequatorial with an intramolecular distance for the nitrogen atoms of 5·75 Å and for the oxygens of 7·00 Å. These distances are to be compared with the 6·14 (5) Å distance estimated from e.s.r. measurements (point dipole approximation).

Introduction. The title compound was prepared from cyclohexane-1,4-dione by the procedure of Keana, Keana & Beetham (1967). Crystals suitable for X-ray analysis were grown from methanol as orange hexagonal plates. The crystal used for the intensity measurements had dimensions $0\cdot2\times0\cdot4\times0\cdot6$ mm; it was the largest crystal grown in several attempts in different solvents. The crystals were examined by precession photographs; systematic extinctions ($0k0$, $k=2n+1$; $h0l$, $h=2n+1$) indicate the space group to be $P2_1/a$. A total of 1071 independent reflections were collected at room temperature for θ between 0 and 22° with a Hilger and Watts 4-circle automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation ($\lambda=0\cdot7107$ Å). The scan was 1·0°/100 s in θ and ω, with 50 s background counts at each end of the scan. The 525 reflections with $I>2\sigma(I)$ were used in the refinement of the structure. The phase problem was solved by direct methods for 102 reflections with $E>1\cdot5$. An E map computed from the set of highest consistency clearly showed the molecule. Initial atomic coordinates for the non-hydrogen atoms were obtained from the E map and refined by least-squares methods with isotropic thermal parameters to a conventional R of 0·172, $r=0\cdot112$.*

Refinement with anisotropic thermal parameters for the nonhydrogen atoms converged with $R=0\cdot147$, $r=0\cdot090$. A difference Fourier map at this point had its highest peaks at the expected hydrogen atom positions. Further refinement with inclusion of hydrogen atoms at idealized positions (tetrahedral) and with isotropic temperature factors converged at $R=0\cdot114$, $r=0\cdot064$. The final R value is large, and is only partially explained by the small size of the crystal and the consequent generally low intensities. However, for our purposes (comparison with e.s.r. results), it did not seem profitable to collect more data using longer scan times. Programs used in the solution and refinement were: *UMLSTQ* (Fourier synthesis and least squares) and *BADTEA* (distances, angles and errors) by L. W. Finger; *NORMA*, *REL* and *RELB* (direct methods) by R. E. Long (1965) as modified by J. Z. Gougoutas. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters are given in Table 1.†

Table 1. *Positional and thermal parameters*

Anisotropic temperature factors are of the form $T=\exp[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)]$.

Parameters are multiplied by 10^3.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	585 (1)	333 (2)	256 (1)	8 (1)	30 (5)	67 (8)	7 (2)	2 (1)	−4 (2)
O(2)	378 (1)	712 (2)	365 (1)	11 (1)	26 (4)	50 (8)	6 (2)	3 (1)	−1 (2)
N(1)	500 (1)	474 (2)	275 (1)	8 (2)	21 (5)	39 (9)	−2 (2)	1 (1)	0 (2)
C(1)	475 (1)	537 (3)	385 (1)	8 (2)	19 (6)	3 (1)	3 (3)	3 (1)	−2 (2)
C(2)	421 (1)	316 (3)	436 (1)	9 (2)	21 (6)	5 (1)	−2 (3)	1 (1)	−1 (2)
C(3)	600 (1)	630 (3)	449 (1)	5 (2)	36 (7)	3 (1)	−8 (3)	8 (9)	2 (2)
C(4)	313 (2)	712 (4)	265 (1)	17 (3)	90 (13)	6 (1)	26 (5)	−1 (2)	−4 (3)
C(5)	400 (2)	597 (3)	193 (1)	9 (2)	35 (7)	4 (1)	5 (3)	1 (1)	1 (3)
C(6)	475 (2)	768 (3)	133 (1)	10 (3)	42 (9)	7 (1)	−4 (4)	−1 (2)	8 (3)
C(7)	324 (1)	419 (3)	120 (1)	12 (2)	40 (8)	7 (1)	−7 (3)	−2 (1)	1 (3)

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* $r=\sum w(|F_o|^2-|F_c|^2)^2/\sum w|F_o|^4$, $R=\sum||F_o|-|F_c||/\sum|F_o|$. The numerator of r was the function minimized. The weights were $1/[\sigma(F^2)]^2$ where $\sigma(F^2)$ was calculated from $\sigma^2(I)=$ peak count + background count + $(0\cdot03I)^2$. The expectation value of R based on the estimated $\sigma(F)$ values was 0·072.

† A table of calculated and observed structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30201 (12 pp., 1 microfiche). Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. The introduction of the spin-labelling technique by McConnell and co-workers has stimulated interest in the synthesis and properties of molecules containing the *N*-oxyl functional group. For a recent general review of the physics and chemistry of spin-labels see McConnell & McFarlane (1971). Three general classes of nitroxides, the piperidine-*N*-oxyls, the pyrroline-*N*-oxyls and *N*-oxyl-oxazolidine derivatives of ketones, have been used as probes of biological systems. Of these classes, X-ray structural information is available for the first two (Lajzérowicz-Bonneteau, 1968; Berliner, 1970; Capiomont, 1972; Turley & Boer, 1972; Chion, Capiomont & Lajzérowicz, 1972). This report describes the structure determination of a dinitroxide member of the third class.

Bond distances and angles are shown in Fig. 1. The N–O distance of 1·25 Å is in reasonable agreement with the N–O distance in pyrroline *N*-oxyls of 1·27 Å (Turley & Boer, 1972; Chion, Capiomont & Lajzérowicz, 1972). A least-squares plane through N(1), O(2), C(1), C(5) and C(4) indicates a puckered ring. Deviations from the least-squares plane are shown in Fig. 1. This distortion is beyond experimental error [C(4) and O(2) are each more than five standard deviations out of the plane] and this is in contrast to the apparent planarity of pyrroline *N*-oxyls previously described. The intramolecular distances for the nitrogens and oxygens of the nitroxide fragments are 5·75 and 7·00 Å. E.s.r. measurements (Barnett & Gleason, unpublished work) using the point dipole approximation of Hirota & Weissman (1964) indicate that the average separation between the unpaired electrons in this molecule is 6·14 (5) Å.

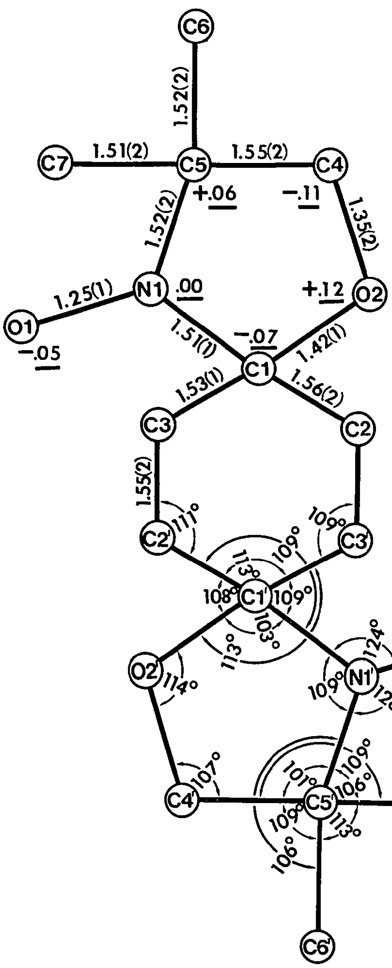

Fig. 1. Bond distances and angles. E.s.d. of angles is 1°. Deviations from least-squares plane through N(1), O(2), C(1), C(5) and C(4) are underlined.

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