Acta Cryst. (1977). B**33**, 2325–2326

cis-*N*-Methyl-*N'*-cyclohexyldiimide *N*-Oxide (I) and *cis*-*N*-Cyclohexyl-*N'*-methyldiimide *N*-Oxide (II)*

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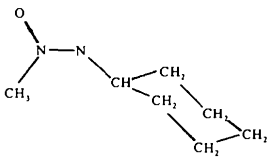
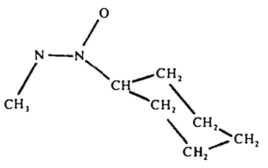
(*Received* 9 *December* 1976; *accepted* 1 *April* 1977)

Abstract. $C_7H_{14}N_2O$ (I): orthorhombic, *Pnma*, $Z = 4$, $a = 21{\cdot}940$ (7), $b = 6{\cdot}656$ (1), $c = 5{\cdot}549$ (2) Å, $D_o = 1{\cdot}14$, $D_c = 1{\cdot}16$ g cm^{-3}. $C_7H_{14}N_2O$ (II): orthorhombic, *Pnma*, $Z = 4$, $a = 20{\cdot}827$ (8), $b = 6{\cdot}924$ (5), $c = 5{\cdot}577$ (1) Å, $D_o = 1{\cdot}15$, $D_c = 1{\cdot}17$ g cm^{-3}. The diimide N=N distances are 1·262 and 1·253 Å in (I) and (II) respectively. There are no unusually short intermolecular distances.

Introduction. The molecular structures of these compounds differ in the placement of the azoxy O atom. In both molecules the methyl and cyclohexyl groups are *cis*. In compound I the azoxy O is bonded to the N with the methyl group; in compound II the azoxy O is bonded to the N with the cyclohexyl group.



(I)



(II)

These compounds are chemically related to the potent carcinogens cycasin and macrozamin found in certain cycad plants (Laquer & Spatz, 1968; Whiting, Spatz & Matsumoto, 1966). Neither compound was observed to form a liquid crystal, as has been observed for aromatic azoxy compounds such as *p*-azoxyanisole (Krigbaum, Chatani & Barber, 1970) and ethyl *p*-azoxybenzoate (Krigbaum & Barber, 1971).

Well formed crystals of (I) and (II) prepared by Taylor, Isaac & Clark (1976) were used. The lattice constants were determined by a least-squares fit to high-angle reflections observed with Cr $K\alpha$ radiation. A θ–2θ scan method was used, with a stationary background measurement preceding and following each scan. Several reflections were periodically monitored and indicated no decomposition of the crystals while exposed to X-rays. Lorentz and polarization corrections were made and errors estimated for each reflection; 761 independent reflections were measured for (I), and 927 for (II).†

The possible space groups were *Pnma* or $Pna2_1$. The statistical distribution of intensities indicated the choice of the centrosymmetric space group *Pnma*, as was confirmed by the final results of the structural analysis. The phase problems were solved using Sayre's method (Long, 1965). The refinements of the structures were carried out by anisotropic full-matrix structure-factor least squares (Busing, Martin & Levy, 1962). The scattering factors of Hanson, Herman, Lea & Skillman (1964) were used for C, N, and O atoms. The scattering factors of Stewart, Davidson & Simpson (1965) were used for H atoms; the H atoms were placed in tetrahedral calculated positions with a C—H distance of 1·04 Å and were assigned the same anisotropic temperature factors as the attached C atoms. Refinement of the 55 adjustable parameters for each structure was continued until the magnitudes of all

Table 1. *Final positional parameters* ($\times 10^4$) *for* (I) *and their standard deviations*

	x	*y*	*z*
N(1)	165 (2)	2500	4744 (9)
N(2)	738 (2)	2500	4554 (9)
O(3)	−81 (2)	2500	6822 (7)
C(4)	1010 (2)	2500	2155 (10)
C(5)	2139 (2)	2500	−630 (12)
C(6)	−270 (3)	2500	2762 (11)
C(7)	1405 (2)	4366 (6)	1947 (8)
C(8)	1762 (2)	4360 (6)	−406 (8)
H(9)	666	2500	869
H(10)	2371	2500	−2308
H(11)	2477	2500	723
H(12)	−723	2500	3420
H(13)	−218	3777	1681
H(14)	1464	4415	−1871
H(15)	2041	5631	−515
H(16)	1143	5670	2006
H(17)	1721	4451	3348

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* This work was supported by research grant GM16260 from the National Institutes of Health.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32597 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final positional parameters* ($\times 10^4$) *for* (II) *and their standard deviations*

	x	y	z
N(1)	147 (1)	2500	366 (5)
N(2)	−451 (1)	2500	117 (5)
O(3)	−687 (1)	2500	−1959 (4)
C(4)	−940 (1)	2500	2121 (6)
C(5)	−2256 (2)	2500	3844 (6)
C(6)	402 (2)	2500	2809 (8)
C(7)	−1342 (1)	4311 (4)	1950 (4)
C(8)	−1848 (1)	4303 (4)	3926 (5)
H(9)	−698	2500	3808
H(10)	−2576	2500	5275
H(11)	−2526	2500	2273
H(12)	900	2500	2747
H(13)	242	3719	3702
H(14)	−1572	4358	287
H(15)	−1051	5523	2139
H(16)	−1637	4352	5628
H(17)	−2156	5478	3806

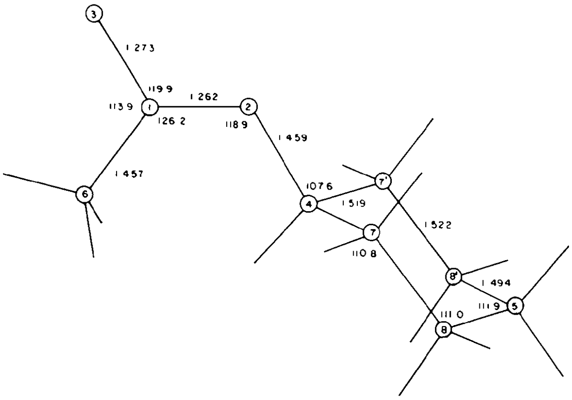

Fig. 1. Bond distances (Å) and bond angles (°) for (I). The estimated standard deviations are 0·006 Å and 0·4°.

shifts were less than 0·1σ. The final values of $R = [\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ were 0·086 for (I) and 0·080 for (II). Final difference Fourier maps were featureless. Tables 1 and 2 list the final positional parameters for the two structures. Figs. 1 and 2 show the observed bond distances and bond angles.

Discussion. The diimide N atoms and the three atoms bonded to them lie on mirror planes at $y = \frac{1}{4}$; therefore, this moiety is accurately planar. The *para* C atoms of the cyclohexyl groups also lie on these mirrors; C(7), C(8), C(7′), and C(8′) lie above and below the mirrors. The cyclohexyl groups show the normal chair conformation.

The structures clearly confirm that the azoxy O atom is bonded to only one N atom of the diimide group. Corresponding distances and angles in (I) and (II) are remarkably similar. However, the cyclohexyl–azoxy C–N bond in (II) (1·512 Å) is longer than the methyl–azoxy C–N bond in (I) (1·457 Å). The N–N–C angles at the trigonal N (126·2, 126·0°) increase to relieve steric strain between the cyclohexyl and methyl groups rather than the N–N–C angles at the digonal N (118·9, 117·6°).

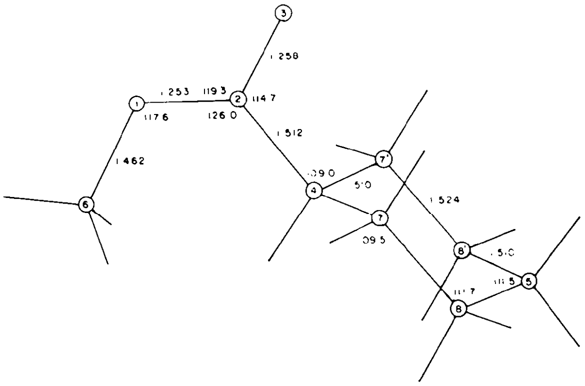

Fig. 2. Bond distances (Å) and bond angles (°) for (II). The estimated standard deviations are 0·006 Å and 0·4°.

The N–O distances (1·273, 1·258 Å) are close to the value reported for *p*-azoxyanisole (1·279 Å, Krigbaum, Chatani & Barber, 1970) and for ethyl *p*-azoxybenzoate (1·291 Å, Krigbaum & Barber, 1971). The diimide N=N distances (1·262, 1·253 Å) are slightly longer in (I) and (II) than in the aromatically substituted azoxy compounds mentioned above (1·218, 1·155 Å).

The thermal-motion ellipsoids were examined and appear quite normal. The molecular-packing arrangements show only normal van der Waals contacts and no unusually short intermolecular distances.

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