

Low order ZnS polytypes can be identified by any of the usual methods of polytype identification: for example the method described by Mardix, Alexander, Brafman & Steinberger (1967). This method consists in comparing the calculated intensity distributions of all possible polytypes with the experimental intensity distribution. It should be noted that the number of possible structures, the intensity distributions of which have to be calculated, can be reduced by using readily available preliminary information:

(a) The order of the polytype can easily be determined from X-ray oscillation photographs. Also, by observing systematic absences in these photographs it can be determined whether or not the polytype is rhombohedral (Verma & Krishna, 1966).

(b) Using the linear dependence of the birefringence on the percentage of hexagonality (Brafman & Steinberger, 1966) and the value 24×10^{-3} for the percentage of hexagonality of the hexagonal 2H structure, the number of Zhdanov numbers in the elementary stacking sequence can be determined by measuring the birefringence of the polytypic regions. The birefringence can almost always be measured when the specimens are platelets. In the case of needle-shaped specimens, most of which are hollow, the birefringence measurement is not feasible (Kiflawi, Mardix & Kalman, 1969).

(c) It is an experimental fact that polytypes found in ZnS crystals grown by sublimation do not have the number 1 in their Zhdanov sequences.

According to Verma & Krishna (Verma & Krishna, 1966), and also from our experience, there is no need for a quantitative determination of the intensities of reflexion spots. In no case was there any ambiguity in polytype

identification as a result of visual determination of the intensities. In all cases, on comparison of the observed intensity distribution of the polytype to be identified with the calculated intensities of all possible structures, only one calculated intensity distribution was found to fit. The calculated intensity distribution of all other possible structures differed considerably from that observed.

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The crystal structure of 2,6-dichloro-4-diazo-2,5-cyclohexadien-1-one. By C. TRAVIS PRESLEY and RONALD L. SASS, Department of Chemistry, William Marsh Rice University, Houston, Texas 77001, U.S.A.

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The crystal structure of 2,6-dichloro-4-diazo-2,5-cyclohexadien-1-one has been determined. Observed unit-cell constants are $a = 13.29$ (1), $b = 10.36$ (1), $c = 10.83$ (1) Å and $\beta = 103.07$ (05)°. The space group is $C_{2h}^5 - P2_1/c$ with 8 molecules per unit cell. Three-dimensional visual data were collected. The structure was refined by least squares to a final conventional R index of 10.5%. Even though the asymmetric unit contains two independent molecules, no evidence of a molecular complex was observed.

The structure of 2,6-dichloro-4-diazo-2,5-cyclohexadien-1-one, $C_6H_2N_2OCl_2$, has been determined by single-crystal X-ray diffraction methods. The compound was prepared by Dr James Perry of Rice University by diazotizing the corresponding dichloroaminophenol with acidic sodium nitrite at zero degrees centigrade. The single crystals used in this study were obtained by recrystallization from hot ethyl acetate as light orange needles. Shortly after the initial X-ray study had begun, it was observed that the crystals were affected by extended periods of exposure to X-rays, the color of the crystals gradually changing to a deep red. Changes were also observable on X-ray photographs as a broadening of the diffraction spots. For this reason, it was necessary to use several different crystals in the collection of the intensity record.

Equi-inclination Weissenberg photographs (Cu $K\alpha$, $\lambda = 1.5418$ Å) indicated the space group to be $C_{2h}^5 - P2_1/c$ (systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). The unit-cell dimensions are $a = 13.29$ (1), $b = 10.36$ (1), $c = 10.83$ (1) Å and $\beta = 103.07$ (05)°. The observed density, determined by flotation in a mixture of carbon tetrachloride and methylene chloride, is 1.72 g.cm⁻³; the calculated density, based on eight molecules per unit cell, is 1.71 g.cm⁻³. Since the space group has fourfold symmetry, the asymmetric unit contains two crystallographically independent molecules.

The intensity data for this compound were collected by multiple-film equi-inclination Weissenberg photography and were estimated visually by comparison with standard intensity exposures in the usual way. Data were collected

Table 1. Final atomic parameters

E.s.d.'s are given in parentheses. The temperature factors are of the form $\exp[-\frac{1}{4}(h^2a^*2B_{11} + k^2b^*2B_{22} + l^2c^*2B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
C(1)	-0.0090 (10)	0.1298 (16)	0.3968 (12)	1.94 (60)	2.30 (79)	2.19 (57)	-0.44 (73)	0.42 (50)	-0.48 (56)
C(2)	0.0822 (10)	0.1035 (16)	0.3468 (12)	1.69 (58)	3.46 (89)	2.22 (56)	-0.20 (76)	-0.25 (51)	-0.37 (61)
C(3)	0.0605 (10)	0.0254 (17)	0.2354 (13)	1.77 (58)	4.18 (98)	2.69 (60)	0.50 (80)	0.49 (52)	-0.98 (68)
C(4)	-0.0327 (10)	-0.0224 (16)	0.1745 (12)	1.78 (57)	3.31 (89)	2.41 (58)	0.35 (78)	0.47 (49)	-0.11 (62)
C(5)	-0.1175 (09)	0.0144 (16)	0.2296 (12)	1.07 (50)	3.23 (86)	2.18 (55)	-0.48 (71)	0.15 (44)	-0.43 (57)
C(6)	-0.1071 (09)	0.0879 (15)	0.3385 (12)	2.30 (64)	2.65 (79)	1.63 (52)	0.60 (73)	0.10 (50)	-0.08 (53)
O(7)	0.1676 (07)	0.1482 (13)	0.3963 (10)	1.75 (45)	6.41 (86)	4.08 (54)	-1.21 (60)	0.06 (42)	-1.86 (57)
N(8)	-0.2122 (09)	-0.0333 (14)	0.1690 (11)	2.08 (56)	4.83 (90)	2.66 (52)	0.29 (70)	0.61 (48)	-1.44 (59)
N(9)	-0.2880 (09)	-0.0697 (17)	0.1196 (13)	2.50 (61)	6.86 (116)	3.98 (68)	-0.61 (78)	0.39 (59)	-1.02 (72)
C(11)	0.4764 (10)	0.0734 (15)	0.3320 (12)	1.31 (52)	2.65 (83)	1.93 (52)	0.76 (68)	-0.23 (46)	0.34 (54)
C(12)	0.5842 (11)	0.1138 (15)	0.3725 (11)	2.12 (59)	3.11 (84)	1.54 (51)	1.02 (75)	0.47 (48)	0.50 (56)
C(13)	0.6063 (10)	0.1966 (16)	0.4823 (12)	1.84 (60)	3.25 (90)	1.99 (54)	0.38 (76)	0.02 (44)	-0.90 (59)
C(14)	0.5361 (10)	0.2320 (15)	0.5501 (12)	1.75 (57)	2.49 (81)	2.43 (57)	0.09 (73)	0.13 (50)	0.16 (58)
C(15)	0.4324 (10)	0.1853 (14)	0.5025 (11)	1.93 (58)	2.06 (75)	1.90 (52)	0.71 (70)	0.58 (48)	-0.17 (54)
C(16)	0.4029 (10)	0.1085 (15)	0.3937 (11)	1.45 (54)	2.67 (77)	1.66 (49)	-0.08 (69)	-0.61 (45)	-0.79 (53)
O(17)	0.6491 (07)	0.0783 (12)	0.3174 (09)	2.06 (44)	5.11 (73)	2.76 (44)	-0.91 (55)	0.36 (38)	-1.59 (47)
N(18)	0.3619 (08)	0.2120 (13)	0.5728 (10)	1.49 (46)	4.14 (81)	2.13 (46)	-0.45 (64)	-0.16 (42)	-0.37 (54)
N(19)	0.3033 (10)	0.2333 (16)	0.6278 (12)	2.92 (61)	6.14 (108)	2.92 (58)	0.39 (80)	0.87 (54)	-1.20 (66)
C(1)	0.0086 (03)	0.2176 (04)	0.5337 (03)	2.74 (17)	3.30 (21)	2.30 (14)	-0.32 (21)	0.15 (14)	-0.53 (16)
C(2)	0.7342 (03)	0.2439 (05)	0.5372 (04)	1.60 (15)	5.04 (30)	4.01 (18)	-1.26 (21)	0.27 (15)	-1.24 (19)
C(3)	0.1678 (03)	-0.0187 (05)	0.1742 (04)	1.81 (15)	6.07 (32)	3.23 (17)	0.30 (22)	0.93 (14)	-0.94 (19)
C(4)	0.4455 (03)	-0.0213 (04)	0.1997 (03)	2.63 (17)	4.14 (24)	1.90 (13)	-0.45 (21)	0.15 (13)	-0.83 (15)

about the *a* axis ($h=0-5$) and the *b* axis ($k=0-4$). Intensities were corrected for Lorentz, polarization, Tunell and spot size effects; no correction for extinction and absorption was attempted. The data were scaled by the method of Dickerson (1959). A total of 1419 reflections in the region of reciprocals space considered had detectable intensities.

A three-dimensional sharpened Patterson function was synthesized from the 1419 observed data. The coordinates of the four chlorine atoms were assigned from a consideration of the $v=0$ and $v=\frac{1}{2}$ Patterson sections. The coordinates of the remaining atoms were then located by fitting a postulated molecular model to the set of remaining Patterson peaks. The structure was refined by full-matrix least squares using the *ORFLS* program (Busing, Martin & Levy, 1962). The function minimized was $\sum w(F_o - F_c)^2$; unit weights were employed. Anisotropic temperature factors were used, but no attempt was made to account for hydrogen scattering. A final residual of $R=10.5\%$ was obtained. Final atomic parameters and estimated standard deviations are given in Table 1. A list of observed and calculated structure factors is available from the authors on request.

Bond lengths and angles calculated from the final atomic coordinates are listed in Table 2. The [010] projection of the unit cell is shown in Fig. 1. The C-Cl bond lengths are all within the range of values found in the literature. A tabulation of carbon-chlorine bond distance in twenty-six aromatic molecules is given by Palenik, Donohue & Trueblood (1968); these distances average to 1.737 ± 0.016 Å compared with an average distance of 1.730 Å for the molecules reported herein. The C(5)-N(8) and C(15)-N(18) distances of 1.374 and 1.362 Å are somewhat shorter than the corresponding bond distance observed in several diazonium salts, which range from 1.385 to 1.45 Å (Polynova, Bokii & Porai-Koshits, 1965). The N(8)-N(9) and N(18)-N(19) distances of 1.096 and 1.103 Å are essentially equal to those observed in these same diazonium salts. The possibility of quinoid character exists in this molecule. The C(2)-O(7) and C(12)-O(17) distances of 1.231 and 1.211 Å are very similar to the C-O distances of 1.222 Å observed in *p*-benzoquinone (Trotter, 1960) and of 1.195 Å observed in chloranil (Chu, Jeffrey & Sakurai, 1962). The average of the eight C-C distances corresponding to single bond distances in the quinoid formulation is 1.432 Å; a value appreciably shorter than that of 1.477 Å observed in *p*-benzoquinone. Similarly, the average of the four distances corresponding to the double bonds in benzoquinone is 1.363 Å, somewhat longer than the distance of 1.322 Å observed in *p*-benzoquinone.

Least-squares planes were fitted to both sets of ring carbon atoms; the results are given in Table 3. For the atoms used in determining the plane, the deviations are not significant. However, other atoms show significant deviations. In molecule I, the oxygen atom and the chlorine atoms are alternately above and below the plane; the diazo group is approximately coplanar with the ring. In molecule II, on the other hand, the oxygen and chlorine atoms are more nearly in the ring plane, but the diazo group shows a remarkable deviation. It seems likely that this deviation is due to packing forces in the crystal.

Although there are no abnormally short intermolecular distances, the crystal packing is such that the closest approach distances are those between the terminal diazino-nitrogen atoms and the oxygen atoms from the adjacent

Table 2. *Interatomic distances and angles*

Molecule I		Molecule II	
	Distance		Distance
C(1)–C(2)	1.461 (18) Å	C(11)–C(12)	1.462 (18) Å
C(2)–C(3)	1.426 (20)	C(12)–C(13)	1.442 (18)
C(3)–C(4)	1.358 (18)	C(13)–C(14)	1.362 (18)
C(4)–C(5)	1.440 (18)	C(14)–C(15)	1.442 (18)
C(5)–C(6)	1.384 (18)	C(15)–C(16)	1.402 (17)
C(6)–C(1)	1.384 (18)	C(16)–C(11)	1.353 (18)
C(2)–O(7)	1.231 (16)	C(12)–O(17)	1.211 (16)
C(5)–N(8)	1.374 (16)	C(15)–N(18)	1.362 (16)
N(8)–N(9)	1.096 (15)	N(18)–N(19)	1.103 (15)
C(1)–Cl(1)	1.709 (13)	C(11)–Cl(4)	1.707 (13)
C(3)–Cl(3)	1.764 (14)	C(13)–Cl(2)	1.740 (14)
	Angle		Angle
C(1)–C(2)–C(3)	113.1 (12)°	C(11)–C(12)–C(13)	114.9 (12)°
C(2)–C(3)–C(4)	127.3 (13)	C(12)–C(13)–C(14)	124.6 (13)
C(3)–C(4)–C(5)	114.6 (13)	C(13)–C(14)–C(15)	115.7 (12)
C(4)–C(5)–C(6)	124.2 (12)	C(14)–C(15)–C(16)	123.6 (12)
C(5)–C(6)–C(1)	117.6 (12)	C(15)–C(16)–C(11)	118.2 (12)
C(6)–C(1)–C(2)	123.2 (12)	C(16)–C(11)–C(12)	122.9 (12)
C(5)–N(8)–N(9)	178.9 (12)	C(15)–N(18)–N(19)	178.6 (13)
O(7)–C(2)–C(1)	121.9 (13)	O(17)–C(12)–C(11)	121.6 (13)
O(7)–C(2)–C(3)	125.0 (14)	O(17)–C(12)–C(13)	123.5 (13)
Cl(1)–C(1)–C(2)	117.3 (10)	Cl(4)–C(11)–C(12)	116.7 (10)
Cl(1)–C(1)–C(6)	119.5 (10)	Cl(4)–C(11)–C(16)	120.3 (10)
Cl(3)–C(3)–C(2)	116.0 (11)	Cl(2)–C(13)–C(12)	116.7 (10)
Cl(3)–C(3)–C(4)	116.7 (11)	Cl(2)–C(13)–C(14)	118.5 (10)

Table 3. *Deviations from the least-square planes through the molecules*

Plane I	Deviation	Plane II	Deviation
C(1)	0.016 Å*	C(11)	0.001 Å
C(2)	–0.013*	C(12)	0.014*
C(3)	–0.002*	C(13)	–0.017*
C(4)	0.015*	C(14)	0.006*
C(5)	–0.013*	C(15)	0.009*
C(6)	–0.003*	C(16)	–0.012*

Table 3 (cont.)

O(7)	–0.073	O(17)	0.059
N(8)	0.005	N(18)	0.120
N(9)	–0.002	N(19)	0.200
Cl(1)	0.070	Cl(2)	–0.043
Cl(3)	0.061	Cl(4)	–0.009

The equations of the planes are:

Plane I: $-0.398x + 8.575y - 5.839z = -1.183$

Plane II: $-1.075x + 8.437y - 5.865z = -1.839$

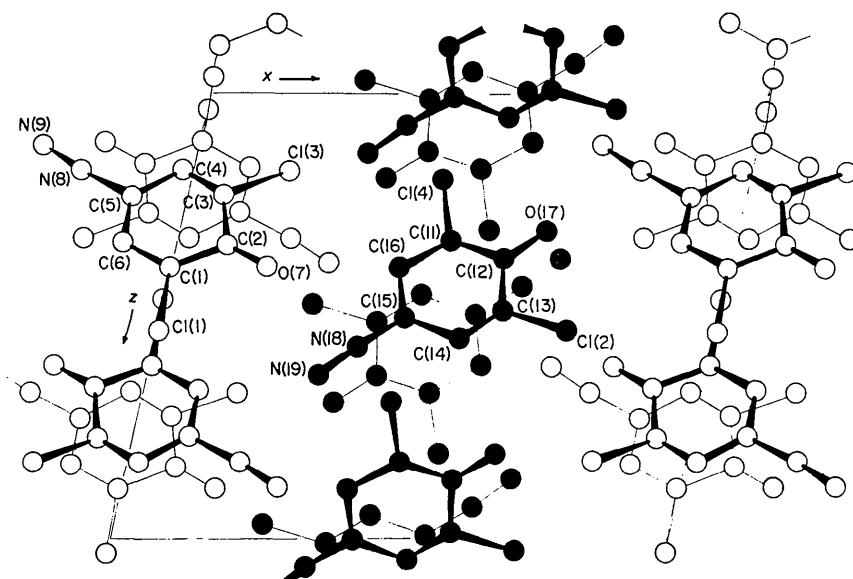


Fig. 1. The [010] projection of the unit cell. Molecule I is represented by open circles; molecule II by darkened circles.

molecules. These nearest-neighbor interactions are between non-symmetry related molecules forming parallel chains along the a axis of the crystal. The distance O(7)–N(19) is 2.875 Å and the distance O(17)–N(9'), where N(9') is related to N(9) by a unit translation along the a axis, is 2.905 Å. Both of these distances are approximately equal to the sum of the normally accepted van der Waals radii for nitrogen and oxygen atoms.

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Refinement and location of the hydrogen atoms in the nitroxide 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl.

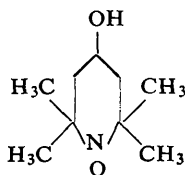
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The structure of 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl as determined by Lajzėrowicz-Bonneteau has been refined using data from a four-circle diffractometer. While the original work yielded a structure with an R value of 0.12 using isotropic least-squares refinement of the non-hydrogen atoms, the results of the current study have yielded (1) the positions and isotropic thermal parameters for all of the hydrogen atoms, (2) the anisotropic thermal parameters of the non-hydrogen atoms, and (3) a refinement of the entire structure to an R value of 0.055. The only major significant differences observed were (1) a large decrease in the C–N–C bond angle, and (2) a moderate decrease in the $\begin{matrix} \text{C} \\ \diagup \\ \text{N}-\text{O} \\ \diagdown \\ \text{C} \end{matrix}$ 'out of plane' angle to a value more consistent with expected configurations derived from anisotropic hyperfine interaction measurements.

Introduction

The structure of the nitroxide radical 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl was determined from photographic data by Lajzėrowicz-Bonneteau (1968) (hereafter referred to as L-B, 1968).



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The structure of this compound as reported here has been determined using diffractometer methods. The interest in this structure stems from its properties as a 'spin label' in structure-function studies of biological molecules (Hamilton & McConnell, 1968). In view of the unexpected value for the $\begin{matrix} \text{C} \\ \diagup \\ \text{N}-\text{O} \\ \diagdown \\ \text{C} \end{matrix}$ 'out of plane' angle of 21° as found by L-B (1968), it was decided to carry out a full refinement of the structure.

Experimental

The compound was prepared by the method of Brière, Lemaire & Rassat (1965), but was crystallized from hexane/chloroform, yielding crystals of similar morphology to other preparations (L-B, 1968).

Table 1. *Summary of refinement procedure*

The reported R values are determined using all reflections with no special treatment of weak reflections.

Parameters refined	Initial R	Final R	Number of cycles
x, y, z, B_{iso} non-hydrogen atoms		0.12 (L-B, 1968)	
x, y, z, B_{iso} non-hydrogen atoms	0.244	0.150	4
x, y, z, B_{H} non-hydrogen atoms	0.150	0.0934	3
As above, including hydrogen positions and B_{iso} values	0.0934	0.0551*	3

* Omitting the very strong 001, 020 and 110 reflections, $R=0.0471$.