

reveals puckering of the chains to different extents. Effectively, the molecule acquires an asymmetric configuration.

The protons of the two phenolic OH groups, which are *trans* axially directed, are involved in intramolecular hydrogen bonding with the nearest N atoms. The short O(1)—N(4) and O(2)—N(2) distances [2.75 (1) Å] and near linearity of the angles O(1)—H(1)···N(4) (147.5°) and O(2)—H(2)···N(2) (149.2°) indicate the fairly strong nature of these hydrogen bonds. No other intermolecular distances shorter than the sum of the van der Waals radii of two atoms could be located.

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## Structure of 2,6-Dihydroxy-2,6-dimethylheptan-4-one

BY RICHARD R. ROMERO, FRANCISCO CERVANTES-LEE AND LEIGH CHRISTOPHER PORTER\*

*Department of Chemistry, The University of Texas at El Paso, El Paso, TX 79968, USA*

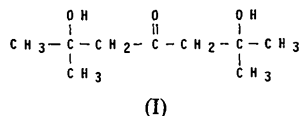
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**Abstract.** C<sub>9</sub>H<sub>18</sub>O<sub>3</sub>, *M<sub>r</sub>* = 174.2, monoclinic, *C2/c*, *a* = 10.496 (3), *b* = 17.305 (4), *c* = 7.500 (2) Å, β = 128.94 (2)°, *V* = 1059.6 (5) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.092 Mg m<sup>-3</sup>, λ(Mo *Kα*) = 0.71073 Å, μ = 0.075 mm<sup>-1</sup>, *F*(000) = 384, *T* = 298 K, *R* = 0.0449 and *wR* = 0.0507 for 88 variable parameters and 547 averaged reflections with *F* > 0σ(*F*). The asymmetric unit consists of one half of the molecule which possesses twofold (*C*<sub>2</sub>) point-group symmetry and resides on a special position. There are no unusual intermolecular contacts in the lattice and no evidence of either inter- or intramolecular hydrogen-bonding interactions.

**Introduction.** A number of azoxy compounds are known to be converted into *ortho*-hydroxyazo compounds upon exposure to light. This rearrangement is formally similar to a Wallach rearrangement, except that the O atom migrates to the *ortho* position on the distant aromatic ring (Spence, Taylor & Buchardt, 1970). Some, but not all, are also photochromic in the solid state. In the mechanism originally proposed for this light-initiated

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transformation, nucleophilic attack by the azoxy oxygen occurs, followed by a subsequent hydrogen-abstraction reaction (Badger & Buttery, 1955). Solution studies on sterically crowded azoxybenzenes, however, have established that a number of side products are formed in lesser amounts implicating diazonium intermediates in the process; as a result, other mechanisms have also been proposed (Goon, Murray, Schoch & Bunce, 1973; Bunce, 1974). In our investigations of the photochemistry of azoxybenzenes, both in solution and in the solid state, we have succeeded in isolating a most unusual and previously unreported product (I) whose structure we now report.



**Experimental.** The title compound was obtained following irradiation of a 0.01 *M* solution of 4-methoxyazoxybenzene in THF for several days. Pale-yellow single well-formed crystals were obtained by crystallization from a CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether solu-

\* To whom correspondence should be addressed.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ )

Equivalent isotropic  $U$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	$x$	$y$	$z$	$U_{eq}$
O(1)	0	2405 (1)	7500	68 (2)
O(2)	302 (2)	746 (1)	10950 (3)	52 (1)
C(1)	0	1702 (2)	7500	43 (3)
C(2)	1527 (3)	1263 (1)	9345 (4)	42 (2)
C(3)	1737 (2)	1138 (1)	11534 (4)	45 (2)
C(4)	1850 (4)	1898 (1)	12653 (6)	66 (2)
C(5)	3243 (3)	641 (2)	13184 (6)	71 (2)

Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

C(1)—C(2)	1.507 (2)	C(3)—C(5)	1.520 (3)
C(2)—C(3)	1.528 (5)	O(1)—C(1)	1.216 (3)
C(3)—C(4)	1.525 (4)	O(2)—C(3)	1.446 (3)
O(1)—C(1)—C(2)	120.3 (1)	C(2)—C(3)—C(4)	112.2 (2)
C(2)—C(1)—C(2a)	119.5 (2)	O(2)—C(3)—C(5)	109.5 (2)
C(1)—C(2)—C(3)	114.2 (2)	C(2)—C(3)—C(5)	109.2 (3)
O(2)—C(3)—C(2)	108.8 (2)	C(4)—C(3)—C(5)	111.0 (2)
O(2)—C(3)—C(4)	106.1 (3)		

tion following a chromatographic separation using 2-propanol. A small regularly shaped crystal of approximate dimensions  $0.4 \times 0.6 \times 0.2$  mm was selected and mounted on the end of a glass fiber in a random orientation. Monoclinic symmetry was suggested on the basis of the interaxial angles and confirmed by axial rotation photographs. Refined cell parameters were obtained from the setting angles of 25 reflections with  $25 < 2\theta < 35^\circ$ . Data collection was carried out using a Siemens  $R3m/V$  diffractometer and graphite-monochromated  $\text{Mo } K\alpha$  radiation using the  $\omega$ -scanning technique in bisecting geometry. Scan rate variable,  $3\text{--}15^\circ \text{ min}^{-1}$ ; scan range,  $1.2^\circ$  in  $\omega$ . Intensities were measured for a total of 609 reflections ( $-10 < h < 8$ ,  $0 < k < 18$ ,  $0 < l < 7$ ) with  $3.5 \leq 2\theta \leq 45^\circ$  and averaged to give 547 unique reflections ( $R_{int} = 0.0132$ ) with  $(\sin\theta/\lambda_{max}) = 0.582 \text{ \AA}^{-1}$ . Three standards (282, 220, 171) measured every 50 data showed no significant variation over the period of data collection. The data were corrected for Lorentz and polarization effects, but not absorption. Intensity statistics favored a centrosymmetric cell and assignment to the  $C2/c$  space group was based on an examination of the systematically absent reflections ( $hkl$ :  $h + k = 2n + 1$ ;  $h0l$ :  $l = 2n + 1$ ). Structure solution and refinement was performed using the *SHELXTL-Plus* collection of crystallographic software (Sheldrick, 1986). Coordinates of most of the atoms were obtained using direct methods; remaining atoms were located on difference Fourier maps. All non-H atoms were refined anisotropically using scattering factors, including terms for anomalous dispersion, taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). H atoms were refined with fixed

isotropic  $U = 0.080 \text{ \AA}^2$ . Refinement based on  $F$  used weights of the form  $w^{-1} = [\sigma^2(F) + 0.0008(F^2)]$ . Convergence to conventional  $R$  values of  $R = 0.0449$  and  $wR = 0.0507$  with a goodness of fit of 1.30 was obtained using 88 variable parameters and 547 observed reflections with  $F > 0\sigma(F)$ . A correction for extinction of the form  $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$  with  $\chi = 0.0036$  (9) was used. For the final cycle, maximum  $\Delta/\sigma = 0.048$  with minimum and maximum residual electron densities of  $-0.10$  and  $0.28 \text{ e \AA}^{-3}$ , respectively. Atomic positional parameters and equivalent isotropic thermal parameters for all non-H atoms are presented in Table 1.† Bond distances and angles are summarized in Table 2.

**Discussion.** The structure of this compound possesses twofold ( $C_2$ ) point-group symmetry and the molecule lies on a twofold axis of rotation which passes through atoms C(1) and O(1). There are no unusually close intermolecular contacts in the lattice and hydrogen-bonding interactions are noticeably absent. A perspective drawing of the structure illustrating the atomic numbering scheme is given in Fig. 1; in Fig. 2 a stereoview packing diagram is presented.

The framework of this structure consists of a seven-atom carbon chain which is substituted at the 2, 5 and 7 positions. C—C bond lengths vary from 1.507 (2) [C(1)—C(2)] to 1.528 (5)  $\text{\AA}$  [C(2)—C(3)],

† Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54972 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0569]

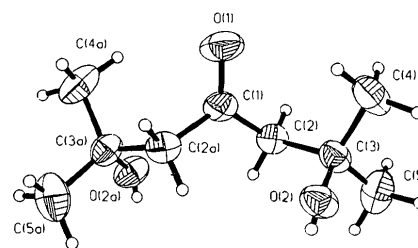


Fig. 1. A perspective view of the structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level.

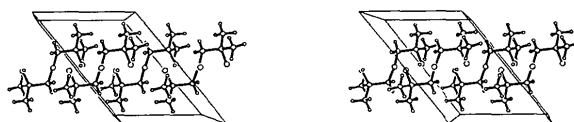


Fig. 2. A stereoview packing diagram projected down the crystallographic  $b$  axis.

and are all within the range of that expected for a  $\sigma$ -bonded carbon framework. There are two types of C—O bonds in this structure. C(1) possesses a trigonal-planar geometry and forms a double bond to O(1) measuring 1.216 (3) Å. As a consequence of the crystallographically imposed symmetry C(1) is perfectly coplanar with the three atoms to which it is attached. Bonds to the hydroxyl groups by C(3) and its symmetry-related equivalent, C(3a), measure 1.446 (3) Å.

This structure constitutes the first example of this type of product to be identified in photochemical studies of the azoxybenzenes. Although it was obtained in fairly good yield as the sole product along with unreacted 4-methoxyazoxybenzene starting material, at this time its origin remains obscure and we are at a loss to propose a reasonable mechanism based on what is currently known regarding the photochemistry of azoxy compounds. It is similar in some respects to diacetone alcohol

which has been isolated following irradiation of neat acetone (Przybytek, Singh & Kagan, 1969).

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## Structure of 5-Chloro-2-methylthio-3*H*-indol-3-one 3-Oxime *O*-Methyl Ether

BY ROY L. BEDDOES AND TIMOTHY KEARNEY

*Chemistry Department, University of Manchester, Manchester M13 9PL, England*

ARTHUR JACKSON

*Fine Organics Ltd, Seal Sands, Middlesbrough, Cleveland TS2 1UB, England*

AND JOHN A. JOULE\*

*Chemistry Department, University of Manchester, Manchester M13 9PL, England*

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**Abstract.** C<sub>10</sub>H<sub>9</sub>ClN<sub>2</sub>OS,  $M_r = 240.71$ , monoclinic,  $C2/c$ ,  $a = 23.671$  (6),  $b = 5.480$  (1),  $c = 20.644$  (8) Å,  $\beta = 123.82$  (2)°,  $V = 2225$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.437$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 46.12$  cm<sup>-1</sup>,  $F(000) = 992$ ,  $T = 296$  K,  $R = 0.053$  for 974 observed [ $I/\sigma(I) \geq 3$ ] reflexions. All skeletal atoms in the title oxime ether lie in one plane, including both methyl C atoms, with a mean deviation from the plane of only 0.006 Å. The *S*-methyl group is oriented away from the oxime unit which has *E* geometry. The structure of the oxime ether, along with a comparison of its UV/VIS absorption spectrum with that of the corresponding oxime and

with other 2-methylthio-3*H*-indol-3-one 3-oximes, demonstrates that the tautomeric equilibrium between 2-methylthio-3*H*-indol-3-one 3-oxime and 2-methylthio-3-nitrosoindole lies on the side of the former.

**Introduction.** We have shown (Kearney, Jackson & Joule, 1992) that treatment of 1-(*N*-arylamino)-1-methylthio-2-nitroethenes with trifluoromethanesulfonic acid effects a cyclization to indole derivatives. The products were shown to have the constitution of 2-methylthio-3*H*-indol-3-one 3-oximes, (1), though for such compounds there is the possibility of their existing in the alternative nitroso form (2), or in an alternative geometrical form, (3)

\* Author to whom correspondence should be addressed.