consistent with the CD assignment of the 2*R*,3*R* configuration to thujaplicatin methyl ether isolated from *Thuja standishii* (Gord.) Carr. (Nishibe, Hisada & Inagaki, 1974). The overall molecular conformation is best described in terms of the principal torsion angles (Table 3). Bond lengths and valence angles in the lactone ring are similar to those reported elsewhere (Conde, Moreno & Márquez, 1980). The ring displays a twist conformation. Atoms O(1), C(1), C(2) and O(5) are coplanar [max. deviation from the least-squares plane 0·0004 Å] while atoms C(3) and C(4) are respectively 0·24 and 0·20 Å above and below the plane as viewed in Fig. 1 (uncertainties in the atomic positions at the 5% level average 0·01 Å). A *trans* relationship between the substituents at C(2) and C(3) is evident from the torsion angle C(6)—C(2)—C(3)—C(15), the deviation from 120° being due to the ring pucker. Mean-plane calculations show that the hydroxydimethoxybenzyl moiety has symmetry approximating C_{2v}. The carbonyl O atom and the two phenolic O atoms participate in two crystallographically distinct hydrogen bonds: C(1)=O(1)···H($10^{\rm i}$)—O($10^{\rm i}$) with O···O 2·847 (3), O···H 1·853 (3) Å, and O(10)···H($19^{\rm i}$)—O($19^{\rm i}$) with O···O 2·854 (3), O···H 1·860 (2)Å [(i) = $1-x$, $\frac{1}{2}+y$, $1-z$]. Each molecule is thus linked to 2_1-related molecules by four hydrogen bonds, atom O(10) acting as both donor and acceptor.

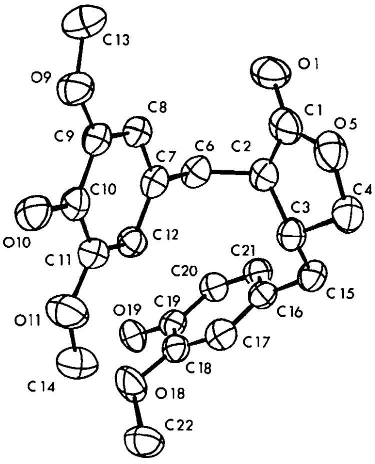

Fig. 1. *ORTEP* plot (Johnson, 1971) of the title molecule. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

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Structure of 1*H*-Azepine-2,5-dione 5-(*O*-Methyloxime), $C_7H_8N_2O_2$

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Abstract. $M_r = 152\cdot15$, triclinic, $P\bar{1}$, $a = 3\cdot877$ (2), $b = 9\cdot522$ (2), $c = 10\cdot674$ (2) Å, $\alpha = 107\cdot99$ (2), $\beta = 97\cdot66$ (3), $\gamma = 98\cdot50$ (3)°, $V = 363\cdot9$ Å^3, $Z = 2$, $D_x = 1\cdot388$ Mg m^{-3}, Mo $K\alpha$ ($\lambda\alpha_1 = 0\cdot70926$ Å), $\mu = 0\cdot0975$ mm^{-1}, $F(000) = 160$, $T \sim 293$ K, $R = 0\cdot030$, 825 unique observed reflections. Compound synthesized in this laboratory. The seven-membered ring is virtually planar, although the bond lengths indicate little

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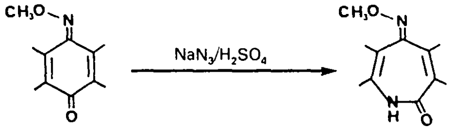
π delocalization. The methyloxime O is *syn* to the ring N. The molecules in the crystal form dimers linked *via* N—H···O hydrogen bonds.

Introduction. Reactions of 1,4-benzoquinone 4-(*O*-methyloximes) with hydrazoic acid in concentrated sulfuric acid (Schmidt reaction conditions) yield novel ring-expanded products, 1*H*-azepine-2,5-dione 5-(*O*-methyloximes) (Wilbur, 1978). The title compound is one of a series of these seven-membered-ring compounds that was synthesized *via* the reaction below.



The structure of this compound was investigated to determine the regiochemistry of the methyloxime O with respect to the ring N. This orientation was important to know because the structural assignments for the new compounds of this series were made by NMR correlations and an unambiguous assignment of which methyloxime geometrical isomer the correlations fit was needed. Additionally, we were interested in the theoretical prospect that these compounds might exhibit some π-electron delocalization. The title compound seemed the compound of choice to investigate for aromaticity as it has no ring substituents to twist the molecule out of planarity by steric interactions.

Experimental. Yellow, needle-like crystals grown from a chloroform/hexane solution. Crystal: approximate dimensions 0·6 × 0·3 × 0·2 mm. CAD-4 diffractometer. Graphite-monochromated Mo $K\alpha$ radiation. Unit cell: 25 reflections, $20 < 2\theta \leq 50°$. No absorption corrections. $\sin\theta/\lambda_{\max} = 0{\cdot}538$ Å^{-1}. Index range: $0 \leq h \leq 4$, $-10 \leq k \leq 9$, $-10 \leq l \leq 11$. Standard reflections $\bar{2}55$ and $\bar{1}4\bar{3}$: 1·4% variation. 1261 reflections measured, 948 unique, 825 observed $[I > 2\sigma(I)]$, $R_{\rm int} = 0{\cdot}0088$. Structure solved by *MULTAN* (Germain, Main & Woolfson, 1971). Least-squares refinement minimized $\sum w(\Delta F)^2$. H atoms located from difference Fourier and refined by least squares. Scale factor, isotropic extinction parameter, positional parameters, anisotropic thermal parameters for heavy atoms and isotropic thermal parameters for H refined. $R = 0{\cdot}030$, $R_w = 0{\cdot}037$, S (goodness-of-fit) = 3·23. Weights calculated as in Cromer & Larson (1977). $(\Delta\zeta_i/\sigma_i)_{\max} = 0{\cdot}0033$. Final ΔF Fourier synthesis, $-0{\cdot}09 \leq \rho \leq 0{\cdot}16$ e Å^{-3}. Isotropic, type 1 Gaussian half-width extinction parameter (Larson, 1969) = 1·7 (2)° × 10^{-5}. Scattering factors f, f' and f'' from *International Tables for X-ray Crystallography* (1974). Calculations on CDC-7600 using the Los Alamos Crystal Structure System developed primarily by A. C. Larson.*

Discussion. The final least-squares structural parameters are given in Table 1 and bond distances and angles are shown in Figs. 1(*a*) and 1(*b*), respectively. The molecules in the crystal are linked by strong, nearly linear [177·0 (6)°] N—H···O hydrogen bonds of 2·860 (2) Å to form planar dimers. These dimers, shown in Fig. 2, are tilted about 13° from the *bc* plane of the unit cell. There are no unusual interatomic distances.

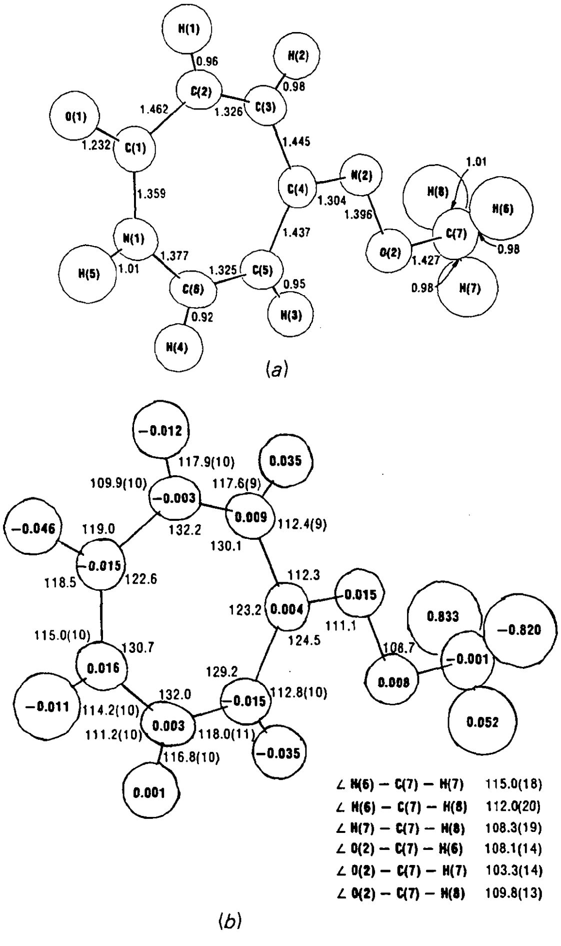


Fig. 1. (*a*) Bond distances (Å). Standard deviations for all heavy-atom bonds are 0·002 Å except for C(1)—C(2) which is 0·003 Å. Standard deviations for bonds to H are 0·02 Å except C(7)—H(7) and C(7)—H(8) which are 0·03 Å. (*b*) Bond angles (°). Atom nomenclature as in Fig. 1(*a*). Values in circles are the distances from the least-squares plane of the seven ring atoms. Standard deviations of the angles are 0·2° except where indicated.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38871 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final least-squares structural parameters*

Isotropic thermal parameters are given for H atoms. Equivalent isotropic thermal parameters are given for the other atoms; $B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}/B_{iso}(Å^2)
C(1)	0·8795 (4)	0·1378 (2)	0·1761 (2)	3·55 (8)
C(2)	0·8077 (5)	0·2294 (2)	0·3039 (2)	3·77 (9)
C(3)	0·7253 (5)	0·3645 (2)	0·3436 (2)	3·53 (8)
C(4)	0·6817 (4)	0·4685 (2)	0·2714 (2)	3·15 (8)
C(5)	0·7239 (5)	0·4376 (2)	0·1344 (2)	3·67 (9)
C(6)	0·7973 (5)	0·3153 (2)	0·0508 (2)	3·94 (10)
C(7)	0·4782 (7)	0·8240 (2)	0·3582 (2)	5·06 (12)
N(1)	0·8624 (4)	0·1829 (1)	0·0667 (1)	3·81 (7)
N(2)	0·6008 (3)	0·5920 (1)	0·3448 (1)	3·76 (7)
O(1)	0·9566 (4)	0·0143 (1)	0·1664 (1)	4·94 (7)
O(2)	0·5605 (3)	0·6903 (1)	0·2727 (1)	4·65 (7)
H(1)	0·829 (4)	0·177 (2)	0·368 (2)	4·6 (4)
H(2)	0·683 (4)	0·403 (2)	0·435 (2)	4·2 (4)
H(3)	0·691 (4)	0·518 (2)	0·102 (2)	4·2 (4)
H(4)	0·811 (4)	0·315 (2)	−0·035 (2)	4·5 (4)
H(5)	0·921 (5)	0·111 (2)	−0·015 (2)	6·2 (5)
H(6)	0·678 (6)	0·871 (2)	0·435 (3)	8·5 (7)
H(7)	0·440 (6)	0·883 (3)	0·299 (2)	8·1 (6)
H(8)	0·247 (7)	0·798 (2)	0·388 (3)	9·5 (7)

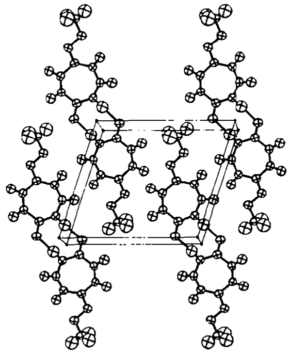

Fig. 2. *ORTEP* (Johnson, 1976) drawing of the structure. Ellipsoids are shown at 50% probability.

The molecular structure of the title compound, Fig. 1(*a*), establishes that the methyloxime is *syn* to the inserted ring N atom. The *syn* regiochemistry had previously been tentatively assigned from NMR correlations with several other azepine-2,5-dione 5-(*O*-methyloximes). This structure can now be used as a basis for NMR structure assignments of new compounds in this series. The *syn* regiochemistry is also interesting with respect to the reaction mechanism. Schmidt reaction products are generally considered to be controlled by steric hindrance about the reacting carbonyl group (Smith, 1963). Clearly, the reacting carbonyl on the starting material [1,4-benzoquinone 4-(*O*-methyloxime)] is sterically symmetric and a mixture of two geometrical isomers would be expected if only the steric hindrance were involved. The fact that only the *syn* isomer is obtained suggests that either the methyloxime has an electronic influence on the direction of N insertion (vinyl carbon migration) or the *syn* isomer is thermodynamically favored and the *anti* isomer isomerizes under the reaction conditions.

The very small deviations from planarity, Fig. 1(*b*), are similar to those reported for the bicyclic benz[*f*]azepine ring (±0·04 Å) (Denne & Mackay, 1972) and the tricyclic dioxodibenz[*b,f*]azepine (±0·20 Å) (Denne & Mackay, 1970). Despite the planarity, the bond lengths shown in Fig. 1(*a*) indicate that there is little, if any, full ring π-electron delocalization. This finding is consistent with other studies which have explored the aromaticity of similar compounds by spectroscopic methods (Rees, 1959; Moriconi & Maniscalo, 1972) or by types of reactions that they will undergo (Hughes, Leward & Rees, 1974).

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