

C4—C23	1.555 (10)	C14—C26	1.555 (12)	Closse, A., Mauli, R. & Sigg, H. P. (1966). <i>Helv. Chim. Acta</i> , 49 , 204–208.
C9—C8	1.551 (8)	C18—C17	1.566 (8)	Courtney, J. L. & Shannon, J. S. (1963). <i>Tetrahedron Lett.</i> pp. 13–20.
C9—C11	1.563 (9)	C18—C19	1.562 (9)	Declercq, J.-P., Puyvelde, L. V., Kimpe, N. D., Nagy, M., Verhegge, G. & Vierman, R. D. (1991). <i>Acta Cryst.</i> C47 , 209–211.
C9—C25	1.554 (11)	C17—C16	1.533 (10)	Johnson, C. K. (1965). <i>ORTEP</i> . Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
C8—C7	1.478 (10)	C17—C22	1.540 (13)	Kamano, Y., Pettit, G. R., Inoue, M., Tozawa, M. & Komeichi, J. (1977). <i>J. Chem. Res. (M)</i> , pp. 840–845.
C8—C14	1.556 (7)	C17—C28	1.546 (10)	Marumo, S., Sasaki, K. & Suzuki, S. (1964). <i>J. Am. Chem. Soc.</i> 86 , 4507–4508.
C16—C15	1.507 (8)	C20—C29	1.514 (14)	Merrien, A., Meunier, B., Pascard, C. & Polonsky, J. (1981). <i>Tetrahedron</i> , 37 , 2303–2306.
C19—C20	1.557 (13)	C20—C30	1.523 (11)	Mo, F., Winther, S. & Scrimgeour, S. N. (1989). <i>Acta Cryst.</i> B45 , 261–270.
C20—C21	1.492 (12)	C21—C22	1.512 (12)	Read, G. & Vining, L. C. (1963). <i>Chem. Ind. (London)</i> , pp. 1239–1244.
C1—C2—C3	111.3 (5)	C12—C13—C27	107.5 (4)	Sengupta, P., Chakraborty, A. K., Duffield, A. M., Durham, L. J. & Djerass, C. (1968). <i>Tetrahedron</i> , 24 , 1205–1213.
C1—C10—C9	112.6 (4)	C12—C13—C18	109.6 (5)	Shannon, J. S., McDonald, C. G. & Courtney, J. L. (1963). <i>Tetrahedron Lett.</i> pp. 173–179.
C1—C10—C5	110.3 (4)	C12—C13—C14	106.7 (5)	Sheldrick, G. M. (1976). <i>SHELX76. Program for Crystal Structure Determination</i> . Univ. of Cambridge, England.
C2—C1—C10	112.1 (4)	C18—C13—C27	113.3 (5)	Sheldrick, G. M. (1985). <i>SHELXS86. Program for the Solution of Crystal Structures</i> . Univ. of Göttingen, Germany.
C2—C3—C4	111.3 (5)	C14—C13—C27	108.5 (5)	
C5—C10—C9	119.8 (4)	C14—C13—C18	110.9 (4)	
C6—C5—C24	110.8 (5)	C8—C14—C13	110.7 (4)	
C4—C5—C24	111.5 (4)	C13—C14—C26	112.3 (5)	
C4—C5—C6	106.6 (5)	C13—C14—C15	107.3 (5)	
C5—C4—C23	114.7 (5)	C8—C14—C26	106.0 (5)	
C5—C4—C3	112.3 (6)	C8—C14—C15	112.8 (5)	
C3—C4—C23	109.4 (5)	C15—C14—C26	107.8 (5)	
C7—C8—O	59.0 (4)	C13—C18—C19	116.4 (5)	
C7—C8—C14	118.4 (5)	C13—C18—C17	117.8 (5)	
C8—C7—O	59.0 (4)	C17—C18—C19	110.3 (5)	
C8—C7—C6	124.0 (5)	C18—C17—C28	108.6 (6)	
C6—C7—O	116.9 (5)	C18—C17—C22	110.9 (5)	
C5—C6—C7	117.8 (6)	C18—C17—C16	112.9 (5)	
C9—C11—C12	117.1 (5)	C22—C17—C28	108.1 (6)	
C8—C9—C25	109.3 (5)	C16—C17—C28	107.4 (5)	
C8—C9—C11	110.4 (5)	C16—C17—C22	108.7 (6)	
C9—C8—O	113.0 (5)	C17—C16—C15	117.6 (5)	
C9—C8—C14	120.5 (5)	C14—C15—C16	112.4 (6)	
C9—C8—C7	118.3 (5)	C18—C19—C20	122.1 (6)	
C10—C5—C24	113.4 (5)	C19—C20—C30	105.7 (8)	
C10—C5—C6	106.1 (4)	C19—C20—C29	113.9 (6)	
C10—C5—C4	108.1 (4)	C19—C20—C21	109.0 (7)	
C10—C9—C25	111.5 (5)	C29—C20—C30	107.3 (7)	
C10—C9—C11	106.1 (5)	C21—C20—C30	110.1 (6)	
C10—C9—C8	111.2 (5)	C21—C20—C29	110.7 (8)	
C11—C9—C25	108.2 (5)	C20—C21—C22	115.2 (7)	
C14—C8—O	110.1 (4)	C17—C22—C21	113.1 (7)	
C11—C12—C13	112.6 (5)	C8—O—C7	61.4 (4)	

The structure was solved with *SHELXS86* (Sheldrick, 1985) using 282 *E* values ($E > 1.20$) which revealed all the 31 non-H atoms. The structure was refined by least-squares methods using *SHELX76* (Sheldrick, 1976). All 50 H atoms were located from a difference Fourier map and positioned with ideal geometry and held fixed for the final refinement of the 31 heavy atoms with anisotropic displacement parameters which led to a final *R* index ($(\sum ||F_o| - |F_c|| / \sum |F_o|)$) of 0.064.

The authors are thankful to CSIR Government of India for financial help.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data, torsion angles, intermolecular contacts less than 3.60 Å and ring-puckering coordinates have been deposited with the IUCr (Reference: AL1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Piperidine Nitroxide Radicals with Heterocyclic Ring Substituents. 4-Hydroxy-2,2,6,6-tetramethyl-4-(2-pyridylmethyl 1-oxide)piperidine 1-Oxide

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Abstract

In the title compound, $C_{15}H_{23}N_2O_3$, an intramolecular hydrogen bond between the hydroxyl group and the O atom of the 2-pyridylmethyl 1-oxide substituent results in a seven-membered ring which shows a twist-chair conformation.

Comment

A perspective view of the molecule showing the atom-numbering scheme and the intramolecular hydrogen bond is given in Fig. 1.

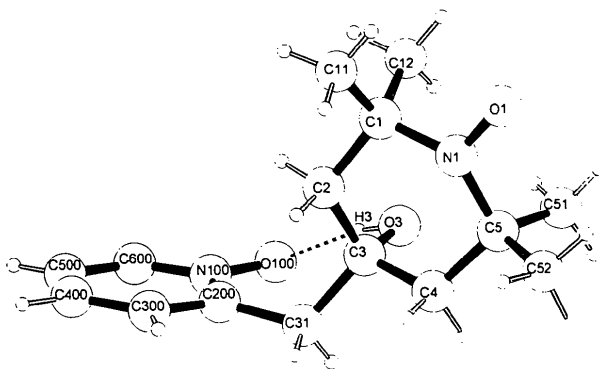
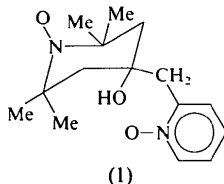


Fig. 1. Atom-numbering scheme and the intramolecular hydrogen bond.

The molecule of the title compound (1) consists of 2-methylpyridyl 1-oxide attached equatorially to the 2,2,6,6-tetramethylpiperidine moiety in position 4. The puckering amplitudes of the piperidine ring describe a slightly distorted chair. The ring is distorted from a pure chair in the direction of a half boat and hence is flattened at the N(1) apex [$\varphi_2 = 0.63(78) \text{ \AA}$, $Q_2 = 0.159(2) \text{ \AA}$, $Q_3 = -0.451(2) \text{ \AA}$, $\theta_2 = 160.6(2)^\circ$, $Q_T = 0.479(2) \text{ \AA}$]. The O atom of the nitroso group is in an equatorial position whereas the hydroxyl group is oriented axially. The pyridine ring is nearly planar, the O(100) atom deviating by $0.052(1) \text{ \AA}$ from this plane.



The crystal contains well ordered molecules of 4-hydroxy-2,2,6,6-tetramethyl-4-(2-pyridylmethyl 1-oxide)piperidine 1-oxide in the form also observed in crystals of 4-hydroxy-2,2,6,6-tetramethyl-4-(2-pyridylmethyl)piperidine 1-oxide (Olszak, Grabowski & Gwoździński, 1993). The bond lengths and angles are in good agreement (within 0.02 \AA and 5.5°) with those observed in the cited compound. The largest deviations in the bond lengths are observed around the N(100) atom and are caused by the introduction of the O atom O(100) to the pyridine ring (1-oxide group). The conformation of the piperidine rings and the configuration around the C(3) atoms are similar in both compounds.

In the previous paper (Olszak *et al.*, 1993) we suggested that an intramolecular bond had occurred, forming a six-membered ring between the N atom of the pyridine ring and the hydroxyl group of the piperidine ring in position 4, but instead an intramolecular hydrogen bond was found. The introduction of an O atom to the

pyridine ring (1-oxide group) gave rise to the 'expected' intramolecular hydrogen bond which, however, forms a seven-membered ring. Examination of the puckering parameters indicates a twist-chair conformation of the ring [$\varphi_2 = 44(1)^\circ$, $\varphi_3 = -71(1)^\circ$, $Q_2 = 0.503(8) \text{ \AA}$, $Q_3 = 0.420(11) \text{ \AA}$, $\theta_2 = 50(1)^\circ$, $Q_T = 0.656(2) \text{ \AA}$].

Experimental

Crystals were obtained by slow evaporation from ethanol solution at room temperature.

Crystal data

C₁₅H₂₃N₂O₃
M_r = 279.4
 Triclinic
*P*1
a = 6.400 (1) \AA
b = 10.767 (1) \AA
c = 11.203 (2) \AA
 α = 91.62 (1) $^\circ$
 β = 91.34 (2) $^\circ$
 γ = 102.2 (2) $^\circ$
V = 753.9 (2) \AA^3
Z = 2

D_x = 1.231 (1) Mg m^{-3}
 Cu *K* α radiation
 λ = 1.54178 \AA
 Cell parameters from 25 reflections
 θ = 30–58 $^\circ$
 μ = 0.6602 mm^{-1}
 Room temperature
 Block
 0.3 \times 0.2 \times 0.2 mm
 Orange

Data collection

Kuma KM-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 none
 3296 measured reflections
 2993 independent reflections
 2592 observed reflections
 $[I > 3\sigma(I)]$
R_{int} = 0.04

θ_{max} = 60 $^\circ$
h = -7 \rightarrow 7
k = -13 \rightarrow 13
l = 0 \rightarrow 14
 3 standard reflections monitored every 100 reflections
 intensity variation: <1%

Refinement

Refinement on *F*
R = 0.045
wR = 0.043
S = 0.38
 2592 reflections
 273 parameters
 H-atom parameters refined isotropically
 Unit weights applied

$(\Delta/\sigma)_{\text{max}}$ = 0.04
 $\Delta\rho_{\text{max}}$ = 0.26 e \AA^{-3}
 $\Delta\rho_{\text{min}}$ = -0.20 e \AA^{-3}
 Atomic scattering factors from CRYSRULER (Rizzoli, Sangermano, Calestani & Andreotti, 1986)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
N(100)	0.1062 (2)	0.2603 (1)	0.2297 (1)	0.0382 (4)
O(100)	0.2377 (2)	0.1923 (1)	0.1857 (1)	0.0529 (5)
C(200)	-0.1104 (3)	0.2192 (1)	0.2150 (1)	0.0358 (5)
C(300)	-0.2397 (3)	0.2912 (2)	0.2678 (2)	0.0469 (7)
C(400)	-0.1553 (4)	0.4040 (2)	0.3306 (2)	0.0534 (7)
C(500)	0.0630 (3)	0.4451 (2)	0.3382 (2)	0.0505 (7)
C(600)	0.1905 (3)	0.3727 (2)	0.2879 (2)	0.0449 (6)

C(31)	-0.1974 (3)	0.1037 (2)	0.1366 (2)	0.0387 (6)
N(1)	-0.3920 (2)	-0.2713 (1)	0.2785 (1)	0.0394 (5)
O(1)	-0.4579 (2)	-0.3821 (1)	0.3204 (1)	0.0580 (6)
C(1)	-0.2798 (3)	-0.1712 (2)	0.3666 (1)	0.0416 (5)
C(11)	-0.4169 (6)	-0.1776 (3)	0.4764 (2)	0.0671 (11)
C(12)	-0.0631 (4)	-0.2012 (2)	0.4020 (2)	0.0567 (8)
C(2)	-0.2585 (3)	-0.0394 (2)	0.3128 (2)	0.0396 (6)
C(3)	-0.1860 (3)	-0.0282 (1)	0.1848 (1)	0.0340 (5)
O(3)	0.0253 (2)	-0.0500 (1)	0.1736 (1)	0.0488 (5)
C(4)	-0.3407 (3)	-0.1279 (2)	0.1084 (2)	0.0380 (6)
C(5)	-0.3674 (3)	-0.2660 (2)	0.1466 (2)	0.0385 (6)
C(51)	-0.1821 (4)	-0.3263 (2)	0.1106 (2)	0.0547 (8)
C(52)	-0.5746 (4)	-0.3431 (2)	0.0873 (2)	0.0611 (8)

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2'-Hydroxy-2-methoxychalcone

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Abstract

In 1-(2-hydroxyphenyl)-3-(2-methoxyphenyl)-2-propen-1-one, C₁₆H₁₄O₃, the methoxylated phenyl ring and the benzoyl group are *trans* with respect to the ethylenic bond. The phenolic OH group forms an intramolecular hydrogen bond with the carbonyl O atom. The torsion angle O9—C9—C8—C7 of the enone moiety is -11.0 (2)°. The phenolic ring is almost coplanar with the carbonyl group: O9—C9—C1'—C2' = -3.0 (2)°. The torsion angle of the methoxyphenyl group C5—C6—C7—C8 = -15.7 (2)°.

Comment

Natural and synthetic analogues of hydroxy and/or methoxychalcones have biological properties (Ischitsuka, Ninomiya, Ohsawa, Fujii & Suhura, 1982; Ninomiya, Ohsawa, Aoyama, Umeda, Suhura & Ischitsuka, 1984; Ramanathan, Das & Tan, 1993; Batt, Goodman, Jones, Kerr, Mantegna, McAllister, Newton, Nurnberg, Welch & Covington, 1993). More recently it has been noted that chalcones frequently crystallize in non-centrosymmetric space groups, which is a favorable criterion for non-linear optical properties. In order to find relationships between hydrogen bonding and non-linear optical properties, a series of substituted chalcones have been synthesized.

2'-Hydroxychalcones are synthetic precursors for preparation of the corresponding flavonols (Wallet, Gaydou, Molins & Miravittles, 1994). In the title chalcone (1) an intramolecular hydrogen bond, O9...H2'—O2', contributes to the planarity of the benzoyl moiety.

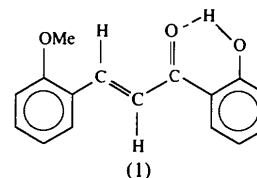


Table 2. Bond lengths (Å) and angles (°)

N(100)—O(100)	1.322 (2)	C(1)—C(11)	1.522 (3)
N(100)—C(200)	1.368 (2)	C(1)—C(12)	1.535 (3)
N(100)—C(600)	1.358 (2)	C(1)—C(2)	1.538 (3)
C(200)—C(300)	1.380 (3)	C(2)—C(3)	1.518 (3)
C(200)—C(31)	1.500 (2)	C(3)—O(3)	1.428 (2)
C(300)—C(400)	1.385 (3)	C(3)—C(4)	1.525 (2)
C(400)—C(500)	1.373 (3)	C(4)—C(5)	1.535 (3)
C(500)—C(600)	1.363 (3)	C(5)—C(51)	1.524 (3)
C(31)—C(3)	1.549 (3)	C(5)—C(52)	1.533 (3)
N(1)—O(1)	1.284 (2)	O(3)—O(100)	2.673 (2)
N(1)—C(1)	1.494 (2)	O(3)—H(3)	0.90 (2)
N(1)—C(5)	1.491 (3)	O(100)—H(3)	1.79 (3)
C(200)—N(100)—C(600)	120.7 (2)	C(11)—C(1)—C(2)	109.0 (2)
O(100)—N(100)—C(600)	118.7 (2)	C(11)—C(1)—C(12)	109.1 (2)
O(100)—N(100)—C(200)	120.6 (1)	C(1)—C(2)—C(3)	116.1 (2)
N(100)—C(200)—C(31)	119.3 (2)	C(31)—C(3)—C(2)	110.9 (1)
N(100)—C(200)—C(300)	117.9 (1)	C(2)—C(3)—C(4)	107.7 (1)
C(300)—C(200)—C(31)	122.7 (2)	C(2)—C(3)—O(3)	111.8 (1)
C(200)—C(300)—C(400)	121.7 (2)	C(31)—C(3)—C(4)	107.4 (1)
C(300)—C(400)—C(500)	118.5 (2)	C(31)—C(3)—O(3)	110.0 (1)
C(400)—C(500)—C(600)	119.7 (2)	O(3)—C(3)—C(4)	109.0 (1)
N(100)—C(600)—C(500)	121.3 (2)	C(3)—C(4)—C(5)	116.2 (2)
C(200)—C(31)—C(3)	118.1 (2)	N(1)—C(5)—C(4)	109.5 (2)
C(1)—N(1)—C(5)	124.6 (1)	C(4)—C(5)—C(52)	107.9 (2)
O(1)—N(1)—C(5)	116.4 (1)	C(4)—C(5)—C(51)	113.1 (2)
O(1)—N(1)—C(1)	115.6 (1)	N(1)—C(5)—C(52)	107.6 (2)
N(1)—C(1)—C(2)	109.6 (1)	N(1)—C(5)—C(51)	109.8 (2)
N(1)—C(1)—C(12)	108.6 (1)	C(51)—C(5)—C(52)	108.9 (2)
N(1)—C(1)—C(11)	107.5 (2)	C(3)—O(3)—H(3)	104 (2)
C(12)—C(1)—C(2)	112.9 (2)	O(3)—H(3)—O(100)	167 (3)

The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985). The first *E* map revealed positions of all non-H atoms. Least-squares refinement used *SHELXL76* (Sheldrick, 1976) and the *CRYSRULER* package (Rizzoli, Sangermano, Calestani & Andreotti, 1986), isotropic and then anisotropic displacement factors. H atoms were located on a difference Fourier map.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: KA1059). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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