

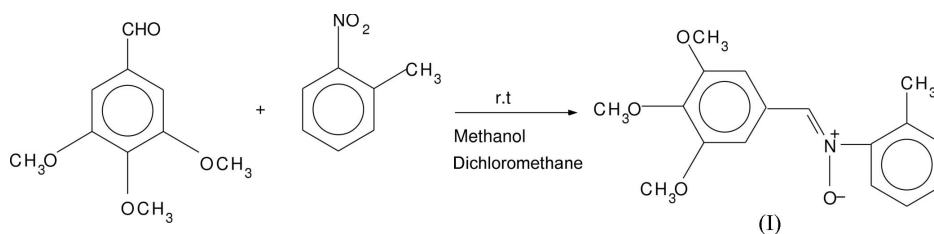
2-Methyl-*N*-(3,4,5-trimethoxybenzylidene)-
aniline *N*-oxideS. Naveen,^a M. P. Sadashiva,^b
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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C})$ = 0.004 Å
R factor = 0.038
wR factor = 0.100
Data-to-parameter ratio = 7.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.In the crystal structure of the title compound, C₁₇H₁₉NO₄, the geometry about the C=N double bond is *Z*. The structure is stabilized by weak intermolecular C—H···O hydrogen bonds, linking the molecules into chains.Received 8 September 2006
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Comment

The stereochemistry, such as regioselectivity and enantioselectivity, of heterocyclic isoxazolidine, isoxazoline and isoxazole compounds (Huisgen, 1984) can be studied by 1,3-dipolar cycloaddition reactions. The cornerstone for cycloaddition reactions, nitrones, are excellent excellent spin trapping (Bernotas *et al.*, 1996) and highly versatile synthetic intermediates (Breuer, 1982). The most popular method for nitrone synthesis is either by direct condensation of hydroxylamine and an aldehyde or by oxidation of the corresponding hydroxylamine. The key intermediate, a hydroxylamine, has been synthesized by controlled reduction of nitroarenes using zinc and ammonium chloride in an aqueous or alcoholic medium, but this method is better for nitrobenzene reduction than substituted nitroarenes (Bamberger, 1919). Furthermore, most of the methods such as using iridium, Raney nickel, or a rhodium catalyst in the presence of protonating agents such as hydrazine, formic acid, phosphonic acid, *etc.* (Rondestvedt & Johnson, 1977) suffer from disadvantages such as a cumbersome work-up procedure, the tendency for the transition metal catalyst to be expensive, the need for high temperature and also the explosive nature of some reactions (Okamoto & Shudo, 1973). The work reported here was undertaken to study the molecular conformation of the title compound, (I).



The molecular structure of (I) is shown in Fig. 1. The C=N distance of 1.295 (1) Å is within 3σ of the value [1.279 (8) Å] reported by Allen *et al.* (1987), as are the C—C bond lengths in the benzene rings. The N7—O21 bond length of 1.305 (3) Å is comparable with the corresponding values reported for *N*-(4-cyanophenyl)- α -(4-methoxyphenyl)nitrone (Kang *et al.*, 2000) and *N*-methylbenzaldehyde nitrone (Bedford *et al.*, 1991). The dihedral angle between the 3,4,5-trimethoxyphenyl ring and the methylphenyl ring is 57.84 (13)°. This value is

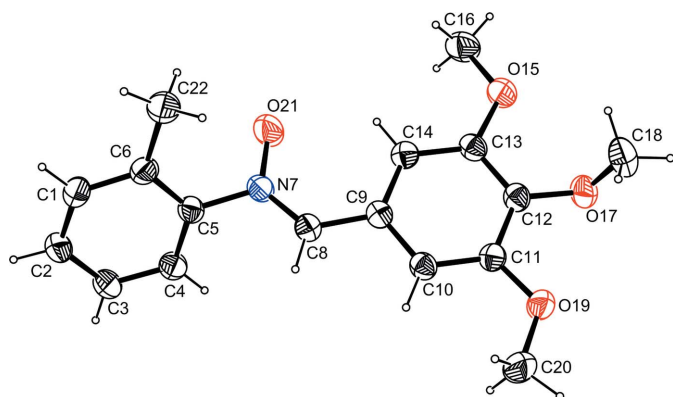


Figure 1

The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms are represented as spheres of arbitrary radii.

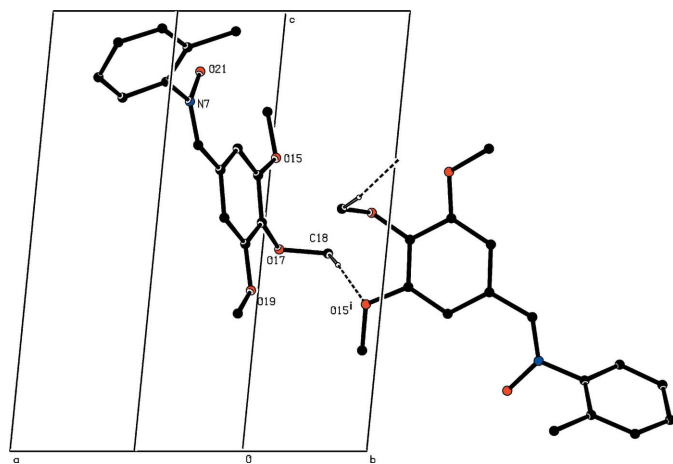


Figure 2

Partial packing view, showing the weak C—H...O hydrogen-bonding interactions (dashed lines), resulting in the formation of an infinite chain. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry code: (i) $-x, \frac{1}{2} + y, 1 - z$.]

slightly larger than that reported for *N*-(*p*-hydroxybenzylidene)phenylamine *N*-oxide [55.3 (1)°; Vijayalakshmi *et al.*, 1997]. This can be attributed to the bulky methoxy groups present at the three, four and five positions on the phenyl ring. The nitron unit is coplanar with the 3,4,5-trimethoxyphenyl ring but is significantly twisted with respect to the methylphenyl ring, as indicated by the O21—N7—C8—C9 and O2—N7—C5—C6 torsion angle values of -0.26 (44) and -59.03 (37)°, respectively. A similar conformation is observed in the structure of *N*-(4-cyanophenyl)- α -(4-methoxyphenyl)nitron, in which the 4-methoxyphenyl ring is approximately coplanar while the 4-cyanophenyl ring is twisted significantly. The double bond connecting the 3,4,5-trimethoxyphenyl ring and the methylphenyl ring has a *Z* geometry.

The crystal structure is stabilized by weak intermolecular C—H...O hydrogen bonds (Table 1), which link the molecules into infinite chains (Fig. 2).

Experimental

1:1.5 molar equivalents of 3,4,5-trimethoxybenzaldehyde, *o*-nitrotoluene and 2–2.5 ml of ammonium buffer solution (pH 10.2) were added to a round-bottomed flask containing 10 ml of 1:1 *v/v* methanol/dichloromethane. To the stirred reaction solution, 2.5 molar equivalents of zinc powder was added slowly. The reaction is exothermic. The stirring was continued for 4–6 h at room temperature. Complete conversion of the reactant to the product was confirmed by thin-layer chromatography using *n*-hexane and ethyl acetate as eluents. The reaction mixture was filtered and the filtrate was evaporated under vacuum. The residue was recrystallized from ethyl acetate and *n*-hexane (1:9), giving the title compound (yield 75%; m.p. 406.15 K).

Crystal data

$C_{17}H_{19}NO_4$
 $M_r = 301.33$
 Monoclinic, $P2_1$
 $a = 7.532$ (8) Å
 $b = 8.256$ (9) Å
 $c = 12.872$ (13) Å
 $\beta = 96.283$ (4)°
 $V = 795.6$ (15) Å³

$Z = 2$
 $D_x = 1.258$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 295$ (2) K
 Block, pale yellow
 $0.25 \times 0.20 \times 0.20$ mm

Data collection

MacScience DIPLabo 32001
 diffractometer
 ω scans
 Absorption correction: none
 2564 measured reflections

1461 independent reflections
 1375 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.029$
 $\theta_{max} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.100$
 $S = 1.11$
 1461 reflections
 203 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.1017P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.006$
 $\Delta\rho_{max} = 0.12$ e Å⁻³
 $\Delta\rho_{min} = -0.15$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C14—H14...O21	0.93	2.21	2.831 (5)	123
C18—H18C...O15 ⁱ	0.96	2.58	3.539 (6)	174

Symmetry code: (i) $-x, y + \frac{1}{2}, -z + 1$.

H atoms were placed at idealized positions and allowed to ride on their parent atoms, with C—H = 0.92–0.98 Å and $U_{iso}(H) = 1.2U_{eq}(\text{carrier atom})$. In the absence of significant anomalous scattering effects, Friedel pairs were merged.

Data collection: XPRESS (MacScience, 2002); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: SCALEPACK and DENZO (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003), ORTEPIII (Burnett & Johnson, 1996) and ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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