

## Refinement

Refinement on $F$	$(\Delta/\sigma)_{\max} = 0.003$
$R = 0.063$	$\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$
$wR = 0.058$	$\Delta\rho_{\min} = -0.25 \text{ e } \text{Å}^{-3}$
$S = 1.46$	Extinction correction: none
983 reflections	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
142 parameters	
H atoms refined isotropically	
$w = 4F_o^2/\sigma^2(F_o^2)$	

Table 1. Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ )

O5—N5	1.368 (3)	C6—C7	1.328 (5)
O8—C8	1.218 (4)	C7—C8	1.463 (4)
N5—C5	1.308 (4)	C8—C10	1.481 (5)
C5—C6	1.449 (5)	C9—C10	1.395 (4)
C5—C9	1.462 (4)		
C2—N1—C10	118.2 (3)	C6—C5—C9	118.3 (3)
O5—N5—C5	111.4 (3)	O8—C8—C7	121.5 (3)
N5—C5—C6	125.2 (3)	O8—C8—C10	121.9 (3)
N5—C5—C9	116.5 (3)	C7—C8—C10	116.6 (3)

All H atoms were located from difference Fourier maps and included in the refinement calculations isotropically.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELX86* (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1032). Services for accessing these data are described at the back of the journal.

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## The Stereochemical Assignment of the Ozonide 5-(2-Naphthyl)-3-phenyl-1,2,4-trioxolane-3-carbonitrile

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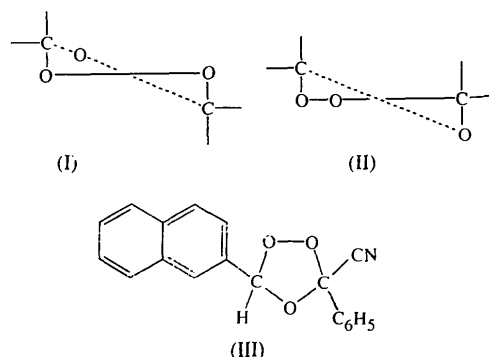
(Received 21 January 1997; accepted 28 April 1997)

## Abstract

The title compound,  $\text{C}_{19}\text{H}_{13}\text{NO}_3$ , has been structurally characterized. The naphthyl and phenyl groups adopt a *trans* arrangement. The five atoms in the ozonide ring have a half-chair conformation. The distances and angles of the ring correspond well with those found in unstrained ozonides.

## Comment

Although conformational and stereochemical assignments of ozonides have attracted much attention (Bailey, 1978; Bailey & Ferrel, 1978; Criegee & Wenner, 1949; Lattimer, Kuczkowski & Gillies, 1974), only simple ozonides with low molecular weights have been isolated as liquids and their structures elucidated by microwave spectroscopy (Mazur & Kuczkowski, 1977; Kuczkowski, Gillies & Gallaher, 1993). Both experimental results and theoretical calculations favour the half-chair conformation, (I). By contrast, several ozonides derived from cyclic or bicyclic olefins have been reported to adopt a symmetrical ether-O envelope conformation, (II).



Stereochemical assignments for *cis-trans* isomeric ozonides bearing H atoms at the ozonide rings have been made with the help of  $^1\text{H}$  NMR spectroscopy. It

has been reported that the signals of the CH groups in *trans* ozonides appear in a higher field than those in the corresponding *cis* isomers (Murray, Youssefeyeh & Story, 1967). More equivocal assignments have been made based on the partial resolution of the racemates of *trans* isomers (Loan, Murray & Story, 1965; Criegcc & Korber, 1971) or the deuterium isotope effects (Choe, Choi & Kuczkowski, 1986).

The synthesis of the title compound, (III), has been reported previously (Griesbaum, Övez, Huh & Dong, 1995). Two stereoisomeric ozonides of (III) have been synthesized, which showed <sup>1</sup>H NMR signals for the H atoms attached to the ozonide rings at  $\delta = 6.52$  and  $\delta = 6.91$ . Of these, only one isomer ( $\delta = 6.52$ ) has been successfully isolated, whereas the other isomer ( $\delta = 6.91$ ) appeared to decompose during the separation process. The *trans* conformation has been assigned to the isolated isomer based upon the NMR spectrum. X-ray diffraction studies of the single crystal have been conducted to characterize its structure and preliminary results have been published (Jung, Yun & Huh, 1996).

The results show that the naphthyl and phenyl groups adopt a *trans* arrangement. This confirms that the NMR spectrum analysis is correct. The dihedral angle between the naphthyl and phenyl groups is 62.9 (1)°. The C1, O1, C2 and O2 atoms of the ozonide ring are in a plane [maximum deviation 0.071 (2) Å], whereas the second peroxidic O3 atom deviates from the least-squares plane by 0.690 (5) Å. This half-chair conformation has been reported to be adopted by many ozonides in the absence of specific steric effects (Griesbaum, Ball, Beck & McCullough, 1995). The O atoms of the ether bridge in ozonides of norbornenes were found to deviate significantly from the plane (Griesbaum, Krieger-Beck & Beck, 1991). The O2—O3 distance [1.477 (4) Å] and the C1—O1—C2 angle [106.8 (3)°] in the title structure are comparable with those found in unstrained ozonides (Griesbaum, Ball, Beck & McCullough, 1995).

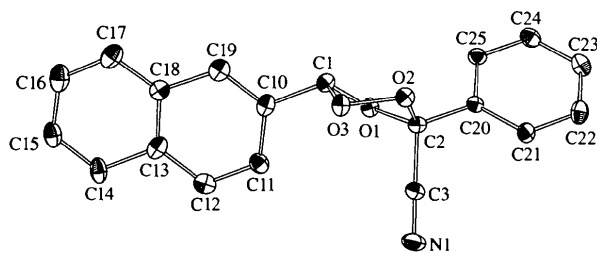


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 20% probability level and H atoms have been omitted for clarity.

## Experimental

Crystals of the title compound were synthesized according to Griesbaum, Övez, Huh & Dong (1995).

## Crystal data

C<sub>19</sub>H<sub>13</sub>NO<sub>3</sub>  
*M<sub>r</sub>* = 303.30  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 18.214 (5) Å  
*b* = 7.416 (2) Å  
*c* = 12.037 (3) Å  
 $\beta$  = 108.49 (2)°  
*V* = 1542.1 (7) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.306 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

## Data collection

Mac Science MXC3 four-circle diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: none  
 2091 measured reflections  
 1982 independent reflections  
 1799 reflections with  $I > 2\sigma(I)$

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.072  
 $wR$ (*F*<sup>2</sup>) = 0.212  
*S* = 1.053  
 1982 reflections  
 209 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.1154P)^2 + 1.352P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Mo *K* $\alpha$  radiation  
 $\lambda = 0.7107$  Å  
 Cell parameters from 26 reflections  
 $\theta = 10$ –14°  
 $\mu = 0.089$  mm<sup>-1</sup>  
*T* = 293 (2) K  
 Polyhedron  
 0.80 × 0.80 × 0.40 mm  
 Pale yellow

*R*<sub>int</sub> = 0.005  
 $\theta_{\max} = 22.99^\circ$   
*h* = -20 → 18  
*k* = 0 → 8  
*l* = 0 → 13  
 2 standard reflections every 100 reflections  
 intensity decay: none

( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{\max} = 0.659$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.265$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXL93* (Sheldrick, 1993)  
 Extinction coefficient: 0.018 (4)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C2	1.409 (4)	C1—C10	1.512 (6)
O1—C1	1.433 (5)	C2—C3	1.493 (6)
O2—C2	1.423 (4)	C2—C20	1.501 (5)
O2—O3	1.477 (4)	C3—N1	1.140 (5)
O3—C1	1.420 (4)		
C2—O1—C1	106.8 (3)	O1—C2—C20	113.2 (3)
C2—O2—O3	100.0 (2)	O2—C2—C20	110.0 (3)
C1—O3—O2	99.3 (2)	C3—C2—C20	112.1 (3)
O3—C1—O1	103.5 (3)	N1—C3—C2	179.4 (4)
O3—C1—C10	109.5 (3)	C19—C10—C1	118.7 (5)
O1—C1—C10	110.7 (3)	C11—C10—C1	120.3 (4)
O1—C2—O2	104.7 (3)	C21—C20—C2	121.0 (3)
O1—C2—C3	108.2 (3)	C25—C20—C2	118.9 (3)
O2—C2—C3	108.3 (3)		

Data collection: *MXC Diffractometer Control Software* (Mac Science Corporation, 1994). Cell refinement: *MXC Diffractometer Control Software*. Data reduction: *MXC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: MS-DOS v6.22 editor.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KH1149). Services for accessing these data are described at the back of the journal.

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## *N,N'*-Bis(2-hydroxybenzyl)-1,4-butanedi-ammonium Dinitrate

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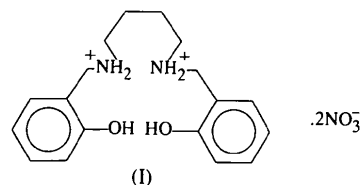
### Abstract

In the title compound,  $C_{18}H_{26}N_2O_2^{2+} \cdot 2NO_3^-$ , both N atoms of the cationic moiety are protonated and linked to two  $NO_3^-$  anions by intermolecular hydrogen bonding. Intramolecular hydrogen bonding also exists be-

tween the amine H and phenol O atoms. The compound displays a centrosymmetric structure with the two aromatic rings parallel to each other.

### Comment

Tetradentate 2N2O amine–phenols have a high coordinating affinity towards transition metals and are commonly used as chelate agents. Although many crystal structures of amine–phenol metals have been determined (Pillai, John, Lo, Schlemper & Troutner, 1990; Pillai, Barnes, John, Troutner & Schlemper, 1993; Pillai, Barnes & Schlemper, 1993, 1994; Pillai & Schlemper, 1994), none of the free ligands has been reported so far. We describe here the title compound, (I), in order to detect its structural variations upon coordination and to provide some insight into the coordination behaviour of this type of ligand.



Under the conditions of preparation (pH 5), both N atoms of *N,N'*-bis(2-hydroxybenzyl)-1,4-butanedi-ammonium (*L*) are protonated resulting in  $-NH_2^+$  moieties. The asymmetric unit contains one anion,  $NO_3^-$ , and half of a doubly charged cation,  $H_2L^{2+}$ . In order to coordinate tetradentate amine–phenol ligands to metal ions, alkaline conditions are required to prevent protonation of the amine N atoms and to facilitate deprotonation of the phenol groups.

The title compound, (I), is centrosymmetric, the inversion center being located at the midpoint of the C9—C9<sup>i</sup> bond [symmetry code: (i)  $-x, -y, -z$ ]. The O—Hn1 distance of 2.50 Å is clearly indicative of intramolecular hydrogen bonding. In addition, both strong and weak intermolecular hydrogen bonds involving O1···Hn1, O1···Hn2, O2···H, O2···Hn1 and O3···Hn2 distances of 2.64, 2.41, 1.85, 2.04 and 1.96 Å, respectively, contribute to the extreme stability of this compound.

The conformation of the amine–phenol ligand is of particular interest in interpretation of its coordination with a metal. The torsion angles C7—N1—C8—C9 and N1—C8—C9—C9<sup>i</sup> are 65.6 (3) and 59.5 (3)°, respectively. As a result, the title compound has a planar structure with the two aromatic rings parallel to each other. The intramolecular O···O<sup>i</sup> distance of 7.624 (1) Å is much larger than that found when the ligand is coordinated to a metal. For example, the corresponding distance is reduced to 2.630 Å when the H-substituted ligand is coordinated to Pd<sup>II</sup> (Pillai & Schlemper, 1994), and to 2.412 and 2.428 Å when coordinated to Tc<sup>V</sup> (Pillai, John, Lo, Schlemper & Troutner, 1990). The