

C4—C3—C2	106.4 (3)	O14—P13—C1	114.92 (14)
N17—C4—C3	103.3 (3)	O16—P13—C1	107.66 (15)
N17—C4—C6	112.6 (3)	O15—P13—C1	100.88 (14)
C3—C4—C6	119.0 (4)	C7—O15—P13	119.3 (2)
O15—C7—C8	109.5 (4)	C10—O16—P13	123.4 (2)
O15—C7—C9	106.2 (3)	C4—N17—C1	107.9 (3)

Collection des données: *CAD-4 Operations Manual* (Enraf-Nonius, 1977). Affinement des paramètres de la maille: *CAD-4 Operations Manual*. Réduction des données: *SDP* (Frenz, 1978). Programme(s) pour la solution de la structure: *SHELXS86* (Sheldrick, 1990). Programme(s) pour l'affinement de la structure: *SHELXL93* (Sheldrick, 1993). Graphisme moléculaire: *ORTEP* (Johnson, 1965). Logiciel utilisé pour préparer le matériel pour publication: Word5,1a sur Macintosh IIvx.

Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: PA1253). Les processus d'accès à ces archives est donné au dos de la couverture.

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N-[2-(*N'*-Hydroxy-*N*-oxidodiaziniumyl)-3-methylbutyl]octanamide

RAKWOO CHANG AND WHANCHUL SHIN

Department of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-742, Korea. E-mail: nswcshin@plaza.snu.ac.kr

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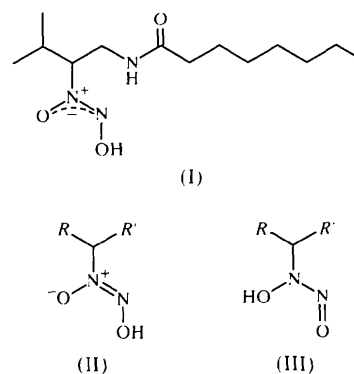
Abstract

The title compound, C₁₃H₂₇N₃O₃, exists in the *N'*-hydroxy-*N*-oxidodiaziniumyl [*R*—N(O)=N—OH] form

instead of the tautomeric *N*-hydroxy-*N'*-nitrosoamino [*R*—N(OH)—N=O] form. Variation of the bond distances and good planarity indicate that resonance takes place in the [N₂O₂]H moiety. The molecule assumes an overall elongated conformation. Two centrosymmetrically-related molecules form a dimer *via* two three-centered N1—H···O2/O3 hydrogen bonds. Crystal packing consists of alternating hydrophilic and hydrophobic layers.

Comment

Compounds containing the NO group, such as the *N*-nitroso compounds, have been studied extensively due to their various physiological effects (Scanlan & Tannenbaum, 1981). Compounds of the R₂N[N₂O₂][−] anion are of current interest as pharmacological probes due to their ability to regenerate nitric oxide (NO), which is known as a multifaceted bioregulatory agent (Saavedra *et al.*, 1992). However, compounds of the R[N₂O₂]H type have rarely been studied. Alanosine, which shows antibiotic and anticancer activities, is one of the few examples to have been isolated from microorganisms (Murthy *et al.*, 1966). X-ray analysis of L-alanosine showed that, unlike the previously proposed structure, the H atom of the [N₂O₂]H moiety is bonded to the terminal O atom instead of the penultimate one (Jalal *et al.*, 1986). The title compound, (I), with an [N₂O₂]H moiety, shows weak herbicidal activity and the present X-ray analysis has been performed to establish its structure.



An ORTEPII drawing (Johnson, 1976) of the title molecule with the atomic numbering scheme is presented in Fig. 1. The molecule exists in the *N'*-hydroxy-*N*-oxidodiaziniumyl form, (II), instead of its tautomeric *N*-hydroxy-*N*-nitrosoamino form, (III), as found in L-alanosine. The N2—N3 distance of 1.271 (4) Å is slightly longer than the average value for a double bond [1.24 (1) Å]. The N2—O2 distance of 1.265 (3) Å is shorter than the N3—O2 distance of 1.369 (4) Å, showing that the N2—O2 bond possesses considerable double-bond character. These bond distances imply that the correct structure is (I), with resonance in the

O2—N2—N3 system, rather than (III), with localized charges. The molecular dimensions of the [N₂O₂]H moiety agree within 5σ with those of L-alanosine for which the same resonance structure was proposed. It has been found that alkylation of the R₂N[N₂O₂][−] anion results in R₂—N—N(O)=N—OR' instead of R₂N—N(OR')—N=O (Saavedra *et al.*, 1992). It therefore seems clear that structure (I) is the predominant form in solution as well as in the crystal.

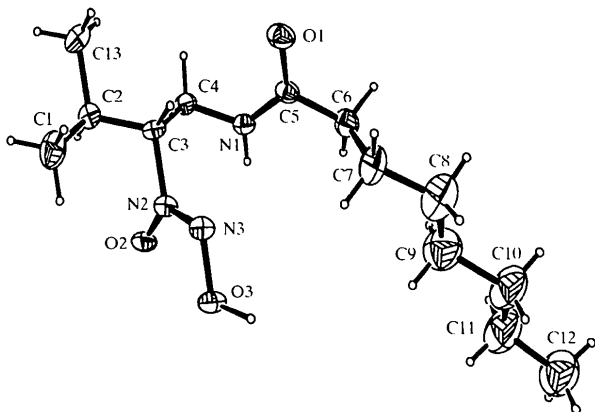


Fig. 1. ORTEP view (Johnson, 1976) of the title compound, with the atomic numbering scheme and displacement ellipsoids drawn at the 30% probability level.

Other molecular dimensions are normal except for the C—C distances in the alkyl chain (C8—C12), which is subject to high thermal motion. There is an indication of minor disorder around the C9 atom, but no discrete disorder model could be obtained for successful refinement. The [N₂O₂]H moiety shows good planarity with a maximum deviation of 0.022 (3) Å for N2, which is consistent with the presence of resonance. The amide group is planar with a maximum deviation of 0.024 (3) Å for N1. The molecule assumes an overall elongated conformation with all torsion angles along the long-chain structure (C1—C12) close to 180°, except for three, namely, C3—C4—N1—C5 of −82.7 (4), N1—C5—C6—C7 of −101.2 (5) and C6—C7—C8—C9 of −66.2 (10)°.

The crystal packing consists of alternating hydrophilic and hydrophobic layers perpendicular to the *a* axis (Fig. 2). Two centrosymmetrically-related molecules form a dimer *via* two three-centered N1—H···O2/O3 hydrogen bonds [N—H 0.82 (4), N···O2ⁱ 2.961 (5), H···O2ⁱ 2.19 (4) Å and N—H···O2ⁱ 156 (4)°; N···O3ⁱ 3.061 (5), H···O3ⁱ 2.40 (4) Å and N—H···O3ⁱ 138 (3)°; symmetry code: (i) $-x, -y, -z$]. These dimers are linked together by O3—H···O1ⁱⁱ hydrogen bonds [O3—H 1.03 (6), O3···O1ⁱⁱ 2.557 (4), H···O1ⁱⁱ 1.55 (6) Å and O3—H···O1ⁱⁱ 166 (5)°; symmetry code: (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$] to form a hydrophilic layer with a two-dimensional hydrogen-bonding network. The *n*-hexyl and isopropyl groups form a hydrophobic layer between the hydrophilic layers.

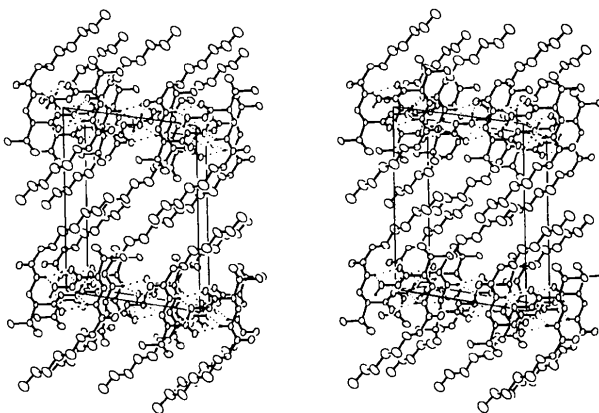


Fig. 2. Stereoscopic view of the crystal packing. Axes *a*, *b* and *c* are approximately vertical, perpendicular and horizontal to the page, respectively. The dashed lines denote hydrogen bonds. H atoms, except those involved in hydrogen bonds, have been omitted for clarity.

Experimental

A sample of the title compound was obtained from the Hannong Corporation. Fragile colorless crystals were grown from an ethanol solution.

Crystal data

C₁₃H₂₇N₃O₃
M_r = 273.38
 Monoclinic
*P*2₁/*c*
a = 14.669 (7) Å
b = 10.722 (8) Å
c = 10.802 (6) Å
 β = 99.55 (8)°
V = 1675.4 (17) Å³
Z = 4
D_x = 1.084 Mg m^{−3}
D_m = 1.06 (2) Mg m^{−3}
D_m measured by flotation in
n-hexane/dichloromethane

Cu *K*α radiation
 λ = 1.5418 Å
 Cell parameters from 22
 reflections
 θ = 11.37–35.47°
 μ = 0.625 mm^{−1}
T = 293 (2) K
 Plate
 0.7 × 0.6 × 0.1 mm
 Colorless

Data collection

Rigaku AFC four-circle
 diffractometer
 ω scans
 Absorption correction: none
 2484 measured reflections
 2484 independent reflections
 1547 reflections with
 $I > 2\sigma(I)$

θ_{\max} = 60.05°
 h = −16 → 0
 k = 0 → 12
 l = −11 → 12
 3 standard reflections
 every 100 reflections
 intensity decay: none

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.198$
S = 1.028
 2483 reflections
 231 parameters
 H atoms: see below

$(\Delta/\sigma)_{\max} = -0.008$
 $\Delta\rho_{\max} = 0.245 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.213 \text{ e } \text{Å}^{-3}$
 Extinction correction:
 SHELXL93
 Extinction coefficient:
 0.042 (3)

$$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2 + 1.1606P]$$

where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
*International Tables for
Crystallography* (Vol. C)

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(±)-3-Indanone-1-acetic Acid: Heterochiral Catemeric Hydrogen Bonding in a δ-Keto Acid

HUGH W. THOMPSON, ANDREW P. J. BRUNSKILL AND
ROGER A. LALANCETTE*

*Carl A. Olson Memorial Laboratories, Department of
Chemistry, Rutgers University, Newark, NJ 07102, USA.
E-mail: lalancette@hades.rutgers.edu*

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Table 1. Selected geometric parameters (Å, °)

C1—C2	1.507 (7)	C5—O1	1.245 (4)
C2—C3	1.511 (5)	C5—N1	1.322 (5)
C2—C13	1.531 (6)	C5—C6	1.498 (6)
C3—N2	1.498 (4)	N2—N3	1.271 (4)
C3—C4	1.518 (5)	N2—O2	1.265 (3)
C4—N1	1.449 (5)	N3—O3	1.369 (4)
C1—C2—C3	112.6 (4)	O1—C5—C6	120.6 (4)
C1—C2—C13	110.4 (5)	N1—C5—C6	117.0 (4)
C3—C2—C13	110.5 (4)	C5—C6—C7	110.9 (4)
N2—C3—C2	109.7 (3)	C5—N1—C4	124.3 (4)
N2—C3—C4	107.4 (3)	N3—N2—O2	126.8 (3)
C2—C3—C4	114.5 (3)	N3—N2—C3	114.5 (3)
N1—C4—C3	113.0 (3)	O2—N2—C3	118.6 (3)
O1—C5—N1	122.3 (4)	N2—N3—O3	108.4 (3)

Diffraction peaks were very broad and the intensity data were collected with the ω -scan mode. H atoms of atoms C7–C12 in the *n*-alkyl chain were generated geometrically and refined using the AFIX 23 or 137 option of *SHELXL93* (Sheldrick, 1993), with the isotropic displacement parameters fixed at 1.3 times the isotropic equivalents of their bonded atoms. All other H atoms were found from a difference Fourier map and refined isotropically.

Data collection: local program (Yoon *et al.*, 1994). Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1075). Services for accessing these data are described at the back of the journal.

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Abstract

The crystal structure of (±)-2,3-dihydro-3-oxo-1H-indeneacetic acid, C₁₁H₁₀O₃, involves carboxyl-to-ketone hydrogen-bonding catemers [O···O 2.691 (2) Å] of an unusual type. Hydrogen bonds progress from the carboxyl H atom of one molecule to the ketone O (O1) atom of a glide-related enantiomer, resulting in heterochiral chains. Parallel screw-related hydrogen-bonding chains proceed in counter-directional pairs through the cell. Two different close contacts (2.49 and 2.58 Å) are found between the carboxyl C=O group and H atoms on neighboring molecules.

Comment

Keto carboxylic acids offer options for varying the standard pattern of dimeric hydrogen bonding that dominates functionally unadorned acids. Usually the ketone fails to participate, resulting in typical carboxyl dimers, but less commonly intermolecular carboxyl-to-ketone hydrogen bonds occur, yielding a catemer. A third, rare arrangement has an internal hydrogen bond and two instances are known of acid-to-ketone dimerization, plus one of carboxyl catemerization (see below). Several cases also exist of hydrates with more complex hydrogen-bonding patterns. We have referenced and discussed numerous examples of these hydrogen-bonding modes (Thompson *et al.*, 1992; Coté *et al.*, 1996). Part of our continuing interest in this behavior lies in the discovery of new hydrogen-bonding patterns. We have recently reported an instance of carboxyl-to-carboxyl catemerization, a pattern not previously observed in keto acids (Lalancette *et al.*, 1998), and we now report a hydrogen-bonding pattern of a heretofore rarely observed type.

The title compound, (I), was of particular interest to us as a one-carbon homolog of (±)-3-indanone-1-carboxylic acid (Lalancette *et al.*, 1997). We have recently reported crystal structures for both the anhydrous and monohydrate forms of that compound, the former of which displays a catemeric hydrogen-bonding