Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1206). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Nitroacetophenone

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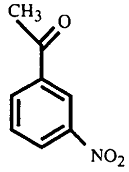
Abstract

Molecules of the title compound, $C_8H_7NO_3$, are connected by a number of C—H···O hydrogen bonds to form planar sheets. Both the nitro and carbonyl O atoms act as hydrogen-bond acceptors.

Comment

Recent reports have demonstrated that many organic reactions can take place in the absence of solvent by simply grinding the crystalline reactants together (Toda, 1993; Etter, Frankenbach & Bernstein, 1989). We are currently investigating the mechanistic aspects of the solvent-free Bayer–Villiger oxidation of ketones to esters by 3-chloroperbenzoic acid. As part of this study we have determined the structure of 3-nitroacetophenone (I), a compound which has been found by us to be particularly inert to such a solid-state oxidation reaction.



(I)

The bond lengths and angles for this molecule are very similar to those found for 4-nitroacetophenone (Kim, Boyko & Carpenter, 1973). Whereas 4-nitroacetophenone is almost planar, the 3-nitroacetophenone molecule is best described by three planar moieties: *A*, the benzene ring (C1–C6) to 0.002 (3) Å; *B*, the nitro group (N1, O1 and O2); *C*, the aceto group (C1, C7, C8 and O7) to 0.008 (4) Å. There is twist of approximately 1.8 (2)° about the C3—N1 bond such that the nitro group lies just out of the plane of the phenyl ring. The dihedral angle *AC* is 9.4 (2)°. This value seems within the typical range of other ring-substituted acetophenones such as 4-hydroxyacetophenone (Vainshtein, Lobanova & Gurskaya, 1974), 4-bromoacetophenone (Lipkowski & Tabaszewska, 1992), 4-aminoacetophenone (Haisa, Kashino, Yuasa & Akigawa, 1976) and also acetophenone (Tanimoto, Kobayashi, Nagakura & Saito, 1973).

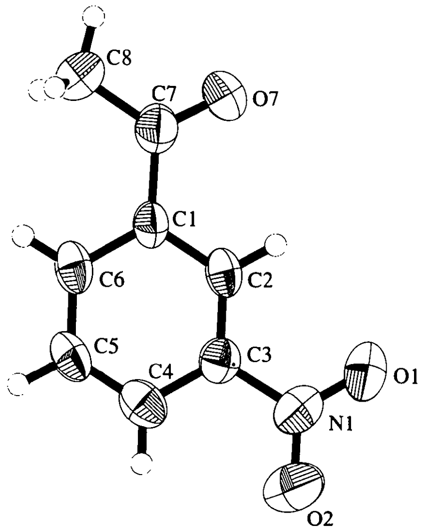


Fig. 1. *ORTEP*II (Johnson, 1976) diagram showing vibration ellipsoids at the 50% probability level.

Fig. 2 demonstrates that molecules connected by a number of C—H···O hydrogen bonds with H···O distances 2.45–2.75 Å are arranged in almost planar sheets, parallel to the (20$\bar{2}$) plane.

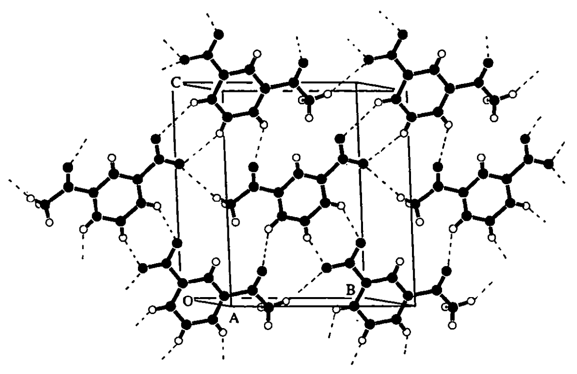


Fig. 2. Molecules connected by C—H···O hydrogen bonds to form sheets parallel to the (20$\bar{2}$) plane. The hydrogen bonds are represented as dashed lines.

Experimental

Crystals of (I) were obtained from Aldrich Chemical Co.

Crystal data

$C_8H_7NO_3$
$M_r = 165.15$
Monoclinic
$P2_1/n$
$a = 7.3920\,(10)$ Å
$b = 9.888\,(2)$ Å
$c = 10.814\,(2)$ Å
$\beta = 99.59\,(3)°$
$V = 779.4\,(2)$ Å^3
$Z = 4$
$D_x = 1.407$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 0.110$ mm^{-1}
$T = 295\,(2)$ K
Plate
0.30 × 0.20 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1444 measured reflections
1370 independent reflections
606 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0691$
$\theta_{\rm max} = 24.97°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 12$
2 standard reflections monitored every 200 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0613$
$wR(F^2) = 0.2315$
$S = 1.003$
1342 reflections
111 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.1054P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.011$
$\Delta\rho_{\rm max} = 0.212$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.197$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N1	0.1177 (6)	0.3249 (4)	0.3214 (4)	0.0637 (11)
O1	0.0257 (5)	0.3622 (4)	0.2233 (3)	0.0856 (12)
O2	0.1544 (7)	0.2074 (4)	0.3447 (4)	0.105 (2)
O7	0.0619 (5)	0.8299 (3)	0.3557 (3)	0.0829 (12)
C1	0.2145 (5)	0.6573 (4)	0.4778 (4)	0.0459 (11)
C2	0.1519 (5)	0.5605 (4)	0.3898 (4)	0.0467 (11)
C3	0.1882 (5)	0.4267 (5)	0.4159 (4)	0.0498 (12)
C4	0.2889 (6)	0.3845 (5)	0.5299 (4)	0.0553 (13)
C5	0.3514 (6)	0.4806 (5)	0.6168 (4)	0.0549 (12)
C6	0.3156 (5)	0.6165 (5)	0.5922 (4)	0.0516 (12)
C7	0.1691 (6)	0.8025 (4)	0.4495 (4)	0.0573 (13)
C8	0.2583 (7)	0.9084 (5)	0.5340 (4)	0.077 (2)

Table 2. *Selected geometric parameters (Å, °)*

N1—O2	1.210 (5)	O7—C7	1.209 (5)
N1—O1	1.217 (5)	C1—C7	1.494 (6)
N1—C3	1.467 (6)	C7—C8	1.472 (6)
O2—N1—O1	123.1 (4)	C2—C3—N1	118.9 (4)
O2—N1—C3	118.1 (5)	C4—C3—N1	119.2 (4)
O1—N1—C3	118.8 (4)	O7—C7—C8	121.6 (4)
C2—C1—C7	119.3 (4)	O7—C7—C1	118.8 (4)
C6—C1—C7	121.9 (4)	C8—C7—C1	119.6 (4)
C2—C1—C7—O7	7.9 (7)	C2—C1—C7—C8	−170.6 (4)
C6—C1—C7—O7	−170.6 (4)	C6—C1—C7—C8	10.8 (7)

H atoms were placed at expected positions, riding. One value of $U_{\rm iso}$ was refined for H2, another for all the other H atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*, *SETANG* (Enraf–Nonius, 1989). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL*93.

We thank Zeneca Specialties for funding.

Lists of structure factors, torsion angles, contact distances, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1154). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Lactone Derived from an Amino Acid with a Cyclohexyl Skeleton: (1*S*,6*R*,9*S*)-6-Benzamido-9-hydroxymethyl-8-oxabicyclo[4.3.0]non-3-en-7-one

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Abstract

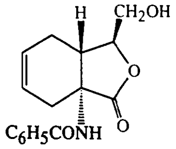
In the title compound, $C_{16}H_{17}NO_4$, the five-membered lactone ring is *trans*-fused to the cyclohexene ring. The cyclohexene ring exhibits a half-chair conformation with the benzamido group in an axial position. The γ-butyrolactone adopts an envelope conformation with the hydroxymethyl substituent in a pseudo-equatorial position. The crystal structure is stabilized by two intermolecular hydrogen bonds (O—H···O and N—H···O) involving the benzamido and hydroxy groups.

Comment

The use of uncommon amino-acid residues in the synthesis of peptides with restricted conformational flexibility has acquired increasing importance in the design of specifically folded analogues of biologically active peptides (Giannis & Kolter, 1993; Liskamp, 1994). Cyclic amino-acid analogues have proved valuable in the construction of conformationally constrained peptide backbones (Holladay *et al.*, 1991; Kazmierski *et al.*, 1988; Hsieh, LaHann & Speth, 1989). In this context, we are interested in the asymmetric synthesis, by Diels–Alder reaction, of new amino-acid derivatives having a cyclic skeleton (Buñuel, Cativiela & Díaz-de-Villegas, 1995).

In the course of experiments directed at the synthesis of cyclic amino-acid analogues having a cyclohexane skeleton, we have found that the isolation of cycloadducts resulting from the reaction between (*Z*)-4-[(*S*)-2,2-dimethyl-1,3-dioxolan-4-ylmethylene]-2-phenyl-5(4*H*)-oxazolone and 1,3-butadiene in the presence of $LiClO_4$ under certain conditions afforded an unexpected byproduct whose chemical and spectroscopic data pointed to a cyclic lactone derived from one of the initially formed cycloadducts. The X-ray analysis was carried out in order to determine unambiguously the absolute configuration at the two new chiral C atoms formed in the Diels–Alder reaction and also to confirm the structure previously assigned to this unexpected compound on the basis of chemical and spectroscopic evidence.

The molecular structure for the title lactone, (I), is shown in Fig. 1. The X-ray analysis confirms the proposed molecular structure and establishes the stereochemistry at the two new chiral C1 and C4 atoms as *R* and *S*, respectively. The absolute configuration is deduced from the known *S* stereochemistry of the chiral centre at C3, which originates from (*R*)-isopropylideneglyceraldehyde; it could not be established from anomalous-dispersion effects in the present work.



(I)

The five-membered lactone ring is *trans*-fused to the cyclohexene ring; the torsion angles C2—C1—C4—C5 and C8—C1—C4—C3 have values of 168.3 (3) and 160.0 (3)°, respectively. The dihedral angle between the best least-squares planes through these two rings is 11.96 (18)°.

The cyclohexene ring exhibits a half-chair conformation [puckering parameters (Boeyens, 1978): Q = 0.529 (5) Å, θ = 50.5 (6), φ = 26.2 (8)°] in which the

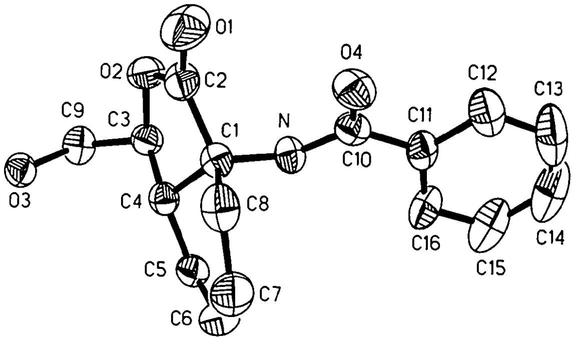


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids, with H atoms omitted for clarity.

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