Refinement

Refinement on F	Unit weights applied
$R = 0.047$	$(\Delta/\sigma)_{max} = 0.107$
$wR = 0.048$	$\Delta\rho_{max} = 0.198$ e Å^{-3}
$S = 0.537$	$\Delta\rho_{min} = -0.253$ e Å^{-3}
3014 reflections	Atomic scattering fac-
317 parameters	tors from *SHELX76*
All H-atom parameters	(Sheldrick, 1976)
refined	

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

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

	x	y	z	U_{eq}
O1	0.8274 (2)	0.2655 (2)	0.6225 (1)	0.050 (1)
O2	1.0589 (2)	0.4393 (2)	0.6625 (1)	0.049 (1)
O3	0.6994 (2)	1.1177 (2)	0.4878 (1)	0.061 (1)
N1	0.8109 (3)	0.9075 (2)	0.4054 (1)	0.047 (1)
C1	0.7555 (3)	0.7321 (2)	0.6019 (2)	0.036 (1)
C2	0.6329 (3)	0.6386 (2)	0.5826 (2)	0.043 (1)
C3	0.6554 (3)	0.4820 (2)	0.5893 (2)	0.042 (1)
C4	0.7985 (3)	0.4183 (2)	0.6153 (1)	0.034 (1)
C5	0.9214 (3)	0.5115 (2)	0.6364 (2)	0.033 (1)
C6	0.8995 (3)	0.6673 (2)	0.6287 (2)	0.035 (1)
C7	1.1712 (4)	0.5325 (3)	0.6986 (3)	0.073 (1)
C8	0.7294 (4)	0.9018 (2)	0.5975 (2)	0.049 (1)
C9	0.7460 (3)	0.9825 (2)	0.4913 (2)	0.041 (1)
C10	0.8285 (4)	0.9729 (3)	0.2992 (2)	0.058 (1)
C11	0.7364 (4)	0.8787 (3)	0.2392 (2)	0.050 (1)
C12	0.7338 (5)	0.9569 (3)	0.1339 (2)	0.071 (1)
C13	0.6511 (3)	0.8642 (3)	0.0689 (2)	0.054 (1)
C14	0.4758 (4)	0.8269 (3)	0.1042 (2)	0.054 (1)
C15	0.3944 (3)	0.7448 (3)	0.0451 (2)	0.054 (1)
C16	0.4929 (4)	0.6990 (3)	−0.0532 (2)	0.057 (1)
C17	0.6674 (4)	0.7357 (3)	−0.0881 (2)	0.064 (1)
C18	0.7469 (4)	0.8167 (3)	−0.0280 (2)	0.063 (1)
C19	0.2038 (4)	0.7075 (5)	0.0884 (3)	0.082 (1)
C20	0.4126 (6)	0.6099 (4)	−0.1219 (3)	0.085 (1)

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

O1—C4	1.368 (2)	N1—C9	1.322 (3)
O2—C5	1.368 (2)	N1—C10	1.456 (3)
O2—C7	1.430 (3)	C1—C8	1.511 (3)
O3—C9	1.245 (2)	C8—C9	1.508 (3)
C5—O2—C7	116.0 (2)	O3—C9—N1	122.4 (2)
C9—N1—C10	123.4 (2)	O3—C9—C8	118.8 (2)
C1—C8—C9	118.1 (2)	N1—C9—C8	118.8 (2)

Intensity data were collected with a scan width of $\Delta\omega = (1.2 + 0.15\tan\theta)°$ (estimated from ω–θ plots). The counter aperture was also adjusted as a function of θ. The horizontal aperture width ranged from 2.0 to 3.1 mm, while the vertical one was set at 4 mm. All reflections were corrected for the usual Lp effects and decay compensation was applied.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN84* (Main, Germain & Woolfson, 1984). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN* (Fair, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including H-atom geometry, have been deposited with the IUCr (Reference: AS1152). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Dray, A. (1992). *Life Sci.* **51**, 1759–1765.
Enraf–Nonius (1989). *CAD-4 Software.* Version 5. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kim, Y. B., Kim, J. A. & Park, I. Y. (1993). *Arch. Pharm. Res.* **16**, 134–139.
Kim, Y. B., Park, I. Y. & Lah, W. R. (1990). *Arch. Pharm. Res.* **13**, 166–173.
Kistenmacher, T. J. & Marsh, R. E. (1972). *J. Am. Chem. Soc.* **94**, 1340–1345.
Main, P., Germain, G. & Woolfson, M. M. (1984). *MULTAN84. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univ. of York, England.
Park, N.-S., Ha, D.-C., Choi, J.-K., Kim, H.-S., Lim, H.-J. & Lee, B.-Y. (1991). *Korean J. Med. Chem.* **1**, 36–43.
Park, N.-S., Ha, D.-C., Kim, H.-S. & Choi, J.-K. (1991). *Korean J. Med. Chem.* **1**, 2–7.
Park, N.-S., Park, I. Y., Choi, J. & Kim, Y. B. (1995a). In preparation.
Park, N.-S., Park, I. Y., Choi, J.-K. & Kim, Y. B. (1995b). In preparation.
Park, N.-S., Park, I. Y. & Kim, Y. B. (1995). In preparation.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.
Suzuki, T. & Iwai, K. (1984). *The Alkaloids*, Vol. XXIII, edited by A. Brossi, pp. 227–299. Orlando: Academic Press.

Stereochemistry of Asymmetric β-Lactam Formation Involving Achiral Glyoxylamide Derivatives

DAISUKE HASHIZUME, HIDENORI KOGO, AKIKO SEKINE AND YUJI OHASHI

*Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan*

HISAKAZU MIYAMOTO AND FUMIO TODA

Department of Applied Chemistry, Ehime University, Matsuyama, Ehime 790, Japan

(Received 2 June 1994; accepted 1 November 1994)

Abstract

The crystals of three glyoxylamide compounds, N,N-diisopropyl(o-methylphenyl)glyoxylamide, $C_{15}H_{21}NO_2$, N,N-diisopropyl(p-methylphenyl)glyoxylamide, $C_{15}H_{21}$-
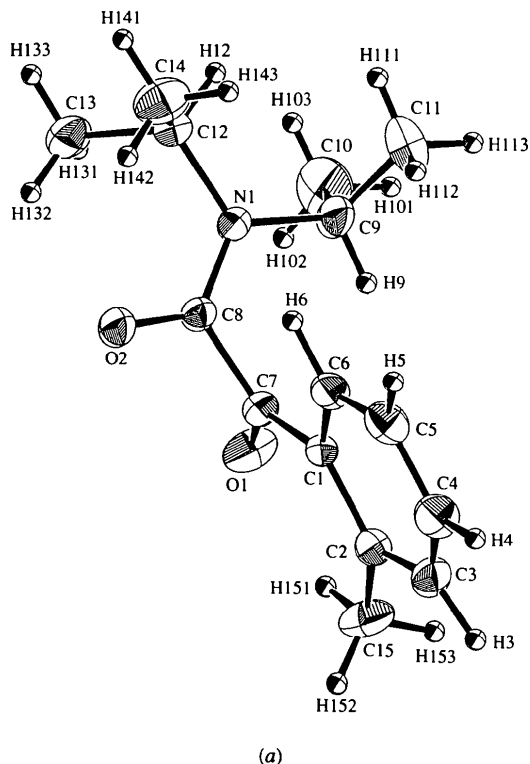
NO₂, and N,N-diisopropyl(m,p-dimethylphenyl)glyoxyl-amide, $C_{16}H_{23}NO_2$, have been analyzed by X-ray structure analysis. In each compound, the two carbonyl groups have a twisted conformation. This results in a short contact between the C atom of one of the carbonyl groups and the C atom of an isopropyl group. On exposure to visible light, a bond may form between these two C atoms and a β-lactam with a four-membered ring is produced. These results are consistent with those observed in the related glyoxylamide containing no methyl substituents.

Comment

When an optically active compound is obtained from an inactive starting material, the route may be an excellent method for the synthesis of chiral compounds. Recently, we discovered that either enantiomer of chiral crystals of N,N-diisopropylphenylglyoxylamide (1) is transformed to β-lactam (2) in the solid state on exposure to visible light in high optical purity and good chemical yield (Toda, Yagi & Soda, 1987). In order to clarify the mechanism, the crystal structures of compounds (1a) and (2) were determined by X-ray structure analysis (Sekine, Hori, Ohashi, Yagi & Toda, 1989). The mechanism was clearly explained from the
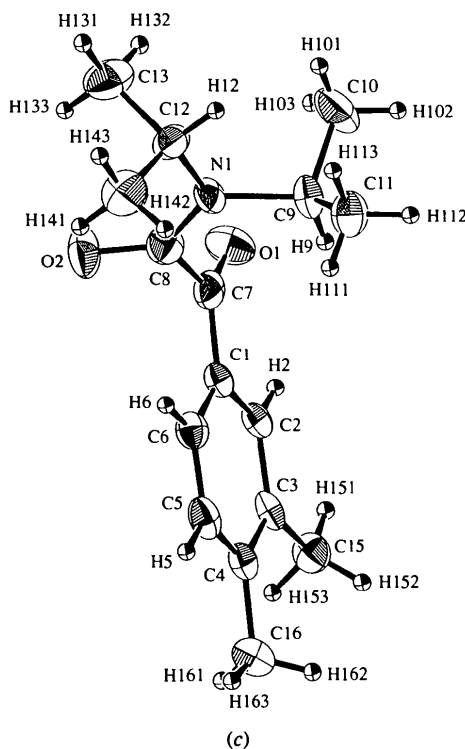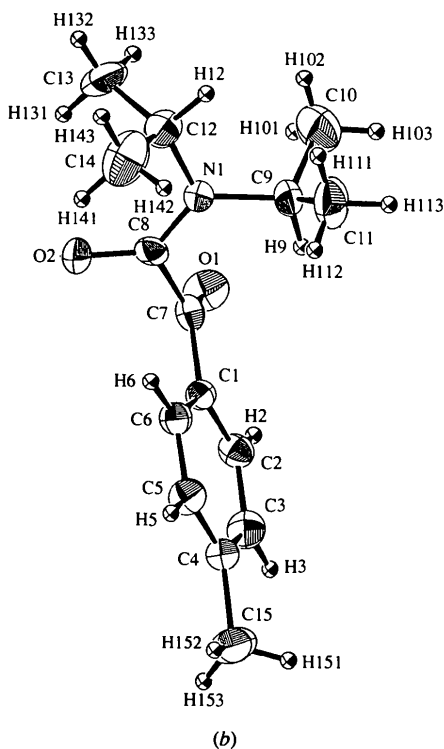

Fig. 1. The molecular structures of (a) N,N-diisopropyl(o-methylphenyl)glyoxylamide, (b) N,N-diisopropyl(p-methylphenyl)glyoxyl-amide, and (c) N,N-diisopropyl(m,p-dimethylphenyl)glyoxylamide. Non-H atoms are shown as displacement ellipsoids of 30% probability.

topochemical point of view on the basis of the two analyzed structures. In order to ascertain the mechanism more precisely, a methyl group was substituted onto the phenyl ring. The *o*-methyl (1*b*) and *p*-methyl (1*c*) derivatives, along with the *m,p*-dimethyl (1*d*) derivative, were prepared. This work reports the structures of these three compounds.

(1a) X = Y = Z = H
(1b) X = Me, Y = Z = H
(1c) X = Y = H, Z = Me
(1d) X = H, Y = Z = Me

(2)
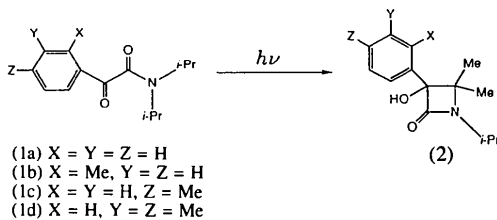
The molecular conformations are very similar to that of compound (1*a*). The torsion angles O1—C7—C8—O2, C7—C8—N1—C9 and C8—N1—C9—C10 are in good agreement with each other in all four molecules; values are 88.1, −5.1 and 115.3° for compound (1*a*), 94.3 (5), −5.2 (6) and 114.0 (5)° for compound (1*b*), 98.1 (7), −7.2 (8) and 110.4 (6)° for compound (1*c*), and 101.2 (12), −8.8 (14) and 109.0 (10)° for compound (1*d*). Short C7···C9 and O1···H9 contacts result in distances of 2.871 (5), 2.847 (7), 2.868 (8) and 2.832 (13) Å, and 2.78 (5), 2.72 (4), 2.70 and 2.68 Å, respectively, for compounds (1*a*), (1*b*), (1*c*) and (1*d*). In the process of the photocyclization, atom H9 would be easily extracted by atom O1, thus forming a new bond between atoms C7 and C9. The reaction would proceed topochemically. Although the absolute configurations have not been determined, the β-lactams with four-membered rings thus obtained from the three title glyoxylamides should be *S*.

Experimental

Compound (1*b*) was synthesized according to Corson, Dodge, Harris & Hazen (1967), compound (1*c*) according to Corson, Dodge, Harris, & Yeaw (1967) and compound (1*d*) according to Fischer, Oehme & Schellenberger (1967). All crystals for X-ray analysis were obtained from the methanol solutions of the corresponding compounds.

Compound (1*b*)

Crystal data

$C_{15}H_{21}NO_2$
$M_r = 247.34$
Orthorhombic
$P2_12_12_1$
$a = 13.6382 (5)$ Å
$b = 13.9275 (8)$ Å
$c = 7.7297 (4)$ Å
$V = 1468.2 (1)$ Å^3
$Z = 4$
$D_x = 1.12$ Mg m^{-3}

Cu *Kα* radiation
$λ = 1.54178$ Å
Cell parameters from 18 reflections
$θ = 22–27°$
$μ = 0.55$ mm^{-1}
$T = 296$ K
Parallelepiped
$0.5 × 0.4 × 0.4$ mm
Colourless

Data collection

AFC-4 diffractometer
$ω–2θ$ scans
Absorption correction: none
1383 measured reflections
1383 independent reflections
1329 observed reflections
$[|F_o| > 3σ(|F_o|)]$

$θ_{max} = 62.5°$
$h = 0 → 18$
$k = 0 → 18$
$l = 0 → 11$
3 standard reflections
monitored every 50 reflections
intensity decay: <1.0%

Refinement

Refinement on *F*
$R = 0.055$
$wR = 0.067$
$S = 8.69$
1329 reflections
183 parameters
H3, H5, H6, H9 and H12 were refined isotropically; other H atoms were fixed

$w = 1/σ^2(|F_o|)$
$(Δ/σ)_{max} = 0.038$
$Δρ_{max} = 0.17$ e Å^{-3}
$Δρ_{min} = −0.25$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	*y*	*z*	U_{eq}
O1	0.2258 (3)	0.3086 (3)	1.0243 (5)	0.0674
O2	0.3566 (3)	0.1344 (2)	0.9477 (4)	0.0545
N1	0.3677 (3)	0.1760 (2)	1.2326 (5)	0.0396
C1	0.3859 (3)	0.3583 (3)	0.9312 (5)	0.0359
C2	0.3592 (3)	0.4473 (3)	0.8576 (6)	0.0452
C3	0.4359 (4)	0.5039 (4)	0.7899 (7)	0.0540
C4	0.5311 (4)	0.4738 (4)	0.7941 (7)	0.0582
C5	0.5567 (4)	0.3875 (4)	0.8663 (7)	0.0545
C6	0.4844 (3)	0.3301 (4)	0.9351 (6)	0.0447
C7	0.3126 (3)	0.2923 (3)	1.0118 (6)	0.0402
C8	0.3494 (3)	0.1932 (3)	1.0651 (6)	0.0380
C9	0.3609 (5)	0.2535 (4)	1.3632 (7)	0.0600
C10	0.2770 (6)	0.2347 (5)	1.4898 (9)	0.0977
C11	0.4592 (6)	0.2692 (5)	1.4546 (9)	0.1038
C12	0.3972 (4)	0.0791 (3)	1.2919 (7)	0.0446
C13	0.3192 (4)	0.0039 (4)	1.2504 (8)	0.0678
C14	0.4972 (4)	0.0516 (4)	1.2187 (9)	0.0741
C15	0.2566 (4)	0.4819 (4)	0.8441 (7)	0.0659

Table 2. *Selected geometric parameters* (Å, °) *for* (1*b*)

O1—C7	1.209 (6)	N1—C12	1.481 (6)
O2—C8	1.226 (5)	C1—C7	1.494 (6)
N1—C8	1.340 (6)	C7—C8	1.527 (6)
N1—C9	1.481 (6)		
C8—N1—C9	121.1 (4)	C1—C7—C8	116.7 (4)
C8—N1—C12	120.8 (4)	O2—C8—N1	125.5 (4)
C9—N1—C12	118.1 (4)	O2—C8—C7	115.5 (4)
O1—C7—C1	125.0 (4)	N1—C8—C7	118.9 (4)
O1—C7—C8	118.0 (4)		

Compound (1*c*)

Crystal data

$C_{15}H_{21}NO_2$
$M_r = 247.34$
Orthorhombic
Pbca
$a = 15.438 (2)$ Å
$b = 15.343 (2)$ Å
$c = 12.685 (1)$ Å

Cu *Kα* radiation
$λ = 1.54178$ Å
Cell parameters from 18 reflections
$θ = 20–24°$
$μ = 0.53$ mm^{-1}
$T = 296$ K

$V = 3004.7$ (6) Å^3

$Z = 8$

$D_x = 1.09$ Mg m^{-3}

Parallelepiped

0.4 × 0.3 × 0.2 mm

Colourless

Data collection

AFC-4 diffractometer

ω–2θ scans

Absorption correction:
none

2390 measured reflections

2390 independent reflections

1459 observed reflections
$[|F_o| > 6\sigma(|F_o|)]$

$\theta_{max} = 62.5°$

$h = 0 \rightarrow 18$

$k = 0 \rightarrow 18$

$l = 0 \rightarrow 15$

3 standard reflections
monitored every 50
reflections
intensity decay: <1.7%

Refinement

Refinement on F

$R = 0.081$

$wR = 0.074$

$S = 6.30$

1459 reflections

163 parameters

H atoms were placed in
fixed positions

$w = 1/\sigma^2(|F_o|)$

$(\Delta/\sigma)_{max} = 0.009$

$\Delta\rho_{max} = 0.23$ e Å^{-3}

$\Delta\rho_{min} = -0.28$ e Å^{-3}

Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1c)

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

	x	y	z	U_{eq}
O1	0.6227 (3)	0.0030 (3)	0.8549 (3)	0.0816
O2	0.5965 (2)	−0.1189 (2)	0.6614 (3)	0.0635
N1	0.7374 (3)	−0.0770 (3)	0.6806 (4)	0.0532
C1	0.5787 (3)	0.0827 (4)	0.7037 (5)	0.0460
C2	0.5492 (4)	0.1529 (4)	0.7622 (5)	0.0576
C3	0.5107 (4)	0.2223 (4)	0.7120 (6)	0.0652
C4	0.5019 (4)	0.2241 (4)	0.6044 (6)	0.0603
C5	0.5316 (4)	0.1537 (4)	0.5466 (5)	0.0626
C6	0.5697 (4)	0.0830 (4)	0.5943 (5)	0.0535
C7	0.6188 (4)	0.0089 (4)	0.7583 (5)	0.0532
C8	0.6525 (4)	−0.0684 (4)	0.6926 (5)	0.0474
C9	0.8005 (4)	−0.0098 (4)	0.7173 (5)	0.0651
C10	0.8522 (5)	−0.0428 (5)	0.8101 (6)	0.1153
C11	0.8565 (4)	0.0254 (4)	0.6295 (6)	0.0979
C12	0.7734 (4)	−0.1558 (4)	0.6271 (6)	0.0698
C13	0.7466 (4)	−0.2383 (4)	0.6873 (7)	0.1139
C14	0.7514 (5)	−0.1593 (5)	0.5134 (6)	0.1073
C15	0.4584 (4)	0.3011 (4)	0.5474 (6)	0.0956

Table 4. *Selected geometric parameters* (Å, °) *for* (1c)

O1—C7	1.230 (8)	N1—C12	1.494 (8)
O2—C8	1.227 (7)	C1—C7	1.464 (8)
N1—C8	1.327 (7)	C7—C8	1.540 (8)
N1—C9	1.493 (8)		
C8—N1—C9	122.7 (5)	C1—C7—C8	118.8 (5)
C8—N1—C12	120.0 (5)	O2—C8—N1	126.6 (5)
C9—N1—C12	117.3 (4)	O2—C8—C7	115.1 (5)
O1—C7—C1	123.3 (6)	N1—C8—C7	118.2 (5)
O1—C7—C8	117.8 (5)		

Compound (1d)

Crystal data

$C_{16}H_{23}NO_2$

$M_r = 261.36$

Monoclinic

$P2_1$

$a = 16.300$ (8) Å

$b = 6.331$ (2) Å

$c = 7.461$ (2) Å

$\beta = 95.31$ (5)°

$V = 766.6$ (5) Å^3

$Z = 2$

$D_x = 1.13$ Mg m^{-3}

Cell parameters from 18
reflections

$\theta = 20$–25°

$\mu = 0.55$ mm^{-1}

$T = 296$ K

Parallelepiped

0.5 × 0.5 × 0.2 mm

Colourless

Data collection

AFC-4 diffractometer

ω–2θ scans

Absorption correction:
none

1347 measured reflections

1347 independent reflections

1312 observed reflections
$[|F_o| > 3\sigma(|F_o|)]$

$\theta_{max} = 62.5°$

$h = -21 \rightarrow 21$

$k = 0 \rightarrow 9$

$l = 0 \rightarrow 11$

3 standard reflections
monitored every 50
reflections
intensity decay: <0.9%

Refinement

Refinement on F

$R = 0.061$

$wR = 0.062$

$S = 9.73$

1312 reflections

171 parameters

H atoms were placed in
fixed positions

$w = 1/\sigma^2(|F_o|)$

$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.18$ e Å^{-3}

$\Delta\rho_{min} = -0.23$ e Å^{-3}

Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1d)

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

	x	y	z	U_{eq}
O1	0.7840 (4)	0.4582	0.6848 (10)	0.0793
O2	0.7288 (4)	0.7909 (19)	0.9636 (7)	0.0824
N1	0.6750 (4)	0.8566 (18)	0.6770 (8)	0.0536
C1	0.8850 (5)	0.718 (2)	0.7540 (10)	0.0478
C2	0.9490 (6)	0.591 (2)	0.7026 (10)	0.0456
C3	1.0311 (5)	0.658 (2)	0.7135 (10)	0.0499
C4	1.0506 (5)	0.8630 (19)	0.7788 (10)	0.0492
C5	0.9850 (6)	0.990 (2)	0.8297 (11)	0.0576
C6	0.9054 (6)	0.924 (2)	0.8191 (11)	0.0494
C7	0.8015 (6)	0.6379 (19)	0.7361 (11)	0.0576
C8	0.7326 (5)	0.773 (2)	0.7968 (12)	0.0618
C9	0.6895 (6)	0.837 (2)	0.4765 (10)	0.0626
C10	0.6263 (7)	0.676 (2)	0.3883 (14)	0.0926
C11	0.6798 (6)	1.061 (2)	0.3859 (12)	0.0754
C12	0.6011 (5)	0.959 (2)	0.7238 (12)	0.0611
C13	0.5518 (6)	0.805 (3)	0.8317 (15)	0.0898
C14	0.6197 (6)	1.167 (2)	0.8297 (15)	0.0839
C15	1.0985 (6)	0.515 (2)	0.6573 (12)	0.0630
C16	1.1374 (5)	0.940 (2)	0.7971 (12)	0.0690

Table 6. *Selected geometric parameters* (Å, °) *for* (1d)

O1—C7	1.225 (12)	N1—C12	1.440 (13)
O2—C8	1.257 (11)	C1—C7	1.447 (13)
N1—C8	1.344 (12)	C7—C8	1.512 (15)
N1—C9	1.541 (10)		
C8—N1—C9	117.0 (8)	C1—C7—C8	119.5 (10)
C8—N1—C12	124.4 (7)	O2—C8—N1	121.8 (9)
C9—N1—C12	118.6 (7)	O2—C8—C7	117.0 (9)
O1—C7—C1	122.8 (10)	N1—C8—C7	121.0 (8)
O1—C7—C8	117.4 (9)		

Since the crystallizability of compound (1c) was poor the *R* value obtained was slightly high.

For all compounds, program(s) used to solve structures: *MITHRIL* (Gilmore, 1984); program(s) used to refine structures: *ORFLS* (Busing, Martin & Levy, 1962); molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, and torsion angles have been deposited with the IUCr (Reference: AS1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS. Fortran Crystallographic Function and Error Program.* Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

Corson, B. B., Dodge, R. A., Harris, S. A. & Hazen, R. K. (1967). *Org. Synth. Coll.* **1**, 241–245.

Corson, B. B., Dodge, R. A., Harris, S. A. & Yeaw, J. S. (1967). *Org. Synth. Coll.* **1**, 336–340.

Fischer, G., Oehme, G. & Schellenberger, A. (1971). *Tetrahedron*, **27**, 5683–5696.

Gilmore, C. J. (1984). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data.* Department of Chemistry, Univ. of Glasgow, Scotland.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Sekine, A., Hori, K., Ohashi, Y., Yagi, M. & Toda, F. (1989). *J. Am. Chem. Soc.* **111**, 697–699.

Toda, F., Yagi, M. & Soda, S. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1413–1414.

---

p-Anisidinium Dihydrogénophosphate

Fatma Ben Amor, El Hassane Soumhi, Mohamed Ould Abdellahi et Tahar Jouini

Département de Chimie, Faculté des Sciences, 1060 Campus Universitaire, Tunis, Tunisia

Abstract

The structure of *p*-anisidinium dihydrogenphosphate, $C_7H_{10}NO^+.H_2PO_4^-$, is composed of inorganic layers of $(H_2PO_4)^-$ anions parallel to the (001) plane alternating with organic layers comprising $(CH_3O—C_6H_4—NH_3)^+$ cations. The $(H_2PO_4)^-$ groups are linked together by strong O—H···O—P bonds and are connected to the organic cations by weak N—H···O—P bonds. All these hydrogen bonds ensure the cohesion and stability of the structure.

Commentaire

La structure, (I), présente une alternance de couches inorganiques $(H_2PO_4)^-$ et organiques $(CH_3OC_6H_4NH_3)^+$, parallèles aux plans (001) (Fig. 1). Dans le premier type de couche les anions $(H_2PO_4)^-$ sont reliés entre

$$CH_3O—\langle\rangle—\overset{+}{N}H_3 \quad H_2PO_4^-$$

(I)
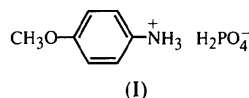
eux par des liaisons hydrogène de type O—H···O—P; HO3···O1(1 − *x*, −*y*, 1 − *z*) 1,81 (3) et HO4···O2 ($\frac{1}{2}$ + *x*, $\frac{1}{2}$ − *y*, *z*) 1,89 (3) Å. Les valeurs extrêmes des distances P—O, P—O2 1,499 (1) et P—O4 1,561 (2) Å, sont en accord avec celles rencontrées pour des composés voisins (Averbuch-Pouchot, Durif & Guitel, 1988; Averbuch-Pouchot, 1993; Ohama, Machida, Nakamura & Kunifuji, 1987). Les cations organiques sont orientés perpendiculairement aux couches inorganiques et leur sont liés par des liaisons hydrogène de type N—H···O—P exercées par les trois protons du groupement —NH3: H1N···O2($\frac{1}{2}$ − *x*, *y* − $\frac{1}{2}$, 1 − *z*) 1,79 (3), H2N···O1 2,02 (3) et H3N···O1(*x* − $\frac{1}{2}$, $\frac{1}{2}$ − *y*, *z*) 1,94 (3) Å.
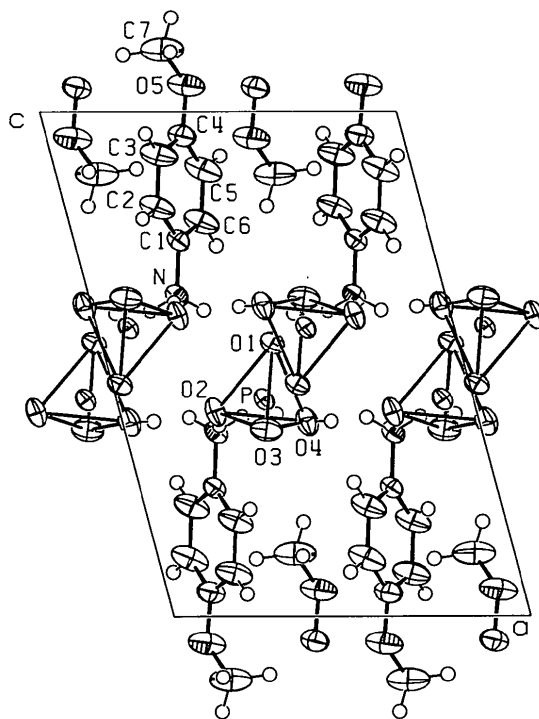

Fig. 1. Projection selon la direction [010] de la structure du *p*-anisidinium dihydrogénophosphate. Les ellipsoïdes thermiques correspondent à 50% de probabilité. Les atomes d'hydrogène sont représentés par des cercles de diamètres arbitraires.