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

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

	x	y	z	$U_{\rm eq}$
S(1)	0.35062 (8)	0.64888 (6)	0.05172 (7)	0.0748
C(1)	0.3516 (2)	0.5789 (2)	0.0214 (2)	0.0604
N(1)	0.3530 (2)	0.5297 (2)	−0.0004 (2)	0.0823
S(2)	0.16997 (7)	0.69593 (9)	−0.25357 (8)	0.0901
C(2)	0.0965 (3)	0.6766 (3)	−0.2637 (3)	0.0730
N(2)	0.0470 (3)	0.6661 (3)	−0.2716 (3)	0.1172
N(11)	0.3539 (2)	0.4045 (2)	−0.0486 (2)	0.0525
C(11)	0.4063 (2)	0.3722 (2)	−0.0120 (2)	0.0602
C(12)	0.4625 (2)	0.4147 (3)	−0.0190 (3)	0.0857
C(13)	0.4216 (3)	0.3082 (2)	−0.0397 (3)	0.0863
C(14)	0.3850 (3)	0.3681 (3)	0.0554 (2)	0.0791
C(15)	0.3201 (3)	0.3405 (3)	0.0639 (3)	0.0892
C(16)	0.2719 (3)	0.3789 (3)	0.0282 (2)	0.0774
C(17)	0.2855 (2)	0.3828 (2)	−0.0416 (2)	0.0580
C(18)	0.2470 (2)	0.4339 (2)	−0.0730 (2)	0.0731
C(19)	0.2748 (3)	0.3209 (2)	−0.0756 (3)	0.0765
N(21)	0.0903 (2)	0.6635 (2)	0.0211 (2)	0.0578
C(21)	0.1122 (2)	0.6450 (2)	0.0864 (2)	0.0571
C(22)	0.0579 (3)	0.6607 (3)	0.1293 (2)	0.0815
C(23)	0.1695 (3)	0.6839 (3)	0.1053 (2)	0.0797
C(24)	0.1257 (3)	0.5754 (2)	0.0857 (3)	0.0756
C(25)	0.1690 (3)	0.5561 (3)	0.0329 (3)	0.0903
C(26)	0.1406 (3)	0.5739 (3)	−0.0303 (3)	0.0882
C(27)	0.1268 (2)	0.6431 (2)	−0.0367 (2)	0.0630
C(28)	0.1853 (3)	0.6829 (3)	−0.0452 (3)	0.0869
C(29)	0.0824 (3)	0.6558 (3)	−0.0908 (2)	0.0906

Table 2. *Geometric parameters* (Å, °)

S(1)—C(1)	1.632 (6)	C(17)—C(18)	1.525 (6)
C(1)—N(1)	1.153 (6)	C(17)—C(19)	1.528 (6)
S(2)—C(2)	1.638 (6)	N(21)—C(21)	1.532 (5)
C(2)—N(2)	1.096 (6)	N(21)—C(27)	1.530 (6)
N(11)—C(11)	1.533 (6)	C(21)—C(22)	1.520 (6)
N(11)—C(17)	1.541 (6)	C(21)—C(23)	1.535 (6)
C(11)—C(12)	1.514 (7)	C(21)—C(24)	1.515 (7)
C(11)—C(13)	1.527 (6)	C(24)—C(25)	1.522 (7)
C(11)—C(14)	1.521 (7)	C(25)—C(26)	1.534 (7)
C(14)—C(15)	1.518 (7)	C(26)—C(27)	1.513 (7)
C(15)—C(16)	1.525 (7)	C(27)—C(28)	1.523 (7)
C(16)—C(17)	1.531 (6)	C(27)—C(29)	1.527 (7)
N(1)—C(1)—S(1)	179.2 (5)	C(19)—C(17)—C(18)	109.1 (4)
N(2)—C(2)—S(2)	177.0 (7)	C(27)—N(21)—C(21)	120.9 (4)
C(17)—N(11)—C(11)	120.5 (4)	C(22)—C(21)—N(21)	105.4 (4)
C(12)—C(11)—N(11)	105.0 (4)	C(23)—C(21)—N(21)	110.3 (4)
C(13)—C(11)—N(11)	111.1 (4)	C(23)—C(21)—C(22)	109.2 (4)
C(13)—C(11)—C(12)	109.2 (5)	C(24)—C(21)—N(21)	107.5 (4)
C(14)—C(11)—N(11)	107.2 (4)	C(24)—C(21)—C(22)	111.6 (4)
C(14)—C(11)—C(12)	111.6 (4)	C(24)—C(21)—C(23)	112.5 (4)
C(14)—C(11)—C(13)	112.5 (5)	C(25)—C(24)—C(21)	112.9 (5)
C(15)—C(14)—C(11)	114.3 (5)	C(26)—C(25)—C(24)	110.6 (5)
C(16)—C(15)—C(14)	110.3 (5)	C(27)—C(26)—C(25)	113.6 (5)
C(17)—C(16)—C(15)	113.2 (5)	C(26)—C(27)—N(21)	107.7 (4)
C(16)—C(17)—N(11)	107.0 (4)	C(28)—C(27)—N(21)	110.9 (4)
C(18)—C(17)—N(11)	104.7 (4)	C(28)—C(27)—C(26)	113.4 (5)
C(18)—C(17)—C(16)	111.7 (4)	C(29)—C(27)—N(21)	104.5 (4)
C(19)—C(17)—N(11)	110.9 (4)	C(29)—C(27)—C(26)	111.4 (5)
C(19)—C(17)—C(16)	113.2 (4)	C(29)—C(27)—C(28)	108.6 (4)

Table 3. *Contact distances* (Å)

N(1)···H(111)	1.929	N(2)···H(211$^{\rm ii}$)	1.909
S(1)···H(112$^{\rm i}$)	2.413	S(2)···H(212$^{\rm iii}$)	2.647

Symmetry codes: (i) $\frac{3}{4} - y, x + \frac{1}{4}, z + \frac{1}{4}$; (ii) $y - \frac{3}{4}, \frac{3}{4} - x, -\frac{1}{4} - z$; (iii) $\frac{3}{4} - y, x + \frac{3}{4}, -\frac{1}{4} - z$.

We thank the National Science Foundation and Office of Naval Research for partial financial support.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71473 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1074]

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Acta Cryst. (1994). C**50**, 95–97

Structure of 8-(4-Acetylphenyl)-1,4-dioxa-8-azaspiro[4.5]decane: a New Potential Non-linear Optical Material

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(*Received* 23 *April* 1993; *accepted* 26 *July* 1993)

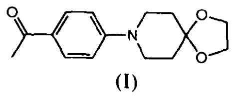
Abstract

The crystals of the title compound (APDA), $C_{15}H_{19}NO_3$, which belong to a non-centrosymmetric space group $Pna2_1$, show significant second harmonic generation efficiency and no absorption for light with a wavelength longer than 400 nm.

Acta Crystallographica Section C
ISSN 0108-2701 © 1994

Comment

In the course of our continuing efforts to produce organic nonlinear optical materials for use in an effective second harmonic generation (SHG) device of a diode laser (Ogawa, Yoshimura, Kaji, Kagawa & Kakuta, 1992; Ogawa, Yoshimura, Takeuchi, Katritzky & Murugan, 1992), it was found that the title compound (I) is a potential candidate. It was obtained as non-centrosymmetric crystals from the reaction of *p*-fluoroacetophenone with 1,4-dioxa-8-azaspiro[4.5]decane. It showed a powder SHG efficiency 12 times that of urea for a fundamental wavelength of 1064 nm of an Nd^{3+}:YAG laser and showed no absorption at wavelengths longer than 400 nm.



(I)

The molecular and crystal structures are shown in Figs. 1 and 2, respectively. All bond lengths and angles are normal. The dihedral angle between the acetyl group and the benzene ring deviates slightly from 0° [5 (1)°]. The piperidine ring adopts a chair conformation, as expected. The dihedral angle between the benzene ring and the least-squares plane of the piperidine ring, in which the N atom has a pyramidal geometry, is −26.6 (6)°. The molecules are arranged in the same direction in the crystals so that the longest molecular axis is along the twofold screw axis parallel to the *c* axis. Such molecular packing effectively contributes to the large nonlinear optical susceptibility of crystalline APDA.

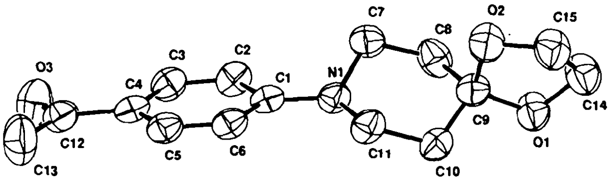


Fig. 1. Perspective view of the title compound. Non-H atoms are represented by thermal ellipsoids with 50% probability.

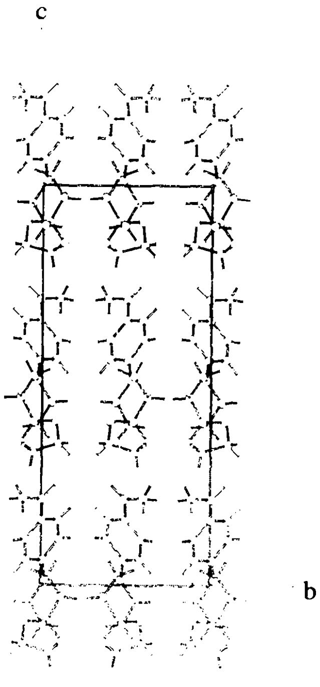


Fig. 2. The crystal structure viewed along the *a* axis, drawn by *MindTool* (Tirado-Rives & Blake, 1990).

Experimental

Crystal data

$C_{15}H_{19}NO_3$
M_r = 261.32
Orthorhombic
$Pna2_1$
a = 6.875 (1) Å
b = 9.036 (1) Å
c = 21.676 (2) Å
V = 1346.5 (3) $Å^3$
Z = 4
D_x = 1.289 Mg m^{-3}
D_m = 1.295 (8) Mg m^{-3}
Density measured by flotation in aq. KBr solution

X-ray tube Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 36.74–39.81°
μ = 0.69 mm^{-1}
T = 296 K
Rectangular
0.35 × 0.3 × 0.3 mm
Colourless

Data collection

Rigaku AFC-6*A* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1067 measured reflections
1034 independent reflections
1000 observed reflections [$I_{net} > 2\sigma(I_{net})$]

R_{int} = 0.009
θ_{max} = 60°
h = 0 → 7
k = 0 → 10
l = 0 → 24
3 standard reflections monitored every 150 reflections
intensity variation: none

Refinement

Refinement on F
R = 0.051
wR = 0.067
S = 3.575
1000 reflections
247 parameters
H atoms not restrained
$w = 1/[\sigma^2(F) + 0.0002F^2]$
$(\Delta/\sigma)_{max}$ = 0.201

$\Delta\rho_{max}$ = 0.244 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.480 e $Å^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, 2.2B, 2.3.1)

Data collection: *MSC/AFC Diffractometer Control Software* (Rigaku Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *Xtal DIFDAT, ADDREF, SORTRF* (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *Xtal CRYLSQ* (Hall, Flack & Stewart, 1992). Molecular graphics: *Xtal*; *ORTEP* (Johnson, 1965); *MindTool* (Tirado-Rives & Blake, 1990). Software used to prepare material for publication: *Xtal BONDLA, CIFIO* (Hall, Flack & Stewart, 1992).

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

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

	x	y	z	U_{eq}
C1	0.2041 (7)	0.5124 (5)	0.5631 (5)	0.042 (2)
C2	0.2238 (8)	0.6072 (5)	0.6148 (5)	0.051 (3)
C3	0.0936 (8)	0.6019 (5)	0.6634 (5)	0.052 (3)
C4	−0.0607 (7)	0.5028 (5)	0.6640 (5)	0.047 (3)
C5	−0.0784 (8)	0.4061 (5)	0.6137 (5)	0.050 (3)
C6	0.0489 (7)	0.4109 (5)	0.5648 (5)	0.048 (3)
C7	0.5353 (8)	0.5460 (7)	0.5240 (5)	0.056 (3)
C8	0.6302 (8)	0.6238 (6)	0.4702 (5)	0.059 (3)
C9	0.5940 (7)	0.5436 (5)	0.4098 (5)	0.049 (2)
C10	0.3798 (8)	0.5148 (6)	0.4012 (5)	0.050 (3)
C11	0.2882 (9)	0.4400 (6)	0.4573 (5)	0.051 (3)
C12	−0.2007 (9)	0.5061 (6)	0.7159 (5)	0.058 (3)
C13	−0.363 (1)	0.393 (1)	0.7184 (6)	0.093 (6)
C14	0.8275 (9)	0.5534 (7)	0.3331 (5)	0.067 (4)
C15	0.797 (1)	0.3956 (6)	0.3524 (6)	0.066 (3)
N1	0.3269 (6)	0.5263 (4)	0.5132 (5)	0.046 (2)
O1	0.6643 (6)	0.6275 (4)	0.3589 (5)	0.062 (2)
O2	0.7031 (6)	0.4087 (4)	0.4104 (5)	0.067 (2)
O3	−0.1877 (8)	0.5990 (6)	0.7558 (5)	0.083 (3)

The starting materials *p*-fluoroacetophenone (1) and 1,4-dioxa-8-azaspiro[4.5]decane (2) were purchased from Aldrich Chemical Company, Inc. A mixture of (1) (47 ml, 0.39 mol), (2) (50 g, 0.35 mol) and potassium carbonate (70 g, 0.51 mol) in dimethyl sulfoxide (150 ml) was stirred vigorously with heating at 323 K for 30 h. Then, the reaction mixture was extracted with ethyl acetate and the organic layer was washed with water. Evaporation of the extract gave a pale-yellow solid. This was recrystallized from ethyl acetate. The single crystals for the X-ray measurements were obtained from slow evaporation of acetone solution at room temperature. ^{1}H NMR($CDCl_3$): δ 7.86 (*d*, 9.4 Hz, 2H), 6.88 (*d*, 9.4 Hz, 2H), 4.00 (*s*, 4H), 3.51 (*dd*, 7.7 Hz, 3.9 Hz, 4H), 2.52 (*s*, 3H), 1.80 (*dd*, 7.7 Hz, 3.9 Hz, 4H). λ_{max}(CH_2Cl_2) = 326 nm (ε = 4.46×10^4). Elemental analysis for $C_{15}H_{19}NO_3$: found C 69.0, H 7.52, N 5.44%; calculated C 68.9, H 7.33, N 5.36%. M.p. 396-397 K.

The powder SHG efficiency was measured by the techinique of Kurtz & Perry (1968) using a 1064 nm *Q*-switched Nd^{3+}:YAG laser (10 Hz, 8 ns pulse duration).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71525 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1039]

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Acta Cryst. (1994). C**50**, 97–100

Structure Analysis of Monoamine Oxidase Inhibitors, (*R*)-5-Hydroxymethyl- and (*R*)-5-Methoxymethyl-3-(4-methoxyphenyl)oxazolidin-2-one

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(*Received* 1 *October* 1992; *accepted* 11 *June* 1993)

Abstract

X-ray single-crystal structures of two recently synthesized inhibitors of monoamine oxidase (MAO) belonging to the aryloxazolidinone family are reported. The first compound is (*R*)-5-hydroxymethyl-3-(4-methoxyphenyl)oxazolidin-2-one, $C_{11}H_{13}NO_4$ (I) and the second is (*R*)-5-methoxymethyl-3-(4-methoxyphenyl)oxazolidin-2-one, $C_{12}H_{15}NO_4$ (II). Both compounds show coplanarity between the phenyl and oxazolidinone rings and electronic delocalization between the heteroatoms of the oxazolidinone moiety as indicated by the bond lengths. The crystal packing is assumed to be by van der Waals interactions. Cohesion is increased in the structure of (I) by the presence of hydrogen bonds.

Comment

This communication is part of a more general study on the structural properties of monoamine oxidase inhibitors (MAOIs) of the oxazolidinone family. Some of these compounds have an antidepressant activity and are therapeutic agents. The selectivity and the reversibility of these inhibitors towards the A and B forms of the enzyme depend on the nature of the substituents (Wouters *et al.*, 1992).

In this study, we have considered the (*R*)-5-hydroxymethyl- (I) and the (*R*)-5-methoxymethyl-3-(4-methoxyphenyl)oxazolidin-2-one (II). Compounds

Acta Crystallographica Section C
ISSN 0108-2701 © 1994