

O—P—O8	114.9 (2)	C1—C2—1	123.4 (3)
O—P—O9	118.8 (2)	C3—C2—1	117.3 (3)
O—P—C7	112.2 (2)	O7—C7—C1	124.0 (4)
O8—P—O9	102.9 (2)	O7—C7—P	114.2 (3)
O8—P—C7	104.0 (2)	C1—C7—P	121.7 (3)
O9—P—C7	102.3 (2)	I···O ⁱ —P ⁱ	129.3 (2)
P—O8—C8	121.1 (3)	O ⁱ ···I—C2	176.7 (1)
P—O9—C9	121.9 (3)	O ⁱ ···I···O7	109.96 (8)
C2—C1—C7	123.3 (3)	O7···I—C2	66.9 (1)
C6—C1—C7	117.7 (4)		
O—P—C7—O7	-94.6 (3)	C6—C1—C7—P	-25.4 (5)
O—P—C7—C1	82.7 (3)	C6—C1—C7—O7	151.7 (4)
O8—P—C7—O7	30.1 (3)	O7···I···O ⁱ —P ⁱ	-131.6 (2)
O8—P—C7—C1	-152.6 (3)	C2—I···O ⁱ —P ⁱ	-115 (2)
O9—P—C7—O7	137.0 (3)	O ⁱ ···I···O7—C7	157.5 (3)
O9—P—C7—C1	-45.7 (3)	C2—I···O7—C7	-21.5 (3)
C2—C1—C7—P	156.3 (3)	O ⁱ ···I—C2—C1	-5 (2)
C2—C1—C7—O7	-26.6 (6)	O ⁱ ···I—C2—C3	172 (2)

Symmetry code: (i) $x, y, z - 1$.

Table 2. Comparative I···O distances and acute dihedral angles (δ) in 2-iodobenzoyl derivatives

CODE ^a	R factor	d(I···O) (Å)	δ (°)
IBBIOX01 ^b	0.09	3.07	6.1
OIBZAC ^c	0.08	3.09	16.7
Title compound	0.03	3.09	26.2
INPHAC ^d	0.06	3.10	19.4
IBRBPX ^e	0.05	3.18	28.8
IBBIOX ^f	0.13	3.20 ^l	43.7
DIBZPO ^g	0.13	3.25	48.3
DIBZPO ^h	0.13	3.25	21.5
IBNZAM ^h	0.10	3.27	46.7
FUMZES ⁱ	0.09	3.28	62.0
IBBIOX ^j	0.13	3.30 ^l	53.2
ICBOYP ^j	0.14	3.33	53.3
FUMZES ^k	0.09	3.64	84.9
LSDIBZ ^l	0.04	3.71	84.1

Notes: (a) Cambridge Structural Database reference codes; (b) 1-(2'-iodobenzoyloxy)-1,2-benziodoxolin-3-one, β -form (Gougoutas & Clardy, 1972); (c) *o*-iodobenzoic acid (Gougoutas, 1977); (d) 3-iodo-2-naphthoic acid (Gougoutas & Toeplitz, 1977); (e) 2-iodo-3'-bromodibenzoyl peroxide, β -form (Gougoutas & Chang, 1979); (f) 1-(2'-iodobenzoyloxy)-1,2-benziodoxolin-3-one, α -form (Gougoutas & Clardy, 1972); (g) 2,2'-diiododibenzoyl peroxide (Gougoutas & Clardy, 1970); (h) *o*-iodobenzamide (Nakata, Tateno & Sakurai, 1976); (i) (3S)-(-)-N-(2,3-dihydro-1-methyl-2-oxo-5-phenyl-1H-1,4-benzodiazepin-3-yl)-2-iodobenzene-carboxamide (Bock *et al.*, 1987); (j) 2-iodo-3'-chlorodibenzoyl peroxide (Gougoutas & Lessinger, 1973); (k) lysergic acid diethylamide *o*-iodobenzoate (Baker, Chothia, Pauling & Weber, 1972); (l) contact to singly bound oxygen.

The final Fourier difference map showed four positive and three negative peaks lying near the I atom (distances 0.91–0.99 Å for positive and 1.07–1.69 Å for negative peaks) in an approximate plane perpendicular to the phenyl-iodine plane. All other peaks were of height $< 0.5 e \text{ \AA}^{-3}$.

Data collection: *CAD-4 Manual* (Enraf-Nonius, 1988). Cell refinement: *CAD-4 Manual*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN* and *SHELXL93* (Sheldrick, 1993). Molecular graphics: *MolEN*. Software used to prepare material for publication: *SHELXL93*.

We wish to acknowledge the use of the EPSRC Chemical Database Service at Daresbury and the EPSRC for a Research Studentship to JEH.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1305). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Baker, R. W., Chothia, C., Pauling, P. & Weber, H. P. (1972). *Science*, **178**, 614–615.
- Bock, M. G., DiPardo, R. M., Evans, B. E., Rittle, K. E., Veber, D. F., Freidinger, R. M., Hirshfield, J. & Springer, J. P. (1987). *J. Org. Chem.* **52**, 3232–3239.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Breuer, E. (1996). *The Chemistry of Organophosphorus Compounds*, Vol. 4, edited by F. R. Hartley, ch. 7, pp. 656–729. New York: Wiley.
- Donohue, J. & Mandel, N. (1981). *J. Cryst. Mol. Struct.* **11**, 189–196.
- Enraf-Nonius (1988). *CAD-4 Manual*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
- Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
- Gougoutas, J. Z. (1977). *Cryst. Struct. Commun.* **6**, 703–706.
- Gougoutas, J. Z. & Chang, K. H. (1979). *Cryst. Struct. Commun.* **8**, 977–980.
- Gougoutas, J. Z. & Clardy, J. C. (1970). *Acta Cryst.* **B26**, 1999–2008.
- Gougoutas, J. Z. & Clardy, J. C. (1972). *J. Solid State Chem.* **4**, 230–242.
- Gougoutas, J. Z. & Lessinger, L. (1973). *J. Solid State Chem.* **7**, 175–185.
- Gougoutas, J. Z. & Toeplitz, B. K. (1977). *Cryst. Struct. Commun.* **6**, 331–334.
- Nakata, K., Tateno, T. & Sakurai, K. (1976). *Mem. Osaka Kyoiku Univ.* **25**, 61–64.
- Nakazawa, H., Nosaka, H., Kushi, Y. & Yoneda, H. (1990). *Organometallics*, **9**, 1958–1963.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1997). **C53**, 1464–1466

2-(3-Nitrophenyl)-1,3-dioxolane at 150 K

MICHAEL BOLTE, RAIMUND MARX AND MARIA SCHOLTYSSIK

Institut für Organische Chemie der Universität Frankfurt, Marie-Curie Strasse II, 60439 Frankfurt/Main, Germany. E-mail: bolte@chemie.uni-frankfurt.de

(Received 30 January 1997; accepted 13 May 1997)

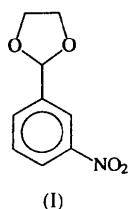
Abstract

The title compound, C₉H₉NO₄, is an intermediate in the synthesis of polyvinylaminobenzaldehyde azo dyes. The dioxolane ring displays an envelope conformation

with the tertiary C atom deviating from the plane of the remaining four atoms. The nitro group is only slightly twisted out of the plane of the phenyl ring. The intermolecular packing is stabilized by two C—H···O hydrogen bonds and two close N···O contacts. The X-ray structure analysis was undertaken to ascertain the nature and conformation of a reaction product.

Comment

In the synthesis of polyvinylaminobenzaldehyde azo dyes (Minami & Kojima, 1954; McQueen & Woodward, 1946; Martin, 1947), the title compound, (I), is catalytically reduced with hydrogen at elevated temperatures and pressures. The resulting aminobenzaldehyde acetal is reacted with an amide-forming derivative of a colour-former acid. The product, a colour-forming amidobenzaldehyde acetal, for example an azo dye, can be used to synthesize polyvinylaminobenzaldehyde azo dyes.



The bond lengths and angles of (I) (Fig. 1) are as expected. The dioxolane ring shows an envelope conformation [$q_2 = 0.36$ and $\varphi_2 = 355.2$ (Cremer & Pople, 1975)] with O2, C3, C4 and O5 in a common plane (r.m.s. deviation 0.015 Å) and C1 0.537(1) Å above it. The phenyl ring forms an angle of 54.95(4)° with the four coplanar atoms of the dioxolane ring and an angle of 10.99(5)° with the nitro group. The intermolecular packing is stabilized by two C—H···O hydrogen bonds [O13A···C16ⁱ 3.577(1), O13A···H16ⁱ 2.764(1) Å and O13A···H16ⁱ—C16ⁱ 144.02(3)°; O13B···C14ⁱⁱ 3.628(1), O13B···H14ⁱⁱ 2.828(1) Å and O13B···H14ⁱⁱ—C14ⁱⁱ 142.52(3)°] and close contacts between the N atom and the two dioxolane O atoms [N13···O2ⁱⁱⁱ 3.053(1) Å and N13···O5^{iv} 2.917(1) Å; symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x, 1 - y, -z$; (iii) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (iv) $x + \frac{1}{2}, y, \frac{1}{2} - z$].

A search of the Cambridge Structural Database (Allen & Kennard, 1993) yielded only one molecule containing a phenyldioxolane group (Halwax & Vollenkle, 1983). A comparison of this structure with (I) shows that in both structures the dioxolane ring exhibits an envelope conformation where the tertiary C atom deviates from the plane of the remaining four atoms. The distance between this C atom and the plane (0.4204 Å) is similar to that in (I), and the angle between the plane formed by the four atoms and the plane of the phenyl ring (51.1°) is close to that in (I).

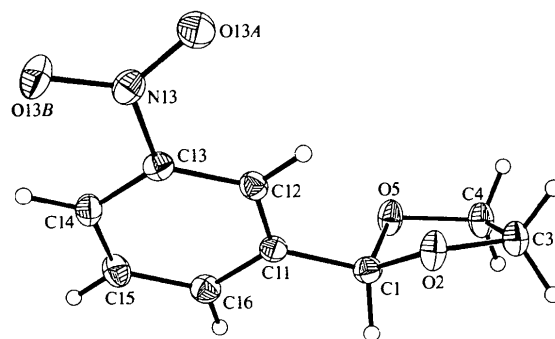


Fig. 1. A perspective view of the title compound with the atom-numbering scheme; displacement ellipsoids are at the 50% probability level.

Experimental

Following Fieser, Fields & Lieberman (1944), the title compound was synthesized by acetalization of *m*-nitrobenzaldehyde by removal of water from an acid-catalyzed mixture of *m*-nitrobenzaldehyde, 1,2-ethylene glycol and a water-entraining solvent. A solution of 0.11 mol of 1,2-ethylene glycol and 0.5 g of *p*-toluenesulfonic acid in 150 ml of benzene was refluxed under a take-off condenser for about 1 h. 0.1 mol of dry *m*-nitrobenzaldehyde was added and the mixture again refluxed under a take-off condenser for 2 h. The dry solution was evaporated *in vacuo*. The residue was a white crystalline solid (m.p. 326–327 K). For purification, it was recrystallized from ethanol and a second time from tetrachloromethane. The product was dried *in vacuo* (m.p. 330–331 K, yield: 85%). Physical and spectral data of the title compound have been published by Horodniak, Wright & Indictor (1971) and Indictor, Horodniak, Jaffe & Miller (1969).

Crystal data

C₉H₉NO₄
 $M_r = 195.17$
 Orthorhombic
Pbca
 $a = 7.8931(2)$ Å
 $b = 11.9354(3)$ Å
 $c = 18.0705(4)$ Å
 $V = 1702.37(7)$ Å³
 $Z = 8$
 $D_x = 1.523$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 8192 reflections
 $\theta = 1-25^\circ$
 $\mu = 0.122$ mm⁻¹
 $T = 133$ K
 Block
 $0.65 \times 0.55 \times 0.40$ mm
 Colourless

Data collection

Siemens CCD three-circle diffractometer
 ω scans
 Absorption correction: empirical using *SADABS* (Sheldrick, 1996a)
 $T_{\min} = 0.777, T_{\max} = 1.000$
 22234 measured reflections
 1725 independent reflections

1557 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\text{max}} = 26.37^\circ$
 $h = -9 \rightarrow 7$
 $k = -14 \rightarrow 14$
 $l = -22 \rightarrow 22$
 419 standard reflections
 frequency: 660 min
 intensity decay: none

Refinement

Refinement on F^2	$\Delta\rho_{\max} = 0.321 \text{ e } \text{\AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$\Delta\rho_{\min} = -0.196 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.080$	Extinction correction:
$S = 1.056$	<i>SHELXL96</i> (Sheldrick, 1996b)
1725 reflections	Extinction coefficient:
128 parameters	0.0156 (14)
H atoms: see below	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.5702P]$	<i>International Tables for Crystallography</i> (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\max} < 0.001$	

The data collection nominally covered over a sphere of reciprocal space, by a combination of nine sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω . The crystal-to-detector distance was 5.94 cm. Coverage of the unique set is over 99% complete to at least 26° in θ . Crystal decay was monitored by repeating the initial 100 frames of the first run at the end of data collection and analyzing the duplicate reflections. The data were corrected for Lorentz and polarization effects. All H atoms could be located by difference Fourier synthesis and were refined with fixed individual displacement parameters [$U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model with C—H(aromatic) = 0.95, C—H(secondary) = 0.99 or C—H(tertiary) = 1.0 \AA .

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996b). Molecular graphics: *XP in SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1235). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Fieser, L. F., Fields, M. & Lieberman, S. (1944). *J. Biol. Chem.* **156**, 191–201.
- Halwax, E. & Vollenkle, H. (1983). *Monatsh. Chem.* **114**, 687–698.
- Horodniak, J. W., Wright, J. & Indictor, N. (1971). *Org. Mass Spectrom.* **5**, 1287–1293.
- Indictor, N., Horodniak, J. W., Jaffe, H. & Miller, D. (1969). *J. Chem. Eng. Data*, **14**, 76–78.
- McQueen, D. M. & Woodward, D. W. (1946). US Patent 2 481 434. Assignors to El du Pont de Nemours & Company, Wilmington, USA.
- Martin, E. L. (1947). US Patent 2 513 189. Assignor to El du Pont de Nemours & Company, Wilmington, USA.
- Minami, E. & Kojima, S. (1954). *J. Chem. Soc. Jpn Ind. Chem. Sect.* **57**, 826–827.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1996a). *SADABS. Program for Empirical Absorption Correction of Area Detector Data*. University of Göttingen, Germany.
- Sheldrick, G. M. (1996b). *SHELXL96. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1995). *SMART and SAINT. Data Collection and Processing software for the SMART System*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1997). **C53**, 1466–1468

(1R,2S,4S,11S)-4-Isopropyl-1-methyl-2-(α -N-morpholino-3-methoxybenzyl)cyclohexan-3-one†

MEVLÛT ERTAN,^a AKGÜL YEŞİLADA,^a BIRSEN TOZKOPARAN,^a ÇELİK TARIMCI,^b BERNT KREBS^c AND MECHTILD LÄGE^c

^aDepartment of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Hacettepe, 06100 Ankara, Turkey, ^bDepartment of Engineering Physics, Faculty of Sciences, University of Ankara, 06100 Besevler, Ankara, Turkey, and ^cWestfälische Wilhelms Universität, Anorganisch Chemisches Institut, D-48149 Münster, Germany. E-mail: tarimci@eros.science.ankara.edu.tr

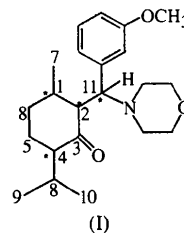
(Received 30 May 1996; accepted 2 April 1997)

Abstract

The title compound, C₂₂H₃₃NO₃, was obtained by reacting (1R,4S)-2-(3-methoxybenzylidene)-1-methyl-4-isopropylcyclohexane-3-one (*E/Z* 68/31%), obtained from (–)-menthone and 3-methoxybenzaldehyde by Claisen–Schmidt condensation, with morpholine by Michael-type addition. The structure was elucidated by IR and ¹H NMR spectral analyses, and the stereochemistry was obtained through an X-ray diffraction study. The absolute configurations of the four chiral centres were determined as 1R, 2S, 4S and 11S. Both the cyclohexane and N-morpholino rings were found to be in chair conformations.

Comment

The title compound, (I), was synthesized in two steps according to a previous method used for synthesizing some aminobenzylcyclohexanols (Özarlan, Ertan, Sayraç, Akgün, Demirdamar & Gümüsel, 1994).



The stereochemistry of one of these compounds, which are ciramadol analogues with opiate analgesic activity, (1R,4S)-2-(α -N-pyrrolidino-3-benzyl)-1-methyl-

† Alternative name: (1R,2S,4S,11S)-2-[(3-methoxyphenyl)(morpholino)methyl]-3-*p*-menthone.