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Acta Cryst. (1999). C**55**, 1154–1156

(Z)-*N*-Benzyl-2,3-dihydro-2-(2-methoxybenzylidene)-4*H*-1,4-benzoxazine

Susim Maiti,[a] Monika Mukherjee,[a] Gopeswar Chaudhuri,[b] Madeleine Helliwell[c] and Nitya G. Kundu[b]

[a]*Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India,* [b]*Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India, and* [c]*Department of Chemistry, University of Manchester, Manchester M13 9PL, England. E-mail: sspmm@mahendra.iacs.res.in*

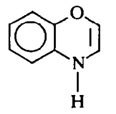
(*Received 12 February 1999; accepted 26 February 1999*)

Abstract

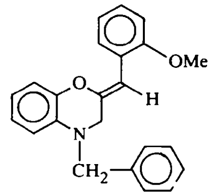
In the title compound, $C_{23}H_{21}NO_2$, the molecule contains three essentially planar benzo rings (*A*, *B* and *C*) and displays the *Z*-configuration. The six-membered oxazine ring adopts a half-boat conformation and is fused to phenyl ring *A*. The dihedral angle between the planar part of the oxazine moiety and ring *A* is 4.70 (6)°. A strong conjugation effect is reflected in the C—O [1.377 (3)–1.385 (3) Å] and C—N [1.396 (2) Å] bond lengths.

Comment

Benzoxazine, (1), a heterocyclic ring system, is present in many natural products (Sainsbury, 1984). Substituted benzoxazines have attracted considerable attention for their therapeutic, antioxidant and stabilizing activities (Abood *et al.*, 1997; Mylari *et al.*, 1990; Palmer *et al.*, 1988). As part of our on-going study of heterocyclic systems of biological importance (Chaudhuri *et al.*, 1998; Khan *et al.*, 1998), we have synthesized the title compound, (2), *via* a palladium-catalysed reaction between 2-methoxyiodobenzene and 2-(*N*-benzyl-*N*-prop-2-ynyl)aminophenyl tosylate. The present X-ray structural study of (2) was undertaken in order to establish the regio- and stereoselectivities of the reaction.



(1)



(2)

The structure of (2) contains discrete molecules separated by normal van der Waals distances. The molecular dimensions (Table 1) are comparable with those in related structures (Chamontin *et al.*, 1998; Lubini & Wouters, 1996; Millini *et al.*, 1993).

The *Z*-configuration of the molecule, with a methoxyphenyl group on the C*sp*^{2} atom of the oxazine ring, is established by the C7—C8—C9—O1 torsion angle of −1.8 (3)°. The three aromatic rings *A* (C11–C16), *B* (C2–C7) and *C* (C18–C23) exhibit the expected planar geometries, with a maximum deviation of 0.007 (3) Å for an in-plane atom (C22) from the corresponding least-squares plane through the endocyclic atoms. The dihedral angles *A*/*B*, *A*/*C* and *B*/*C* are 23.95 (6), 84.82 (6) and 102.54 (6)°, respectively. The six-membered heterocyclic ring (C9, C10, N, C16, C11 and O1) adopts an approximately half-boat conformation and is fused to the phenyl ring *A*. Atoms C10 and C11 lie on the same side of the best plane through C9, O1, C16 and N, with displacements of 0.606 (2) and 0.082 (2) Å, respectively.

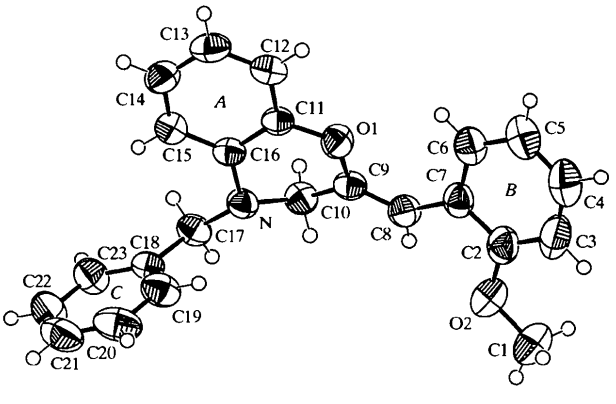


Fig. 1. *ORTEP*II (Johnson, 1976) view of molecule (2). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

Acta Crystallographica Section C
ISSN 0108-2701 © 1999

The dihedral angle between the planar part of the oxazine moiety and the phenyl ring *A* is 4.70 (6)°. The *cis* orientation of C1—O2 with respect to C2—C3 about the O2—C2 bond [C1—O2—C2—C3 = −6.7 (4)°] results in repulsion between the C1 and C3 atoms, and because of this the O2—C2—C3 bond angle is increased by about 10° compared with O2—C2—C7 (Sakaki *et al.*, 1976).

The π-electron delocalization of the aromatic rings extends its influence to the adjacent atoms. This is reflected in the bond lengths and torsion angles involving atoms N, O1 and O2. The C16—N bond length of 1.396 (2) Å is significantly shorter than C10—N [1.465 (2) Å] and C17—N [1.456 (2) Å]; the C—N single bond and C=N double bond distances are 1.48 and 1.28 Å, respectively (Allen *et al.*, 1987). Similarly, the observed C—O bond lengths [C11—O1 1.385 (2), C9—O1 1.385 (2) and C2—O2 1.377 (3) Å] (Table 1) are shorter than a C—O single bond (1.43 Å) and longer than a C=O double bond (1.23 Å) (Allen *et al.*, 1987), indicating that O1 and O2 are conjugated with the π-electron systems of the neighbouring benzene rings. The C14—C15—C16—N [178.5 (2)°], O1—C11—C12—C13 [−178.2 (2)°] and O2—C2—C3—C4 [179.9 (2)°] torsion angles indicate a nearly planar configuration.

Experimental

A mixture of 2-methoxyiodobenzene (1.76 mmol), 2-(*N*-benzyl-*N*-prop-2-ynylamino)phenyl tosylate (2.11 mmol), $(PPh_3)_2PdCl_2$ (0.05 mmol) and CuI (0.09 mmol) in triethylamine (7 ml) was stirred for 16 h at room temperature. The product obtained after usual work-up was cyclized by refluxing with KOH/H_2O (15 equivalents KOH in 3 ml H_2O) in ethanol for 8 h to yield the title compound, (2). Single crystals suitable for X-ray analysis were obtained by slow crystallization from a dilute solution of (2) in a light petroleum (333–353 K)/ether mixture (1:1).

Crystal data

$C_{23}H_{21}NO_2$
$M_r = 343.41$
Monoclinic
$P2_1/c$
$a = 12.103\ (1)$ Å
$b = 5.630\ (1)$ Å
$c = 26.795\ (1)$ Å
$\beta = 93.655\ (6)°$
$V = 1822.1\ (4)$ Å^3
$Z = 4$
$D_x = 1.252$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 30–40°$
$\mu = 0.628$ mm^{-1}
$T = 296.2$ K
Prism
0.45 × 0.35 × 0.15 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans

2486 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$

Absorption correction: empirical (North *et al.*, 1968)
$T_{min} = 0.817$, $T_{max} = 0.910$
3249 measured reflections
3102 independent reflections

$\theta_{max} = 78.18°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 6$
$l = -34 \rightarrow 33$
3 standard reflections every 150 reflections intensity decay: <1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.120$
$S = 1.079$
3102 reflections
235 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.3786P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.133$ e Å^{-3}
$\Delta\rho_{min} = -0.185$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C11	1.385 (2)	N—C10	1.465 (2)
O1—C9	1.385 (2)	C7—C8	1.456 (3)
O2—C2	1.377 (3)	C8—C9	1.327 (2)
O2—C1	1.401 (3)	C9—C10	1.487 (3)
N—C16	1.396 (2)	C11—C16	1.398 (2)
N—C17	1.456 (2)	C17—C18	1.513 (2)
C11—O1—C9	118.73 (14)	C9—C8—C7	130.2 (2)
C2—O2—C1	119.1 (2)	O1—C9—C10	115.62 (15)
C16—N—C10	111.81 (13)	N—C10—C9	110.17 (15)
O2—C2—C3	124.3 (2)	O1—C11—C16	121.74 (15)
O2—C2—C7	114.6 (2)	N—C17—C18	114.2 (2)
C1—O2—C2—C3	−6.7 (4)	C7—C8—C9—C10	174.6 (2)
O2—C2—C3—C4	179.9 (2)	O1—C11—C12—C13	−178.2 (2)
C5—C6—C7—C8	−177.9 (2)	C14—C15—C16—N	178.5 (2)
C3—C2—C7—C8	178.7 (2)	C16—N—C17—C18	−75.9 (2)
C7—C8—C9—O1	−1.8 (3)	C10—N—C17—C18	148.7 (2)

H atoms were refined using a riding model and their isotropic displacement parameters were set to 1.2 times (1.5 times for CH_3 groups) the equivalent displacement parameters of their parent atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1280). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1156–1158

Tris(prop-2-ynyl)ammonium chloride

Thomas Steiner,[a] Antoine M. M. Schreurs[b] and Jan Kroon[b]

[a]Institut für Kristallographie, Freie Universität Berlin, Takustraße 6, D-14195 Berlin, Germany, and [b]Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 Utrecht, The Netherlands. E-mail: steiner@chemie.fu-berlin.de

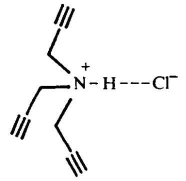
(*Received 11 February 1999; accepted 2 March 1999*)

Abstract

The title compound, $C_9H_{10}N^+\cdot Cl^-$, contains two symmetry-independent formula units in the unit cell. The independent organic cations have similar conformations and coordination geometries, whereas the chloride ions have very different coordination spheres. All six independent alkyne groups form $C\equiv C—H\cdots Cl^-$ hydrogen bonds, with $C\cdots Cl^-$ separations in the narrow range 3.46–3.63 Å.

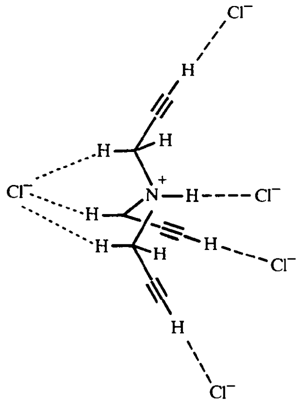
Comment

The title compound, (I), was prepared and its crystal structure determined in order to elucidate the hydrogen-bond interactions. Interest is focused especially on the three alkyne groups of the cation because $C\equiv C—H\cdots X$ hydrogen bonding often plays an important role in terminal alkynes (Steiner, 1998*a*).



(I)

The crystal structure of (I) contains two symmetry-independent formula units, as shown in Fig. 1. The conformations of the two cations are very similar, as are their coordination geometries with the chloride ions (Table 1). The bond lengths and angles are all normal. Each cation is in contact with five chloride ions, as shown in the Scheme below. The dominant $N^+—H\cdots Cl^-$ hydrogen bond and the three $C\equiv C—H\cdots Cl^-$ hydrogen bonds all have distances in the usual ranges (Steiner, 1998*b*). In addition, each cation forms a short contact to a chloride ion positioned opposite the N—H vector, leading to three $C—H\cdots Cl^-$ contacts. The two corresponding $N^+\cdots Cl^-$ separations are $N1\cdots Cl2 = 3.760\,(2)$ and $N2\cdots Cl2 = 3.832\,(2)$ Å, which are in the distance range typical of this interaction (Desiraju & Steiner, 1999).



In structures with more than one molecule or formula unit per asymmetric crystal unit ($Z' > 1$), it is of interest to see if this is associated with different conformations and intermolecular interactions. In (I), the conformation and immediate surroundings of the two organic cations are almost identical, but the two chloride ions have

Acta Crystallographica Section C
ISSN 0108-2701 © 1999