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ORIGINAL PAPER

Synthesis, Characterization, Structure, Ab Initio and DFT Calculations of 2-Amino-*N*-(3-phenylprop-2-enylidene)aniline

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Abstract New Schiff base compound 2-amino-*N*-(3-phenylprop-2-enylidene)aniline, **1**, was prepared by condensation of cinnamaldehyde with o-phenylenediamine and characterized by elemental analyses, UV–Vis and FT-IR spectroscopy. The crystal structure of **1** was determined by X-ray crystallography from single-crystal data and displays a *trans* configuration about the C=N double bond. In the crystal structure of 1, the molecule is located on an inversion center, so that it is disordered around the center of central C–C bond. The results from both the experimental and theoretical calculations are compared in this paper.

Keywords Schiff base · Spectroscopy · Crystallography · Disordered

Introduction

Schiff bases, having imine groups (–C=N–) and phenyl rings, have been widely studied as ligands in the development of coordination complexes of transition metals [1–4]. Schiff bases are typically formed by the condensation of a primary amine and an aldehyde [5, 6]. As reported in literature [7–9], the –C=N– functional group (called an imine) binds the metal ions via the lone pair of *N* atom. Recently, physical properties, such as thermal properties, of Schiff-base compounds in the crystalline state have been studied [10]. Schiff bases are also known to have biological activities [11, 12], to give dyes and pigments [13, 14] to have nonlinear optic [15, 16] and photochromic [17] effects and to be possible anion sensor [18]. Here, we present the synthesis, characterization, crystal structure and theoretical studies of the new Schiff base compound **1** (Fig. 1).

Experimental

General Procedures and Materials

All reagents and solvents for synthesis and spectroscopic studies were commercially available and used as received without further purification. The infrared spectrum was recorded on a PerkinElmer FT-IR spectrophotometer as a KBr pellet and electronic spectra was recorded on a JASCO 7580 spectrophotometer.

Synthesis of 2-Amino-*N*-(3-phenylprop-2-enylidene)aniline (**1**)

The Schiff base compound 2-amino-*N*-(3-phenylprop-2-enylidene)aniline (**1**) was obtained by stirring equimolar quantities of the cinnamaldehyde (132 mg, 1 mmol) and *o*-phenylenediamine (108 mg, 1 mmol) in 20 mL diethyl ether. The mixture was stirred at room temperature for 30 min to give a clear orange solution. Suitable crystals of **1** for X-ray study were formed by slow evaporation of diethyl ether over 3 days at 273 K (178 mg, yield 83%). Orange crystals. Yield: 83%. *Anal.* Calc. for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60%. Found: C, 81.09; H, 6.29; N, 12.63%. IR (KBr pellet, cm^{-1}): 3,480, 3,375 (s, NH_2), 2,926–3,056 (m, C–H aromatic and aliphatic), 2,854

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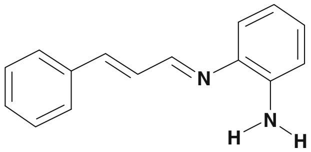

Fig. 1 Chemical diagram of the title compound **1**

(s, –HC=N), 1595 (s, C=N), 1,447–1,557 (m, C=C and C=N aromatic). UV–Vis [$CHCl_3$, λ_{max} (nm), log ε (M^{-1} cm^{-1})]: 295 (4.92), 386 (3.54).

X-ray Structure Determination of 2-Amino-*N*-(3-phenylprop-2-enylidene)aniline (**1**)

A single crystal of **1** with the dimensions 0.45 mm × 0.25 mm × 0.14 mm was chosen for X-ray diffraction study. Crystallographic measurements were done at 180 K with Rigaku RAXIS-RAPID II diffractometer, with Mo *Kα* radiation ($\lambda = 0.71075$ Å). The crystal structure was solved by direct methods and refined by full-matrix least-squares technique on F^2, using the SHELX-97 set of program [19]. The molecule was found to be located on a crystallographic inversion center and the asymmetric unit is half of the molecule. Since the molecular structure expected from the preparation process and the results of elemental analysis and IR spectra is not centrosymmetric, the location of the molecule on the inversion center in the crystal structure causes a twofold disorder with equal site occupancies. The disordered feature is also confirmed by the equivalent isotropic displacement parameter U_{eq} of the amino *N* atom. When the occupancy was set at 0.5 for the *N* atom, the U_{eq} value [0.0536(5) Å^2] was comparable with those [0.0409(3)–0.0455(3) Å^2] of C atoms, whose occupancies were set to one. However, when the occupancy of the *N* atom was set at one, assuming a symmetric molecule, the refinement resulted in the large U_{eq} value [0.0997(14) Å^2] for the *N* atom and worse *R* and *wR* factors [$R[F^2 > 2\sigma(F^2)] = 0.093$ $wR(F^2) = 0.3338$]. *C* atoms of the terminal phenyl group and those of the aminophenyl group could not be distinguished, but the imine *N* atom and the corresponding vinylene *C* atom (N2 and C7, respectively) were successfully refined with the occupancy of 0.5 as described below. Hydrogen atoms of the NH_2 group were located in a difference Fourier map and their positional parameters were refined with a distance restraint of N–H = 0.88(2) Å. Other hydrogen atoms were treated as riding. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as $1.2U_{eq}$ of the parent atom. Crystallographic data and details of the data collection and structure refinements are listed in Table 1. The molecular structure plots were prepared by ORTEP-3 [20].

Table 1 Crystal data and structural refinement for **1**

Empirical formula	$C_{15}H_{14}N_2$
Formula weight	222.29
Crystal system	Monoclinic
Space group	*C2/c*
a (Å)	26.667 (3)
b (Å)	5.6788 (7)
c (Å)	7.9307 (7)
β (deg)	92.288 (3)
V (Å^3)	1200.1 (2)
Z	4
D_x (Mg m^{-3})	1.230
μ (mm^{-1})	0.07
T_{min}	0.872
T_{max}	0.990
Measured reflections	8863
Independent reflections	1745
Parameters	97
Reflection with $I > 2\sigma(I)$	1382
R_{int}	0.071
Index range	$-37 \le h \le 37$
	$-7 \le k \le 7$
	$-9 \le l \le 11$
$R[F^2 > 2\sigma(F^2)]$	0.044
$wR(F^2)$	0.139

Ab Initio and DFT Calculations

The geometry of **1** has been optimized by using HF and DFT(B3LYP) model with the method at 6-31G basis set. All HF and DFT calculations were performed using the Gaussian 98 R-A.9 package [21].

Results and Discussion

The title compound, 2-amino-*N*-(3-phenylprop-2-enylidene)aniline, was obtained in high yield, 83%, by the condensation of cinnamaldehyde with o-phenylenediamine; it is stable in air in the solid state. The stability of **1** in solution depends on the solvent used. It is stable in methanol and acetonitrile solution at room temperature for about 3 days and at 273 K for 12 days. Also, they remain unchanged in chloroform and dichloromethane for about 20 h at room temperature and about 3 days at 273 K. The product, as orange crystals, was characterized by elemental analyses (CHN), UV–Vis and FT-IR spectroscopy.

FT-IR

The two sharp bands at *ca.* 3,480 and 3,375 cm^{-1} in the FT-IR spectrum of **1** can be attributed to stretching vibrations of NH_2 group. The characteristic band of the azomethine (C=N) group appears at 1,595 cm^{-1} in the FT-IR spectra. The spectrum of **1** also shows several bands corresponding to aromatic and aliphatic C–H stretching and aromatic C–C stretching.

UV–Vis

The UV–Vis spectrum of **1** in $CHCl_3$ shows two bands. The absorption band at 295 nm can be attributed to $\pi \rightarrow \pi^*$ transition in the benzene ring, while the absorption band observed at 386 nm can be attributed to $\pi \rightarrow \pi^*$ transition in the azomethine (C=N) group.

Description of the Crystal Structure of 1

The crystal structure of **1** has been studied by X-ray diffraction. An ORTEP view of **1** including the atom-numbering scheme is illustrated in Fig. 2. The molecule is located on an inversion center, resulting in a twofold disorder around the center of central C–C [C8–C8^i; symmetry code: (i) 1 − x, −y, −z] bond. A summary of bond lengths, angles and torsion angles of **1** are presented in Table 2.

The N(2)–C(8) bond length is in agreement with the double bond for the imine group, while the N(2)–C(1) and N(1)–C(2) bond lengths are in agreement with the single bonds for the amine groups. The H(1A) atom of NH_2 group is co-planar with the N=C group allowing the formation of a weak intramolecular N(1)–H(1A)···N(2) hydrogen bond between amine nitrogen atom and imine nitrogen atom, The N(1)···N(2) distance is 2.670(11) Å. The phenyl rings and the chain connecting are approximately coplanar.

Table 2 Selected bond lengths (Å), angles (°) and torsion angles (°) of **1**

Bond	Experimental *d*	HF/6-31G *d*	B3LYP/6-31G *d*
N(2)–C(8)	1.237(10)	1.268	1.300
N(2)–C(1)	1.416(8)	1.409	1.409
C(2)–N(1)	1.292(2)	1.269	1.270
C(7)–C(8)	1.368(12)	1.333	1.357
C(7)–C(1)	1.472(8)	1.470	1.462
C(8)–C(8^i)	1.443(2)	1.454	1.442
Angle	*ω*	*ω*	*ω*
C(8)–N(2)–C(1)	132.5(9)	124.8	124.87
N(1)–C(2)–C(3)	125.30(14)	121.4	122.13
N(1)–C(2)–C(1)	114.56(13)	119.8	118.85
C(8)–C(7)–C(1)	117.6(11)	119.5	120.58
N(2)–C(8)–C(8^i)	125.4(5)	121.2	121.06
C(7)–C(8)–C(8^i)	118.3(5)	122.5	122.87
Torsion	*ω*	*ω*	*ω*
N(1)–C(2)–C(1)–N(2)	−0.4(6)	−0.77	−0.006
C(8)–N(2)–C(1)–C(6)	−9.4(13)	−22.44	−0.105
N(2)–C(8)–C(8^i)–C(7)	179.9(5)	179.66	179.99
C(1)–N(2)–C(8)–C(8^i)	−178.3(7)	178.61	179.99
C(1)–C(7)–C(8)–C(8^i)	179.9(5)	179.86	179.99
C(8)–N(2)–C(1)–C(2)	171.7(8)	159.49	179.90

Symmetry codes: (i) −*x* + 1, −*y*, −*z*

Table 3 Calculated total energies and relative stabilities of four conformers of the title compound at various levels of the theory

	trans	*cis*
HF/6-31G(d)	−684.8025[a]	−684.8763
B3LYP/6-31G	−689.3497	−689.4217

[a] Total energies in hartree

Molecular conformation of **1** obtained from HF and DFT calculations and shows an excellent agreement with X-ray study. The calculated structural parameters of **1** are listed in Table 3. The small differences between the theoretical and experimental parameters can be attributed to the fact that the HF and DFT calculations were carried out with isolated molecules in the gaseous phase whereas the X-ray parameters were based on molecules in the solid state. In the gas phase the two isomers (*cis* and *trans*) for **1** were found. The structure and selected numbering of these isomers are presented in the Fig. 3.

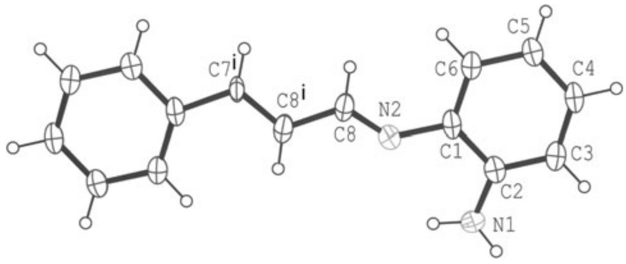

Fig. 2 An ORTEP diagram of **1**, showing 50% probability displacement ellipsoids. [Symmetry code: (i) 1 − x, −y, −z]

Ab Initio and DFT Studies

The results of calculated total energies and relative stabilities of two isomers of **1** are presented in the Table 3. In consistence with results obtained in the solid state, DFT calculations predict that in the gas phase isomer *trans* is the most stable ones. In addition based on DFT results a planar structure for the conformers was found.

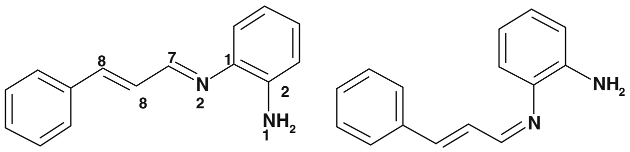

Fig. 3 The structure and selected numbering of two isomers (*trans* and *cis*) considered in the gas phase of **1**

Supplementary Material

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 760518. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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