



P-Dimethylaminobenzaldehyde semicarbazone: The bonding abilities of imine nitrogen atom

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ABSTRACT

The crystal and molecular structures of *p*-dimethylaminobenzaldehyde semicarbazone and *p*-dimethylaminobenzaldehyde semicarbazone hydrochloride have been determined. On the basis of quantum-mechanical calculations the availability of the imine nitrogen atom for bonding with molecular species was analysed and also the complete assignment of the experimental IR spectrum was performed. The *p*-dimethylaminobenzaldehyde semicarbazone was characterised by thermogravimetric analysis in conjunction with evolved gases in the air atmosphere.

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1. Introduction

Hydrazones are widely studied and used, attracting much attention because of their biological activity [1–5] and metal ion binding properties [6,7]. Most of them possess antimicrobial, anticancer, anti-inflammatory and antitoxic activities. They have also been studied as a group of the most useful spectrophotometric reagents because of their sensitivity and selectivity toward metal cations. In both cases the mechanism of action for these compounds has not yet been identified. These compounds have also advantage of obtaining by usage of “green” synthesis method: solventless conditions or recyclable medium, such as poly(propyleneglycol) [8].

The aryl semicarbazones show *inter alia* the anticonvulsant activity [9–11]. It is believed that the interaction mechanism at the binding site is related to the presence and properties of hydrogen-bonding area and hydrophobic binding site, as well as the presence of electron-rich atom/group attached at the *para* position of the aryl ring and electron donor moiety. The HOMO–LUMO energy gap is also considered [12]. The precise mechanism by which these compounds act is not well understood. Because only the three-dimensional model of GABA_A receptor proposed on the basis of the X-ray crystal structure of the Acetylcholine binding protein (AChBP) [13] is known, the search for structure–activity relationships continuously is an active area of investigation. It is supposed that the biological activity of a compound depends on energetically preferred conformation. Knowledge about charge distribution, geometrical parameters, stereoelectronic properties, conformation

flexibility is crucial to determine the mechanism of ligand–receptor interactions and pharmacophoric elements. For this purpose, the model compound possessing semicarbazono group – the *p*-dimethylaminobenzaldehyde semicarbazone (I) have been obtained and investigated. Since the hydrogen bonding is necessary for ligand activity the protonated form (II) was obtained to establish the primary site available for molecular interactions.

2. Experimental

2.1. Synthesis

The *p*-dimethylaminobenzaldehyde semicarbazone (I) and *p*-dimethylaminobenzaldehyde semicarbazone hydrochloride (II) were prepared by one pot synthesis of aldehyde with semicarbazide hydrochloride in methanol. A hot solution of semicarbazide hydrochloride (5 mmol) in methanol (30 ml) was added dropwise to a hot solution of *p*-dimethylaminobenzaldehyde (5 mmol) in methanol (30 ml). The mixture was refluxed for 2 h. The solution was then reduced by evaporation to half-volume and allowed to cool. After 1 day, red crystals were formed. Yield: 84%. The part of obtained product was dissolved in methanol–HCl solution (pH 2) and left to stand at 278 K. After 3 day, yellow crystals were formed.

2.2. X-ray crystallography

A crystal of (I) measuring 0.112 × 0.107 × 0.006 mm was mounted on a Bruker AXS Smart APEX CCD, and used for data

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collection, whereas the crystal of (II) measuring $0.289 \times 0.276 \times 0.103$ mm was mounted on a KM-4-CCD automatic diffractometer equipped with CCD detector diffractometer, and used for data collection. X-ray intensity data were collected with graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) at temperature 291.0 K, with ω scan mode. A 10 s, 7 s, respectively, exposure time was used and all reflections inside Ewald sphere were collected up to $2\theta = 50^\circ$ with scan width 0.4° . The unit cell parameters were determined from 3382, 2101 strongest reflections, respectively. Both crystals used for data collection did not change their appearance. Lorentz, polarisation and numerical absorption [14] corrections were applied. The structures were solved by direct methods and subsequently completed by the difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using full matrix, least-squares technique on F^2 . The hydrogen atoms were found on difference Fourier synthesis and treated as 'riding' on their adjacent non-hydrogen atoms and assigned isotropic displacement parameters equal to 1.5 (amine, methyl group, water molecules) or 1.2 (rest of atoms) times the value of equivalent displacement parameters of the parent atoms. The carbon bonded hydrogen atoms geometry was idealised after each cycle of least-squares refinement. The methyl groups were allowed to rotate about their local threefold axis. SHELXS97 [15], SHELXL97 [16] and SHELXTL [17] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs. Details concerning crystal data and refinement are summarised in Table 1 and selected bond lengths and bond angles are given in Table 2. In plane polarised light the crystals exhibited strong pleochroism. The colours ranged from deep green to a straw colour as the plane of polarisation of the light was rotated.

2.3. Theoretical calculations

Geometry optimisation, vibrational data and natural bond orbital (NBO) analysis [18–20] were performed at the B3LYP/6-31++G(d,p) level of theory [21,22] using GAUSSIAN03 [23] program package. The geometric parameters were employed from crystal structure data. The optimised geometrical parameters were in agreement with those found from X-ray measurement in the range of three standard deviations. The amide group of semicarbazone molecule (I) was rotated along C(1)–N(2) bond (rotation angle

Table 2
Selected bond lengths and angles

Bond length (Å)/angle (°)	I	II
C(1)=O(1)	1.2397(16)	1.2319(20)
C(1)–N(1)	1.3250(18)	1.3213(23)
C(1)–N(2)	1.3621(17)	1.3593(22)
C(2)=N(3)	1.2754(17)	1.2652(22)
C(6)–N(4)	1.3821(19)	1.4769(19)
N(2)–N(3)	1.3796(16)	1.3715(18)
N(1)–C(1)=O(1)	124.04(12)	122.75(17)
C(1)–N(2)–N(3)	120.32(12)	119.33(15)
N(2)–N(3)=C(2)	115.40(12)	116.61(15)
C(6)–N(4)–C(9)	120.44(15)	112.48(13)

equal to 10°) and the total energy of molecule was calculated by the above-mentioned method. Density and potential contour plots were visualised with the gOpenMol program [24,25].

2.4. Physical measurement

The IR spectrum (400 – 4000 cm^{-1}) was recorded on a Shimadzu DR-8011 spectrophotometer. The thermal analysis was carried out in a TG/DTA-SETSYS-16/18 thermoanalyser coupled with Thermo-Star (Balzers) mass spectrometer. The sample (2.41 mg) was heated in corundum crucible up to 1000 °C, at the heating rate 10 °C min^{-1} in air atmosphere. The products of decomposition were calculated from TG curve. The temperature ranges were determined by thermoanalyser Data Processing Module [26]. A coupled TG–MS system was used to analyse the principal volatile thermal decomposition and fragmentation products.

3. Results and discussion

3.1. Structures and bonds properties

The unit cell parameters of semicarbazone of *p*-dimethylamino-benzaldehyde (I) and its optical properties were previously determined by Manivannan and Dhanuskodi [27]. Both the crystallographic analysis (cubic system, $a = 5.645(2)$ Å, $V = 179.88$ Å³) and UV–vis spectroscopy results indicate that the authors obtained rather simple inorganic salt such as sodium chloride than hydrazone. One molecule of compound I occupies volume of 264.91 Å³, what is larger than available space in above-mentioned unit cell.

The semicarbazone molecule (I) (Fig. 1) shows the configuration *E* with respect to the C1–N2 bond and C2=N3 bond, which is stabilised by the N(1)–H(1B)···N(3) intramolecular hydrogen bond. The occupancies of the lone pair ($n_{\text{N}(3)}$), antibonding bond orbital ($\sigma_{\text{N}(1)\text{--H}(1\text{B})}^*$) and the stabilisation energy value (1.46 kcal/mol) indicate the weak (donor–acceptor) non-covalent interactions between p_y lone pairs on nitrogen atom and σ^* N–H bond. This is rather low N–H···N hydrogen-bond energy, but deletion of this interaction leads to increase of total molecule energy by 8 kcal/mol. Moreover, both N atoms, of imine and amine group, are negatively charged, according to natural population analysis (NPA [18]) and Breneman, Merz-Kollman-Singh (MKS) charge values (Table 3). This confirms the existence of hydrogen bond, although the geometrical parameters of this interaction are not common N···N distance equal to 2.659 Å, H···N distance equal to 2.275 Å, N–H···N angle equal to 108°). A CSD [28] search for intramolecular N–H···N hydrogen bond in similar benzaldehyde semicarbazone revealed that N–H···N angle adopts value in the range 92 – 115° and the H···N distance is smaller than the corresponding van der Waals radii sum of 2.75 Å (but it should be mentioned that all these structures were determined from X-ray studies and the accuracy of H atoms positions is low).

Table 1
Crystal data and refinement for I and II

	C ₁₀ H ₁₄ N ₄ O (I)	C ₁₀ H ₂₁ ClN ₄ O ₄ (II)
Empirical formula	C ₁₀ H ₁₄ N ₄ O (I)	C ₁₀ H ₂₁ ClN ₄ O ₄ (II)
Formula weight	206.25	296.76
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
Unit cell dimensions		
<i>a</i> (Å)	14.9861(4)	9.4069(12)
<i>b</i> (Å)	5.37830(10)	18.775(3)
<i>c</i> (Å)	13.4025(4)	18.429(3)
β (°)	101.2080(10)	103.628(11)
Volume (Å ³)	1059.64(5)	3163.2(8)
<i>Z</i>	4	8
Absorption coefficient (mm ^{−1})	0.089	0.257
<i>F</i> (000)	440	1264
θ Range for data collection (°)	1.39–25.04	2.94–31.65
Index ranges	$-17 \leq h \leq 17$ $-6 \leq k \leq 6$ $-15 \leq l \leq 15$	$-10 \leq h \leq 13$ $-23 \leq k \leq 27$ $-26 \leq l \leq 22$
Goodness-of-fit on F^2	1.054	0.865
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0366$, $wR_2 = 0.1071$	$R_1 = 0.0405$, $wR_2 = 0.1035$
<i>R</i> indices (all data)	$R_1 = 0.0518$, $wR_2 = 0.1121$	$R_1 = 0.1415$, $wR_2 = 0.1263$
Largest difference peak and hole (e Å ^{−3})	0.198 and -0.167	0.183 and -0.200

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