Thiobenzamide: Structure of a free molecule as studied by gas electron diffraction and quantum chemical calculations

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The equilibrium (r_e) molecular structure of thiobenzamide along with r_{h1} structure has been determined in gas phase using gas electron-diffraction (GED) at about 127 °C and quantum-chemical calculations (QC). Rovibrational distance corrections to the thermal averaged GED structure have been computed with anharmonic force constants obtained at the MP2/cc-pVTZ level of theory. According to the results of GED and QC thiobenzamide exists as mixture of two non-planar enantiomers of C_1 symmetry. The selected equilibrium geometrical parameters of thiobenzamide (r_e, Å and $\angle_e$, deg) are the following: (C=S) = 1.641(4), (C−N) = 1.352(2), (C−C) = 1.478(9), (C=C)$_{av}$ = 1.395(2), CCN = 114.7(5), CCS = 123.4(5), C2C1C7S = 31(4), C6C1C7N = 29(4). The structure of thiobenzamide in the gas phase is markedly different to that in the literature for the single crystal. The differences between the gas and the solid structures are ascribed to the presence of intermolecular hydrogen bonding in the solid phase.

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1. Introduction

Thioamides and its substituted compounds possess various pharmacological activity [1–4]. The accurate experimental molecule structures of the simplest aliphatic primary thioamides were determined in the gaseous phase [5,6] and in the solid state [7,8]. The comparison of crystalline and gaseous molecular structures for thioacetamide [6] revealed that the structure of thioacetamide in the gas phase is markedly different to that for the single crystal. It was suggested that the changes are caused by the formation of intermolecular hydrogen bonds in the solid state [6]. Investigations on related thioamides are required for further understanding of the effect of hydrogen-bonding on the molecular structures of thioamides.

Thiobenzamide is a fundamental aromatic thioamide but its structural data is rather scarce. According to the X-ray diffraction (XRD) data [9], the asymmetric unit of thiobenzamide contains four non-planar crystallographically independent molecules, with the dihedral angle between the aromatic ring and the thioamide group varying from −23.5(2)° to 38.5(2)°. Two types of infinite ladder motifs are formed between the neighboring thioamide groups via H···S contacts (Fig. 1).

However, there is no experimental data for the structure of free thiobenzamide molecule which we expect to be quite different from its crystalline structure due to the absence of intermolecular contacts. The comparison of both gaseous and crystalline molecule structures would be beneficial for revealing how the formation of hydrogen-bonding affects the molecule structure of thiobenzamide. The purpose of the present work is the investigation of the molecular structure and conformational composition of thiobenzamide in the gas phase by GED method and *ab initio* calculations. A special attention attracts the angular twist of carbothioamide group around benzene ring plane, when thiobenzamide molecule is free from intermolecular interactions with other thiobenzamide molecules, and changes of the structural parameters of thiobenzamide caused by the formation of hydrogen-bonding.

2. Experimental section

2.1. Synthesis of thiobenzamide

A Schlenk tube was charged under Ar atmosphere with benzamide (0.6 g, 4.4 mmol), Lawesson's reagent (1 g, 2.5 mmol), THF (4 mL), and stirred at 55 °C. After 4 h, when the reaction was completed as determined by TLC, aluminium oxide (10 g) was added and the solvent was evaporated. The resulting solid was placed into a short column and eluted with acetonitrile (30 ml). The

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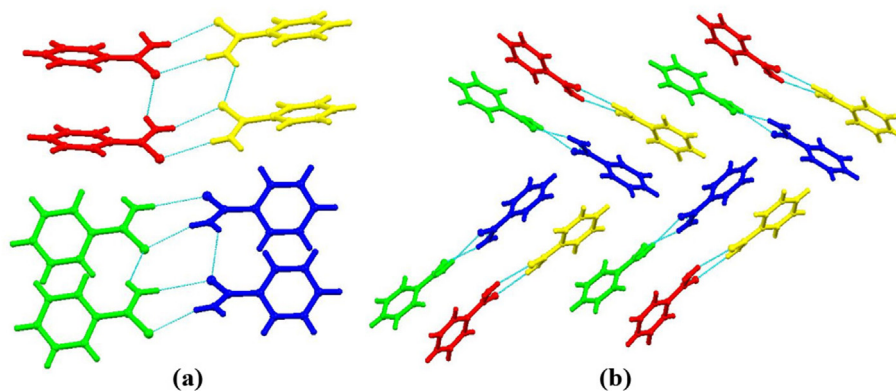   *E-mail address:* kolesnikova@phys.chem.msu.ru (I.N. Kolesnikova).

Fig. 1. (a) Hydrogen-bonding ladder motifs and (b) supramolecular network observed in thiobenzamide.

solution was dried in *vacuo* to give thiobenzamide as a yellow solid. The yield was 71%, m. p. 118 °C (*cf.* Ref. [10]: m. p. 118 °C). The course of the reaction was monitored, and the purity of the product was checked, by TLC on ALUGRAM SIL G/UV$_{254}$ plates. Benzamide and Lawesson's reagent (Aldrich) were used as purchased.

2.2. NMR measurments

NMR spectra were recorded in CDCl$_3$ on a Bruker Avance 400 NMR spectrometer operating at a frequencies of 400.13 MHz (^{1}H) and 100.61 MHz (^{13}C). The chemical shifts of the nuclei are reported here in ppm relative to SiMe$_4$: ^{1}H NMR, δ: 7.38–7.53 (m, 3H, C$_6$H$_5$), 7.87–7.85 (m, 2H, C$_6$H$_5$); ^{13}C NMR, δ: 203.0 (C=S), 139.3(C$_i$), 132.2(C$_p$), 128.6(C$_m$), 127.0 (C$_o$).

2.3. GED measurements

GED data for thiobenzamide were acquired using the electron diffraction apparatus EG-100 M at the Moscow State University. The diffraction patterns were recorded on photo films (MACO EM-FILM EMS) at short and long camera distances. The electron wavelength was calibrated against gaseous CCl$_4$ which diffraction patterns were recorded after collecting the diffraction patterns for thiobenzamide. A summary of the experimental parameters can be found in Table 1.

The photo films containing diffraction data were scanned using an Epson Perfection 4870 photo commercial scanner at 16-bit/600dpi and the obtained images were transformed into mean optical densities as a function of the scattering vector, s, using the UNEX [11] program. The background was approximated by cubic splines. Illustrations of the intensity curves and the final background lines for r_e structure are shown in Fig. 2. Numerical values of the intensities and backgrounds for r_e and r_{h1} representations are given in Section 1 of ESI.

Table 1
Conditions of the GED experiment.

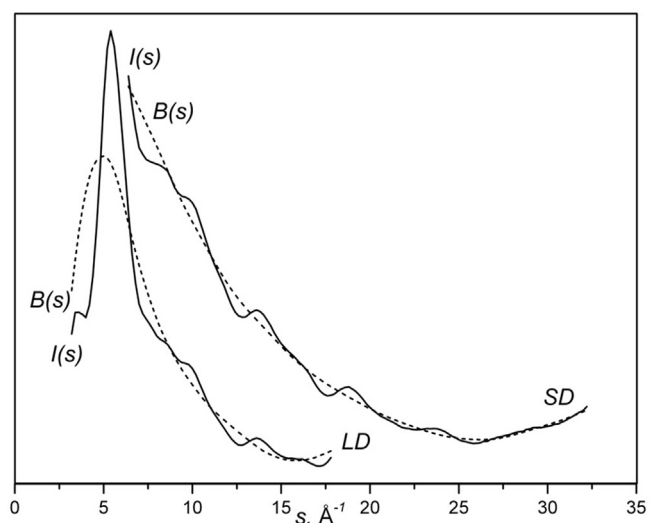|	Short camera distance	Long camera distance
Nozzle-to-plate distance, [mm]	193.9	362.3
Nozzle temperature, [K]	401	399
Acceleration voltage, [kV]	60	60
Electron beam current, [μA]	2.9	1.8
Electrons wavelength, [Å]	0.050278	0.049589
s range, [Å^{-1}]	6.4–29.6	3.2–17.8
Residual gas pressure, [Pa]	3.3·10^{-3}	3.3·10^{-3}
Exposure time, [s]	100	95

Fig. 2. Experimental intensity (solid line) and background curves (dashed line) for thiobenzamide as obtained from long nozzle-to-plate distance (LD) and short nozzle-to-plate distance (SD).

3. Theoretical calculations

All the QC were performed using the Gaussian03 program package [12]. Computational methods B3LYP [13,14], B3LYP-D3 [15] and MP2 [16] as well as basis sets 6-31G(d,p) [17], cc-pVTZ [18] and aug-cc-pVTZ [18] were used as implemented in this program. One-dimensional potential energy surface scan for torsion vibration of thioamide group, made at B3LYP/6-31G(d,p) level of theory, revealed the existence of two non-planar enantiomeric conformers of C$_1$ symmetry (Fig. 3). In the calculations the values of ∠C2−C1−C7−S were fixed at an interval of 10° from 0° to 180°, whereas all the other structural parameters were varied (Fig. 4).

The geometry of thiobenzamide was optimized using the tight convergence criteria and option UltraFine-Grid. Quadratic force fields and vibrational frequencies of the optimized species were calculated at B3LYP/6-31G(d,p), B3LYP/cc-pVTZ, B3LYP-D3/aug-cc-pVTZ and MP2/cc-pVTZ levels of theory. Cubic force field was obtained atMP2/cc-pVTZ level of theory.

Natural bond orbital (NBO) analysis of the electron density distribution at the DFT-B3LYP/cc-pVTZ level of theory was carried out to explain the structural features of the molecule under study. Parameters for GED refinement, namely mean vibrational amplitudes l, interatomic distance corrections $r_{h1} − r_a$ and $r_e − r_a$ for all