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Structure and conformation of (trifluoromethyl)thiobenzene, $C_6H_5SCF_3$: Gas electron diffraction and quantum chemical calculations

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Abstract

The geometric structure and conformation of (trifluoromethyl)thiobenzene, $C_6H_5SCF_3$, has been determined by two independent gas electron diffraction (GED) studies at the Universities of Moscow and Ivanovo and by quantum chemical calculations. Both experimental studies result in perpendicular orientation of the $S—CF_3$ bond relative to the benzene plane. This result is confirmed by several quantum chemical calculations (HF/6-31G(d), B3LYP/cc-pVTZ, MP2/6-31G(d), MP2/6-311+G(d,p) and MP2/cc-pVTZ) which predict single-minimum potential functions for internal rotation around the $C(sp^2)—S$ bond. A double-minimum potential function predicted by the B3LYP/6-31G(d) calculation is not compatible with the experiment. B3LYP and MP2 calculations with large basis sets (6-311+G(d,p) and cc-pVTZ) predict barriers to internal rotation around the $C(sp^2)—S$ bond between 2.4 and 2.6 kcal/mol. The geometric parameters of both experimental studies agree with each other within the experimental uncertainties, except for the C—F bond distance. The effect of fluorination of the methyl group in thioanisole, $C_6H_5SCH_3$, i.e., conformational change from planar orientation of the $S—CH_3$ bond to perpendicular orientation of the $S—CF_3$ bond, is rationalized on the basis of a natural bond orbital (NBO) analysis. The predominant effect is loss of conjugation between the p-shaped sulfur lone pair and the π system of the ring upon fluorination.

Keywords: (Trifluoromethyl)thiobenzene; Gas electron diffraction; Quantum chemical calculations; Conformation

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1. Introduction

The effect of fluorination on the conformational properties of anisole, $C_6H_5OCH_3$, has been studied by gas electron diffraction (GED), spectroscopic methods and quantum chemical calculations in a cooperative project between the universities of Moscow, Ivanovo and Tübingen [1–7]. Two independent studies demonstrated that fluorination of the methyl group causes a mayor conformational change from planar orientation of the $O—CH_3$ bond ($\varphi(C—O) = 0°$) in anisole to perpendicular orientation of the $O—CF_3$ bond ($\varphi(C—O) = 90°$) in α,α,α-trifluoroanisole (trifluoromethoxy benzene) [1,2]. Although GED and some quantum chemical calculations do not exclude the presence of a small amount of a second conformer with planar orientation, no such form is observed in microwave and IR(matrix) spectra [2].

In a recent study we investigated the geometric structure and conformation of thioanisole, $C_6H_5SCH_3$, by GED and quantum chemical calculations [8]. Whereas GED resulted clearly in the presence of a single conformer with planar orientation of the $S—CH_3$ bond ($\varphi(C—S) = 0°$), quantum chemical calculations do not provide a conclusive result. Predictions made by different computational methods included all feasible conformational properties, either a single conformer with planar or perpendicular orientation,

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or a mixture of both forms with either perpendicular or planar conformer prevailing.

We were now interested in the effect of fluorination of the methyl group on the conformation of thioanisole. Several experimental and theoretical studies concerning the orientation of the S—CF_3 bond have been reported in the literature. UV and IR spectra have been interpreted in terms of a mixture of planar and perpendicular conformers, with the latter predominating [9]. Semiempirical MINDO-PM3 calculations predict a similar mixture of two forms and multinuclear NMR spectra are interpreted in terms of a single conformer with near-perpendicular orientation of the S—CF_3 bond [10]. Potential functions for internal rotation around the $C(sp^2)$—S bond have been calculated with different computational methods and 6-31G(d) basis sets [11,12]. Whereas the reported functions derived with HF and MP2 approximations possess a single minimum for perpendicular orientation ($\varphi(C—S) = 90°$), the function derived with the B3LYP method possesses a flat double-minimum potential at perpendicular orientation. We report the results of two independent investigations of (trifluoromethyl)thiobenzene, $C_6H_5SCF_3$, which were performed at the universities of Moscow and Ivanovo, applying GED and quantum chemical calculations. Additional calculations were performed at the University of Tübingen. An explicit goal of performing two independent studies for this compound is to check how different experimental intensities and slightly different constraints in the analyses of these intensities influence the results.

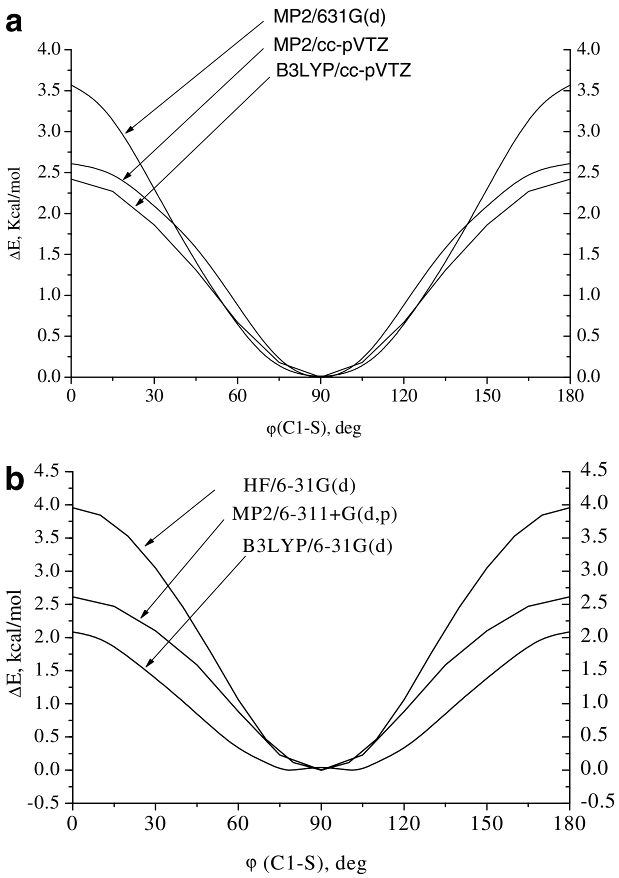

Fig. 2. (a) Calculated potential curves for internal rotation around $C(sp^2)$—S bond (Moscow). (b) Calculated potential curves for internal rotation around $C(sp^2)$—S bond (Ivanovo).

2. Quantum chemical calculations

The geometry of $C_6H_5SCF_3$ was optimized for different fixed dihedral angles $\varphi(C—S)$ between 0° and 90°, using the GAUSSIAN03 program system [13]. A molecular model with atom numbering is shown in Fig. 1. The GED analysis at the University of Moscow was supplemented by MP2/6-31G(d), MP2/cc-pVTZ and B3LYP/cc-pVTZ calculations, the analysis at University of Ivanovo by HF/6-31G(d), B3LYP/6-31G(d) and MP2/6-311+G(d) calculations. The potential functions for internal rotation around the $C(sp^2)$—S bond are shown in Figs. 2a and b. All potential functions possess a single minimum at perpendicular orientation ($\varphi(C—S) = 90°$), except for that which was derived with the B3LYP/6-31G(d) method. Our MP2/6-31G(d) function is very close to that reported in Refs. [11] and [12]. The HF method predicts a barrier for internal rotation around the $C(sp^2)$—S bond of 4 kcal/mol and all MP2 and B3LYP calculations result in barriers between 2.1 and 3.6 kcal/mol. A similar potential barrier of 2.3 kcal/mol was derived with the B3LYP/6-31G(d) method for internal rotation of the CF_3 group around the S—CF_3 bond. Calculated structural parameters for the orthogonal conformer are included in Table 1. Force fields for the perpendicular structure derived with B3LYP/cc-pVTZ (Moscow) and MP2/6-311+G(d,p) (Ivanovo) methods were used to calculate vibrational amplitudes and corrections Δr at the respective temperature of the experiment using the approach of Sipachev which is incorporated in the program SHRINK [14]. This method takes the nonlinear relation between Cartesian and internal coordinates into account and corrects r_a distances to r_{h1} values. It has to be pointed out that some calculated frequencies, especially for low frequency torsional vibrations, depend appreciably on the computational method. This leads to some amplitudes derived from the B3LYP force field which are smaller at 70 °C than the corresponding amplitude derived from the MP2 force field at 0 °C.

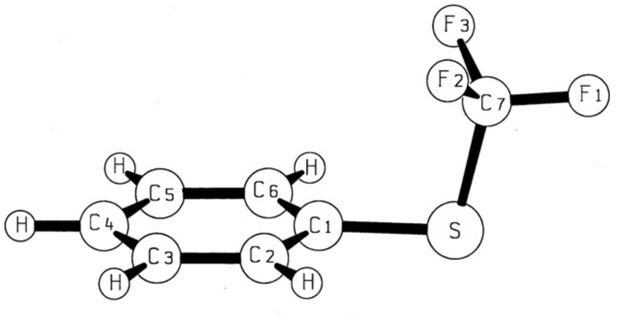

Fig. 1. Molecular model with atom numbering.