Potential Functions of Internal Rotation around the \( C_{sp^2} \)–S Bond and Intramolecular Interactions in Thioanisoles \( p-RC_6H_4SCH_3 \)

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Abstract — The potential functions of internal rotation around the \( C_{sp^2} \)–S bond in the compounds \( p-RC_6H_4S \cdot CH_3 \ (R = NH_2, OCH_3, CH_3, H, F, Cl, CN, NO_2) \) are studied by \textit{ab initio} quantum-chemical calculations taking into account the correlation energy for all the electrons (MP2/6-31G* and in the approximation of the density functional theory (B3LYP/6-31G*). As the electron-donor power of the \( p \)-substituents decreases and their electron-acceptor power grows, the molecular conformation changes in the sequence orthogonal–free rotation–planar. The interaction of the sulfur lone electron pairs with the aromatic ring is studied by the natural bond orbital method. The effect that the conformational changes occurring upon replacement of \( p \)-substituents exert on the electron density redistribution is demonstrated. The first Koopmans ionization potentials and the geometric parameters of the molecule are reported.

In our previous work [1], we studied by \textit{ab initio} calculations (HF/6-31G* and MP2/6-31G*) the potential functions of internal rotation around the \( C_{sp^2} \)–O bond in anisoles \( p-RC_6H_4OCH_3 \). The potential energy minimum was found in the region of the planar conformation. The electronic effects of the \( p \)-substituents were found to affect mainly the height of the internal rotation barrier rather than the geometry of the most stable conformer. In this work, we studied the potential functions of internal rotation around the \( C_{sp^2} \)–S bond in thioanisoles \( p-RC_6H_4SCH_3 \), where \( R = NH_2, OCH_3, CH_3, H, F, Cl, CN, \) or \( NO_2 \), by \textit{ab initio} calculations on the MP2/6-31G* level, and also by DFT calculations on the B3LYP/6-31G* level. Intramolecular interactions were studied by the method of natural bond orbitals (NBO).

\( p-RC_6H_4S \cdot OAlk \) are more labile conformationally than \( p-RC_6H_4O \cdot OAlk \) molecules. For example, the conformation of alkyaryl sulfides gradually changes from planar to orthogonal, or the population of the planar form decreases with that of the orthogonal form growing, in going to bulkier alkyl substituents at the \( S \) atom in the order \( CH_3 < C_2H_5 < iso-C_3H_7 < t-C_4H_9 \). This is indicated by data of photoelectron [2, 3], UV and IR [4–11], NMR [12–18], and X-ray fluorescence spectroscopy [16, 19, 20]. The series of thioanisoles \( p-RC_6H_4SCH_3 \) were studied by the methods of birefringence in electric field (Kerr effect) [21], UV and IR spectroscopy [4, 9–11], dipole moments [22–24], and NMR [25–29]. The \(^{13}\)C NMR spectra showed that the conformation of the \( p-RC_6H_4SCH_3 \) molecules is much more sensitive to the electronic effects of \( p \)-substituents than that of the \( p-RC_6H_4OCH_3 \) molecules [27]. The results obtained by the method of Kerr constants led Aroney et al. [21] to a conclusion that the effective conformation of the \( p-RC_6H_4SCH_3 \) molecules in solution is characterized by the following torsion angle \( \phi \) between the planes of the benzene ring and \( C_{sp^2} \)–S–C_{sp^2} bonds: 23° (H), 47° (Cl), 46° (Br), and 17° (NO\(_2\)). The UV data suggest that the relative content of the planar conformer in the molecules with \( p-R = H \) and \( F \) under normal conditions is 86 and 95%, respectively, and that in the molecules with \( p-R = Cl \) and \( C(O)CH_3 \) is 100% [10]. The experimental data led many authors to a conclusion that electron-withdrawing \( p \)-substituents stabilize the planar conformation [9–11, 15, 21, 27]. Cheryukanova et al. [30] made similar conclusion from the data for \( m \)-substituted aryl methyl sulfides, obtained by the methods of the Kerr effect and dipole moments. Chmutova and Podkuvryina [31] studied spectrophotometrically the charge-transfer complexes of tetracyanoethylene with aryl methyl sulfides. The molecular-orbital characteristics of aryl methyl sulfides with donor substituents are reported in [32]. The electronic and steric structures of aryl alkyl sulfides were considered in reviews [33, 34]. The steric structure of the thioanisole molecule was studied by electron diffraction by Zaripov [35]. He found that the torsion angle \( \phi \) in the effective conformation of the molecule in the gas phase is 45° ± 10°, which may be due to free rotation around the \( C_{sp^2} \)–S bond. A quantum-chemical study of this molecule confirms free rotation of the fragments around the \( C_{sp^2} \)–S bond [36]. The microwave spectrum ob-
Calculation procedures. \textit{Ab initio} quantum-chemical calculations were performed in the approximation of the second-order Møller–Plesset perturbation theory (MP2/6-31G*) [39, 40] taking into account the electron correlation energy for all the orbitals within the framework of the GAUSSIAN 98W program complex [41]. DFT calculations [42] by the B3LYP/6-31G* method [43, 44] were performed with the GAUSSIAN 92W/DFT program complex [45]. The calculations were performed in the range of variation of the torsion angle \( \varphi \) from 0° to 90° with a step of 15°. The population analysis of the wave functions obtained in the MP2/6-31G* geometry was performed by the NBO method [46–49].

Steric structure. The total energies (\( E_{\text{tot}}, \text{au} \)) of the \( p\text{-RC}_6\text{H}_4\text{SCH}_3 \) molecules are listed in Table 1.

According to MP2/6-31G* calculations (Fig. 1a), the potential functions of internal rotation around the \( C_{sp^2} \text{--S} \) bonds in molecules with the \( p\)-substituents \( \text{NH}_2, \text{OCH}_3, \text{CH}_3, \text{H}, \text{F}, \text{and Cl} \) (curves 1–6) have a twofold rotation barrier. The energy minimum is in the region of the orthogonal conformation, and the energy maximum, in the region of the planar conformation. With the accuracy determined by the step of 15° and without taking into account the zero vibration energy, the height of the barrier to rotation around the \( C_{sp^2} \text{--S} \) bond in these molecules is as follows (kJ mol\(^{-1}\)): 7.37 (\( \text{NH}_2 \)) > 5.97 (\( \text{OCH}_3 \)) > 4.55 (\( \text{F} \)) > 3.36 (\( \text{CH}_3 \)) > 2.88 (\( \text{H} \)) > 2.74 (\( \text{Cl} \)). It is clearly seen that the rotation barrier tends to grow with increasing electron-donor power of the \( p\)-substituent. It should be noted that, in the molecules with \( p\)-H and \( p\)-Cl substituents, according to MP2/6-31G* calculations, the barrier height is close to \( kT \) (2.5 kJ mol\(^{-1}\) [50]). The full optimization of the geometry (including the torsion angle \( \varphi \)) of the \( \text{C}_6\text{H}_4\text{SCH}_3 \) molecule with solution of the vibration problems reveals the stationary points of the potential function of internal rotation around the \( C_{sp^2} \text{--S} \) bond at \( \varphi 0^\circ, 85.6^\circ, \) and \( 90^\circ \). The structure corresponding to a minimum at \( \varphi 85.6^\circ \) has \( E_{\text{tot}} - 668.3035682 \) au; the Hesse matrix in this point has only positive eigenvalues. The main maximum is observed at \( \varphi 0^\circ \). The Hesse matrix in this point has one negative eigenvalue (−29.86 cm\(^{-1}\)). The barrier separating the planar and nonplanar (almost orthogonal) forms is 3.08 kJ mol\(^{-1}\) taking into account the zero vibration energy. In the structure with the torsion