

Internal rotation and equilibrium structure of 2-chloro-3-nitrothiophene from gas electron diffraction and quantum chemistry



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ABSTRACT

The equilibrium structure of the 2-chloro-3-nitrothiophene molecule and the internal rotation of the nitro group have been studied in gas phase using electron diffraction data and quantum chemical calculations in the framework of the large-amplitude motion model for internal rotation.

Quantum chemical calculations at the MP2 and B3LYP levels of theory with various Pople and Dunning basis sets predict the planar minimum energy molecular conformation, with the internal rotation barrier height in the interval 1140–1560 cm⁻¹.

The experimental GED data are consistent with the dynamic model governed by the twofold cosine potential energy function with the barrier height in the range from 600 to 1400 cm⁻¹.

The main equilibrium structure parameters are as follows (values in parentheses correspond to 3 times standard deviations): $r_e(\text{N}=\text{O}) = 1.225/1.227(3)$ Å, $r_e(\text{C}-\text{C})/r_e(\text{C}-\text{N}) = 1.362/1.376/1.403/1.438(3)$ Å, $r_e(\text{C}-\text{Cl})/r_e(\text{C}-\text{S}) = 1.700/1.712/1.715(2)$ Å, $\angle_e \text{C2SC5} = 92.2(5)^\circ$, $\angle_e \text{C3C2S} = 110.8(6)^\circ$, $\angle_e \text{C4C5S} = 111.3(5)^\circ$, $\angle_e \text{C3C4C5} = 113.0(7)^\circ$, $\angle_e \text{C2C3C4} = 112.7(8)^\circ$, $\angle_e \text{C3NO11} = 116.9(6)^\circ$, $\angle_e \text{C3NO10} = 118.5(6)^\circ$, $\angle_e \text{SCCl} = 118.6(5)^\circ$, $\angle_e \text{C4C3N} = 121.8(7)^\circ$, $\angle_e \text{ONO} = 124.6(6)^\circ$, $\angle_e \text{C2C3N} = 125.1(6)^\circ$, $\angle_e \text{C3C2Cl} = 130.7(6)^\circ$.

Thermally averaged parameters are provided for comparison with the results of traditional studies.

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1. Introduction

In recent years, the authors developed the idea of calculating experimental observables of various techniques (gas phase electron diffraction (GED)), microwave spectroscopy (MW), vibrational spectroscopy) and the results of quantum chemical (QC) calculations on the common basis of the intramolecular potential energy function (PEF). The first efforts were focused on the investigation of rigid molecules [1–4], one of them being thiophene molecule [4]. This approach eliminates compatibility problem for data originating from various experimental techniques and theoretical calculations. It was shown that determination of the equilibrium geometry for relatively complex molecules from experimental data combined with theoretical results is feasible.

Later the theory and software for more sophisticated structure analysis for the systems with large amplitude motion (LAM) has been developed [5,6] and applied to different types of nonrigid

molecules, including nitrocompounds [7–9].

The molecule under consideration, 2-chloro-3-nitrothiophene, is widely used as a precursor in the pharmaceutical organic chemistry; nevertheless, the gas phase structure of this molecule was not experimentally determined except for short communication in Ref. [10]. The vibrational spectra of this molecule have not been systematically studied.

In this article we are reporting our results of QC calculations as well as the results of the combined GED + QC investigation of the intramolecular dynamic and equilibrium structure of this molecule. The PEF and conformational analysis of this molecule are discussed.

2. Experimental technique

The commercial sample of 2-chloro-3-nitrothiophene obtained from Acros Organics (97%) was used for the GED experiments without further purification. Electron diffraction patterns were obtained on EG–100 apparatus with an accelerating voltage of 57.3 kV and temperature of the nozzle equal to 50 °C.

Diffraction patterns were recorded at the nozzle to film

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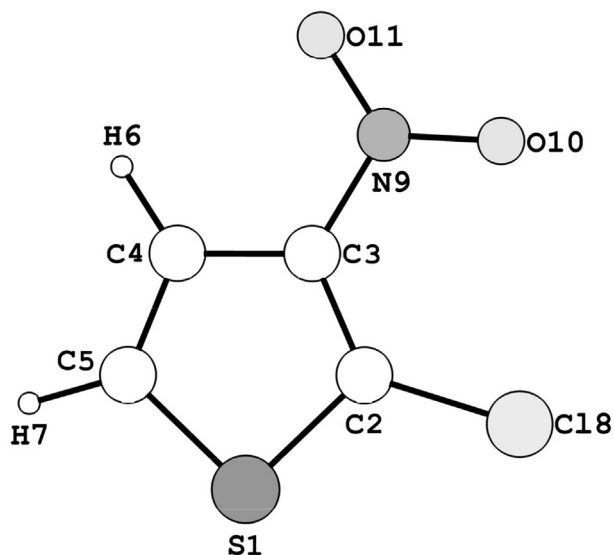


Fig. 1. Planar configuration of the 2-chloro-3-nitrothiophene molecule (reference configuration) predicted by the majority of quantum chemical calculations.

distances 196.20 and 364.24 nm on the electronic imaging films Maco EM-film EMS, emulsion ES 209. Electron beam current was equal to 5 μA with the exposure times of 60 s for short camera distance and 3 μA and 60 s for long camera distance. The films were scanned and digitized using CanoScan 9950F commercial scanner. Preprocessing of the scanned images was performed with the use of PLATE software (Kochikov et al. [11]).

For wavelength calibration, the CCl_4 gas standard was used; the wavelength was found to be 0.04937 and 0.04942 \AA for long and short distances respectively. Electron scattering intensities were recorded at 3.4–18.0 \AA^{-1} (long distance) and 7.8–32.0 \AA^{-1} (short distance) with 0.2 \AA^{-1} increments. For the analysis, six patterns were used: three for long distance and three for short distance. Individual intensity curves obtained for short and long distances were averaged; two resulting curves were used in optimization. Background was approximated by polynomial functions and adjusted in the course of structural parameters optimization. Scattering intensity and background curves are provided in [Supplementary Materials](#). Elastic scattering and phase factors were taken according to [12].

3. Quantum chemical calculations

Quantum chemical calculations include scanning of the potential energy function with respect to the rotation angle of NO_2 group with optimization of all remaining geometrical parameters. The torsional PEFs were obtained with 10° step in the dihedral angle interval 0° – 90° .

The calculations were performed at the levels of theory MP2(FC)/6-311 + G(d), MP2(FC)/6-311++G(d,p), MP2(FC)/cc-pVTZ, MP2(full)/6-311++G(3df,2pd), MP2(full)/cc-pVTZ, MP2(full)/aug-cc-pVTZ, B3LYP/6-31G(d), B3LYP/6-311 + G(d), B3LYP/cc-pVTZ, B3LYP/aug-cc-pVTZ using Gaussian 03 software [13].

Most of these calculations result in planar minimum energy configuration of 2-chloro-3-nitrothiophene (see Fig. 1). Internal rotation barrier heights predicted by all B3LYP calculations are grouped in 1510–1560 cm^{-1} interval, the highest being for B3LYP/cc-pVTZ. MP2 barrier heights are somewhat lower, mostly grouped near 1200 cm^{-1} (see Fig. 2 and [Supplementary Materials](#)).

For comparison, MP2(full)/cc-pVTZ predicts the barrier height for 3-nitrothiophene approximately equal to 2100 cm^{-1} compared to 1170 cm^{-1} for 2-chloro-3-nitrothiophene. Apparently, so significant decrease of barrier height is caused by the steric repulsion between the chlorine and oxygen atoms in plane configurations.

Only MP2(FC)/6-311++G(d,p) calculations predict skewed equilibrium conformations with double PEF minima near $\pm 30^\circ$ and barriers $\sim 130 \text{ cm}^{-1}$ in the planar conformation and 780 cm^{-1} in the orthogonal conformation.

For further use in the structural analysis, quadratic and cubic force constant matrices, as well as the frequencies of normal vibrations, were calculated at the MP2(full)/cc-pVTZ level for the planar conformation corresponding to the minimum of PEF. For evaluating the influence of chosen quantum chemistry results, the whole analysis was repeated with the geometry constraints, relaxation dependencies and force matrices calculated at B3LYP/6-311 + G(d) level.

Relaxation dependencies of the structural parameters in the course of internal rotation should be accounted for in the accurate structural analysis (see the papers [5,6,14–16] and some more recent GED [7–9,17,18] and MW [19] investigations).

The most important relaxation dependencies in 2-chloro-3-nitrothiophene molecule obtained at MP2(full)/cc-pVTZ level are presented in [Supplementary Materials](#). Relaxations for all distances in this molecule except C2 – C3 do not exceed a few thousandths of an Ångström; C2 – C3 distance in orthogonal position of nitro

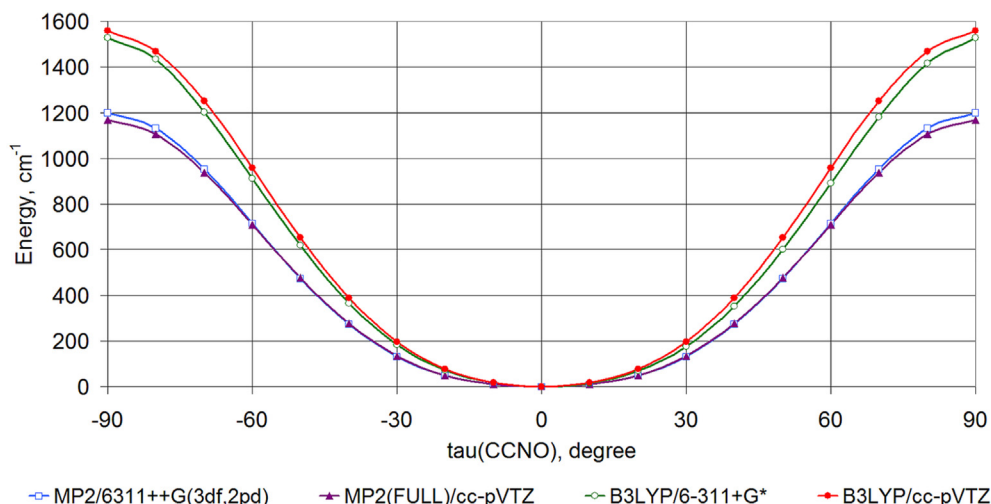


Fig. 2. Potential energy functions for internal rotation of NO_2 group in 2-chloro-3-nitrothiophene according to quantum chemistry calculations.

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