



Internal rotation potential and structure of six fluorine substituted nitrobenzenes studied by microwave spectroscopy supported by quantum chemical calculations



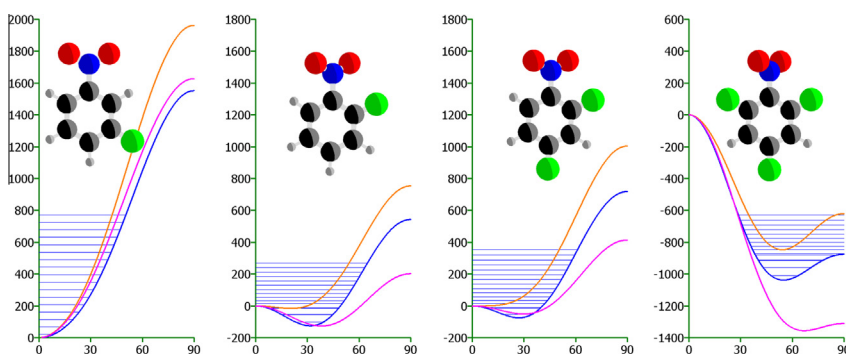
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HIGHLIGHTS

- Several torsional states were assigned for all molecules.
- Coriolis type interaction was used to determine torsional tunnelling splittings.
- Structural relaxation from *ab initio* was helpful for all molecules.
- Simultaneous fit to rotational constants for several torsional states.
- Low barriers to internal rotation and nitro group torsional equilibrium angles were determined.

GRAPHICAL ABSTRACT



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ABSTRACT

Microwave spectra of the vibrational ground state and several torsionally excited states were used to investigate the internal rotation potential and the structure of six fluorine substituted nitrobenzenes: 3-fluoro- and 4-fluoronitrobenzene were planar molecules just as nitrobenzene whereas 2-fluoro-, 2,4-difluoro- and 2,5-difluoronitrobenzene were found to be non-planar with a dihedral angle, γ_0 , between the benzene ring and the nitro group of 31.8°, 27.1° and 30.0° respectively and 2,4,6-trifluoronitrobenzene was non-planar with $\gamma_0 = 55.0^\circ$. The lower of the two barriers separating the potential minima in the non-planar molecules were 125.5, 74.9, 98.4 and 163 cm⁻¹ respectively. Parameters for structural relaxation during the internal rotation were calculated by the B3LYP method using aug-cc-pVDZ basis and by the MP2(full) method using aug-cc-pVTZ basis. Using these relaxation parameters clearly improved the fit by the internal rotation model, SAF, to observed rotational constants as compared with fits without relaxation of structure. For 2-fluoro-, 2,4-difluoro- and 2,5-difluoronitrobenzene the coefficients V_2 , V_4 and V_6 in the Fourier expansion of the potential were determined. For the planar molecules and for 2,4,6-trifluoronitrobenzene V_2 and V_4 were determined using assumptions about V_6 based on the quantum chemical calculations. For all non-planar molecules tunnelling through the lower of the two barriers was observed as a splitting of the torsional energy levels.

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Introduction

Fluorine substitution in the planar molecule nitrobenzene is interesting theoretically as well as experimentally because the potential function for the internal rotation of the nitro group

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against the phenyl ring changes by substitution. Fluorine substitution in meta or para position to the nitro group gives rise to relatively small changes of the potential function and the molecules remain planar, but with fluorine in ortho position the nitro group is no longer co-planar with the phenyl ring. The planarity of nitrobenzene (NB) was established and the barrier to internal rotation was determined in 1971 by Høg et al. [1,2]. In these investigations the potential to internal rotation was assumed to be described by the first term, the V_2 term, of the Fourier expansion of a general potential function with 2-fold symmetric,

$$V(\gamma) = \sum_{n=1}^{\infty} \frac{1}{2} V_{2n} (1 - \cos(2n\gamma)) \quad (1)$$

where γ is the internal rotation angle.

In 1979 Correll et al. [3] reported the microwave (MW) spectra of 3-fluoronitrobenzene (3FNB) and 4-fluoronitrobenzene (4FNB) in the ground state and two torsionally excited states and of 2-fluoronitrobenzen (2FNB) and 2,4,6-trifluoronitrobenzene (246F3NB) in the vibrational ground state. The inertial defect was used to prove the planarity of 3FNB and 4FNB and the non-planarity of 2FNB and 246F3NB. The inertial defect was further used to determine the barrier to internal rotation for the planar species and the torsional angle, γ_0 , for the equilibrium configuration of the non-planar molecules ($\gamma_0 = 32^\circ$ and 57° for 2FNB and 246FNB respectively).

For the non-planar species the potential function for the internal rotation has two barriers, B_{planar} with maximum in the planar configuration ($\gamma = 0^\circ$) and B_{perp} with maximum in the perpendicular configuration ($\gamma = 90^\circ$). $V(\gamma)$ has minimum for $\gamma = \gamma_0$. In [3] $V(\gamma)$ was assumed to be described by the two first terms, the V_2 term and the V_4 term, of eq. (1). The value of γ_0 was used to determine the ratio V_2/V_4 while actual values of V_2 and V_4 were roughly estimated by assuming increments on fluorine substitution to be additive.

Ab initio calculations were used in 1999 by Staikova et al. for 2FNB and 2,6-difluoronitrobenzene (26F2NB) to find γ_0 to 23° and 48° respectively while B_{planar} was found to 177 and 1333 cm^{-1} and B_{perp} to 888 and 319 cm^{-1} respectively [4]. In 2002 Chen et al. calculated the potential to internal rotation for 2FNB ($\gamma_0 = 21.6^\circ$ and $V_2 = 1021 \text{ cm}^{-1}$) based on B3LYP at the 6-311-G** level [5].

Combined Gas Phase Electron Diffraction (GED) and Quantum Chemistry (QC) was used in 2003 by Shiskov et al. to determine $\gamma_0 = 38(3)^\circ$ for 2FNB and in 2004 to confirm the planarity of 3FNB and 4FNB [6,7]. GED and QC was again used in 2008 by Dorofeeva et al. who reported potentials to internal rotation for 26F2NB and 3,5-difluoronitrobenzene (35F2NB). 35F2NB was found to be planar with $V_2 \approx 800 \text{ cm}^{-1}$ while 26F2NB was non-planar with $\gamma_0 = 54^\circ$, $B_{\text{planar}} = 1379 \pm 125 \text{ cm}^{-1}$ and $B_{\text{perp}} = 184 \pm 42 \text{ cm}^{-1}$ [8].

In 2009 rotational constants for two isotopologues and several torsional states of thiophenol were fitted simultaneously by an internal rotation model extended by parameters for structural relaxation (SAF). The barrier to internal rotation and some relaxation parameters were determined by the fit and QC-calculations were helpful as a guideline in the choice of these parameters [9].

In 2010 Larsen used the experimental microwave data from Ref. [1] combined with QC calculations of structural relaxation to determine the barrier to internal rotation for nitrobenzen. The SAF-model with three free relaxation parameters and a potential function containing a V_2 and a V_4 term was in this case able to fit the rotational constants for four torsional states in each of nine isotopologues simultaneously [10].

The fluoronitrobenzene study in Ref. [3] was based on only one or a few torsional states for each molecular species. In the 1980s the microwave spectra of the fluorine substituted nitrobenzenes

in Ref. [3] were studied more carefully and the microwave spectra of the non-planar molecules 2,4-difluoronitrobenzene (24F2NB) and 2,5-difluoronitrobenzene (25F2NB) were investigated as well. The microwave spectra of these “new” molecules have not yet been published, and since the SAF model combined with QC-calculations was doing well for thiophenol and nitrobenzene, it was decided to use the same model for all six fluorine substituted nitrobenzenes and to include nitrobenzene for comparison.

Experimental

All compounds were commercially available and were used without further purification. The microwave spectra were recorded on a Stark modulated MW-spectrometer of type HP8460A covering the spectral region 8–40 GHz. The spectra were obtained at temperatures between -10 and -20°C and at pressures between 1 and 2 Pa. The measurements are believed to be accurate to 0.02–0.1 MHz depending on the line width. In a number of cases, radio frequency microwave double resonance [11] was very helpful in the assignments. In most cases a technique called Stark averaging was used when measuring individual lines: a number of spectra obtained with different Stark voltage were accumulated, with the result that the Stark components were more or less eliminated and the zero-field lines became more prominent.

In order to measure closely spaced lines independently a simple line narrowing technique was used: the second derivative of the spectrum times a constant depending on the approximate line width was subtracted from the original spectrum.

MW-spectra of the molecules 2FNB, 3FNB and 246F3NB in ref [3] were re-measured and several new torsional states were assigned. In the MW-spectra of each of the “new” molecules 24F2NB and 25F2NB several torsional states were assigned.

Model

The internal rotation model, SAF, used in the present study is very similar to the one used for thiophenol and 4-fluorothiophenol [9] and for nitrobenzene [10]. It is essentially a semirigid model i.e. a model with only one internal degree of freedom, which has been extended to include structural relaxation.

The phenyl ring plane including the fluorine atom(s) and the CNO_2 group are both assumed to remain planar during the internal rotation and the internal rotation angle, γ , is defined as the dihedral angle between the plane of the nitro group and the phenyl ring plane.

The internal rotation potential as a function of γ is defined in the standard way by the Fourier coefficients V_2 , V_4 etc. given in eq. (1).

The number of structural parameters is different for molecules with and without a C_2 symmetry axis. For the symmetric molecules (NB, 4FNB, 246F3NB) 13 structural parameters are required to define the planar reference configuration, but for the non-symmetric species (2FNB, 3FNB, 24F2NB, 25F2NB) 25 parameters are needed.

This basic model which includes the molecular structure and the potential coefficients V_2 , V_4 , ... as the only adjustable parameters has been extended by 3 other types of parameters:

- (1) Relaxation parameters for each structural parameter. Most structural parameters, $R(\gamma)$, are periodic with a period π in the internal rotation angle and are therefore represented by a Fourier expansion analogous to Eq. (1) with three relaxation parameters, R_2 , R_4 and R_6 defining the gamma dependence:

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