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Transient chirality of anilides - The rotational spectrum of *trans*-benzanilide

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ABSTRACT

The rotational spectrum of *trans*-benzanilide $C_{13}H_{11}NO$ is reported for the most part of the cm-wave range (3–19 GHz). Heavy atom frame conversion between the two possible enantiomers surprisingly leads to significant tunnelling splittings in the observed spectrum. The large amplitude motion parameters for the occurring tunnelling as well as the nuclear quadrupole coupling constants for the ^{14}N were determined in addition to the rotational constants and quartic centrifugal distortion coefficients. Contrary to other *trans*-anilides, calculations indicate the existence of a non planar amide group in *trans*-benzanilide.

1. Introduction

Amide bonds (R_1—CO—NH—R_2) are ubiquitous in nature, and so molecular structures exhibiting the amide bond are subject to research from various fields. The amide bond orientations are generally differentiated into *cis*- and *trans*- as illustrated on the example of benzanilide in Fig. 1. Intuitively amide bonds are often thought to be planar, but this is not always the case. In crystalline protein structures the amide bond is observed to have a standard deviation from planarity by $\approx 6–8^\circ$ described by the dihedral angle D_{OCNR_2} [1–3]. On the other hand gas phase investigations show, that the amide bond of smaller anilides in fact is frequently planar. The most preferred orientation of acetanilide [4,5] and of 2- and 4-methylacetanilide [6] is planar and *trans* in orientation and also formanilide [7] seems to favour a planar *trans*-orientation. Benzanilide $C_{13}H_{11}NO$ is a compound with an isolated amide bond with two phenyl substituents, making it a perfect candidate for further investigation of amide bond behaviour.

Benzanilide is also of interest because of earlier observations: E.g., its anomalous fluorescence in UV–vis spectroscopy has puzzled scientists for some time and was first attributed to an amid-imidol tautomerism of the *cis*-benzanilide dimer, but later identified to originate from a twisted intra molecular charge transfer state [8–10]. Additionally, the standard enthalpy of formation for benzanlide in the gas phase at 298.15 K was analysed by means of micro calorimetry and accompanying B3LYP/6-311G(d,p) calculations revealed a non planar amide bond and a tilted rest R_1 [11]. This work focuses on the microwave spectrum of benzanilide. Benzanilide is an example for the case that, even if rather big masses are involved, tunnelling can lead to enantiomer conversion if the barrier is narrow and small enough.

2. Experimental

All experiments were carried out with benzanilide purchased from Alfa Aesar (98%) without further purification. The rotational spectrum from 3 to 19 GHz was recorded with the Fabry-Pérot resonator based COBRA-FTMW spectrometer [12]. Benzanilide has a high melting point of 162–166 °C, therefore a commercial pulsed solenoid valve with a custom made heated nozzle was utilized as molecular supersonic-jet source operating at 170 °C. Neon was used as carrier gas at a backing pressure of 0.5–1 bar.

3. Computational details

All quantum chemical calculations were performed using the Gaussian09 program package [13]. Since the conformational diversity of benzanilide is limited to two typically well separated types, i.e. the *trans*- and the *cis*-conformers, the search for stable starting geometries for subsequent geometry optimization calculations was performed for both species separately. For both conformers a

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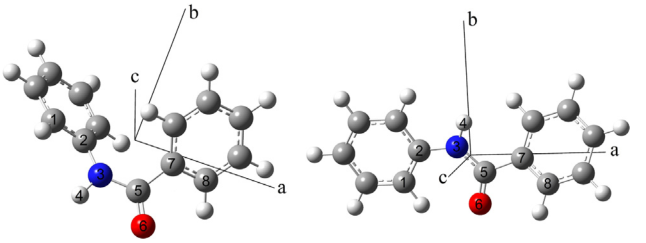

Fig. 1. Conformers of benzanilide in their inertia principal axes system. Left: the *cis*-conformer of benzanilide. Right: the *trans*-conformer of benzanilide with atom numbering labels. Hydrogen: white, carbon: grey, nitrogen: blue, oxygen: red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

frequency calculation with anharmonic corrections to predict the vibrational ground state rotational constants A_0, B_0, C_0 was carried out and the results are given in the supplementary material. The Becke three parameter Lee-Yang-Parr hybrid functional (B3LYP) [14–18] in terms of density functional theory (DFT) with a 6-311++G(d,p) basis set as implemented in the Gaussian09 program package was utilized for all calculations. D3 dispersion corrections provided by Grimme et al. [19] were utilized to increase the accuracy of the B3LYP calculations (B3LYP-D3). Additional energy calculations with Counterpoise (CP) corrections were performed on the B3LYP-D3 optimized structures to determine the effect of the basis set superposition error (BSSE) on the calculated energy differences. The two fragments used in the Counterpoise correction are connected via the N3—C5 bond.

4. Results and discussion

The optimized structure for *trans*-benzanilide and *cis*-benzanilide is non-planar with a tilted shape. In Table 1 an overview of different dihedral angles for both conformers is given. While the phenylaminyl moiety (D_{C1C2N3C5}, D_{O6C5N3C2}, D_{O6C5N3H4}) remains almost planar in the *trans*-conformer, the phenylcarbonyl dihedral angle D_{O6C5C7C8} shows a pronounced deviation from planarity with 27.0°.

The angle D_{O6C5C7C8} can be used to describe the internal large amplitude motion pathway for the conversion of the two tunnelling *trans*-enantiomers of benzanilide. A structurally relaxed energy scan was performed along that angle and the results are shown in Fig. 2. The tunnelling barrier was calculated as energy difference between the all planar transition state and the equilibrium structure and has a value of $V_{\mathrm{tnl}} = 2.4\ \frac{\mathrm{kJ}}{\mathrm{mol}}$ ($2.3\ \frac{\mathrm{kJ}}{\mathrm{mol}}$ CP corrected).

The CP corrections were significant for the *cis* to *trans* energy difference, changing it by 12% to $12.2\ \frac{\mathrm{kJ}}{\mathrm{mol}}$ for the electronic energy. The zero point energies with added CP corrections from the equilibrium energy calculations are $E_{\mathrm{trans},0} = 540.4\ \frac{\mathrm{kJ}}{\mathrm{mol}}$ and $E_{\mathrm{cis},0} = 551.4\ \frac{\mathrm{kJ}}{\mathrm{mol}}$. The electronic energy of *trans*-benzanilide was set to zero. The results are summarized in Table 2.

In the jet-cooled expansion exclusively transitions originating from the more stable *trans*-conformer could be found. In addition to the hyperfine structure caused by the quadrupole coupling an approximatively 8 MHz wide splitting of the *c*-type transitions and a much narrower additional splitting exclusively of the *a*- and *b*-type transition signals was observed. A typical signal group for *b*-type and *c*-type transitions is shown in Fig. 3.

Any instantaneous molecular structure with three different, non-zero dipole moment components is chiral. If the barrier to interconversion between the two energetically equivalent enantiomers is high with respect to room temperature, an isolation of the individual species is possible. A barrier less high in energy and/or narrow with respect to atomic displacement coordinates allows for significant tunnelling between these two conformers. The splitting of the rotational transition lines caused by the large amplitude motion arises as follows: Starting with the two enantiomers in their vibrational ground state, labelled with “0”, the overlap of the vibrational wave functions leads to a splitting of the energy eigenvalues. The corresponding Eigenstates of opposite parity “0^+” and “0^-” are not only separated by ΔE but also have individual sets of slightly different rotational constants. Since the states are often rather close in energy, significant Coriolis coupling can occur. In the current experiment the pronounced *c*-type transition splitting reveals transitions from the $0^{\pm}$ to $0^{\mp}$ vibrational levels and a change of the sign in the dipole vector component μ_c between both enantiomers. In comparison the μ_a and μ_b transitions of type $0^{\pm}$ to $0^{\pm}$ are split by less than 1 MHz with a large variation in the values of the splitting. This smaller splittings are

Table 1
Predicted dihedral angles in *trans*-benzanilide and *cis*-benzanilide, atom labels used as in Fig. 1.

Basis set	D_{1235}	D_{6578}	D_{6532}	D_{7532}
	trans-benzanilide			
6-311++G(d,p)[a]	6.0°	27.0°	2.5°	-178.2°
6-311G(d,p)[b]	4.7°	22.0°	1.3°	−179.7°
	cis-benzanilide			
6-311++G(d,p)[a]	−147.4°	35.2°	−158.9°	23.8°

[a] B3LYP-D3 prediction of this work.
[b] B3LYP prediction Ref. [11].

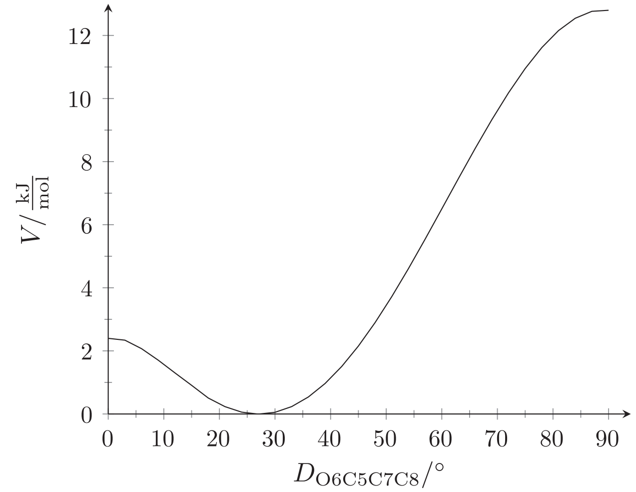

Fig. 2. Results of relaxed potential energy scan along D_{O6C5C7C8}. The barrier to conversion of the two *trans*-enantiomers is $2.4\ \frac{\mathrm{kJ}}{\mathrm{mol}}$ ($2.3\ \frac{\mathrm{kJ}}{\mathrm{mol}}$ CP corrected). The step size of the scan was 3°.

Table 2
Relative energies and BSSE of *trans*- and *cis*-benzanilide and potential barrier V_{tnl} for B3LYP-D3 calculations and CP corrections in kJ/mol.

	E_{trans}	$E_{\mathrm{trans},0}$[a]	E_{cis}	$E_{\mathrm{cis},0}$[a]	V_{tnl}
B3LYP-D3	0	540.4	10.9	550.1	2.4
BSSE	6.4		7.7		6.3
CP corrected	0	540.4[b]	12.2	551.4[b]	2.3[c]

[a] E_0 is the sum of electronic (E) and zero point vibrational energy (E_{zpve}): $E_{i,0} = E_i + E_{i,\mathrm{zpve}} - E_{\mathrm{trans}}$.
[b] CP corrections for equilibrium energies were added to the E_0 energies.
[c] Zero point corrected value for V_{tnl} is $2.1\ \frac{\mathrm{kJ}}{\mathrm{mol}}$.