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Torsional broadening in absorption and emission spectra of bithiophene as calculated by time-dependent density functional theory

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ABSTRACT

The optimized geometries of bithiophene in the electronic ground and excited state have been calculated by time-dependent density functional theory using the hybrid functional B3-LYP. The dependence of the singlet excitation energies and transition dipoles on the torsion between the two thienyl groups has been determined and compared with the torsional potential curve previously found for biphenyl. Based on these data the torsional progressions in absorption and emission have been computed quantum-mechanically in order to show their contribution to the inhomogeneous broadening in the respective spectra of bithiophene.

1. Introduction

In a previous work, Hans Lischka and I have calculated the torsional potential curves of the ground and singlet-excited states of biphenyl [1]. There we found that the inhomogeneous broadenings of the biphenyl absorption and emission spectra are determined to a large extent by torsional disorder. In the electronic ground state the torsional potential is very shallow with a minimum at 30° and low barriers at 0° and 90°. At room temperature, this results in a broad distribution of torsion angles between the planes of the phenyl-ring. In contrast to the ground state, for the lowest optically excited state the torsional potential curve is steep in the respective range of 20°-60°. This effect is responsible for approximately half of the total spectral broadening in absorption – smearing out any spectral substructure, e.g. the vibrational progression for the high-frequency vibrational modes. For the relaxed excited state, however, the torsional potential curve is flat in the vicinity of the minimum at 0°. The ground state torsional potential curve is flat in this range as well for being maximum. Consequently, the torsional spectral broadening is much smaller in emission than in absorption. Therefore the high-frequency vibrational progression is fully visible in the emission spectrum even at room temperature. It is reasonable to assume that this difference between absorption and emission spectra of biphenyl may also be found for other conjugated molecules with single-bond-linked cyclic aromatics allowing torsions – in particular for conjugated polymers like poly-para-phenylene (PPP), poly-phenylene-vinylene (PPV) and poly-thiophenes. For PPV comparable effects have been already calculated [2].

In the present work, bithiophene as the shortest representative of oligo- and poly-thiophenes is the object of interest. The torsional potential curves for the electronic ground state and the vertical as well as relaxed excited states will be calculated. From these the torsional broadening of the spectra will be deduced in the same way as we previously did for biphenyl. In contrast to biphenyl, bithiophene shows a syn–anti-isomerism, which influences its torsional dynamics. Therefore, one may expect additional features in the torsional progression. For the ground state potential energy surface of bithiophene – like for biphenyl – a huge amount of partly contradicting, experimental data [3–13] and theoretical calculations [9,12,14–27] exist; whereas, for the relaxed excited state – important to deduce the fluorescence spectrum – quantum-chemical calculations are rare [5,28]. There exist two studies [25,27], which show single-point calculations done by CASPT2. To my mind their results do not provide an unequivocal picture

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for the energetics and dynamics neither in the vertically excited state nor in the totally relaxed excited state. Concerning experimental data, the situation is slightly better [28–32]. Nevertheless, they are not many, though in principle the determination of the vibrational progression should be easier and more significant in emission than in absorption spectra due to the smaller torsional broadening as shown in what follows.

2. Method

In the present study the same quantum-chemical method is applied to bithiophene as for biphenyl [1], which has resulted in best agreement to experimental data: DFT and corresponding TD-DFT using the B3-LYP functional [33–35] and SVP basis set as implemented in the program package TURBOMOLE [36,37]. This implementation has a great advantage that for the relaxed excited state analytical gradients are available [38,39]. Control calculations with the 6-311G basis set result in deviations in energy of only ±0.01 eV for the torsional potential curves of ground state and the first vertically excited state. This error is of the same order of magnitude as the deviation between the torsional potential curves of biphenyl, which we calculated previously, and the results of highly resolved spectroscopy [1,40]. The sufficiently good agreement between experiment and theory is also the reason, for not using improved non-empirical hybrid-functionals recently developed for DFT calculations of extended π-systems of conjugated molecules, e.g. TPSS [41,42], even though these may result in more accurate potential surfaces (see also Ref. [43–45]).

For the calculation of the torsional progression the same procedure as described in the previous work that has been mentioned [1] has been used. This is based on the Fourier expansion of the torsional potential curve

$$V(\tau) = V_0 + 2\sum_{k=1}^{\infty} V_k \cos 2k\tau \qquad (1)$$

for periodic boundary conditions of the torsional motion and a subsequent solution of the Schrödinger equation in the Fourier-space. The oscillator strength of a single transition within the torsional progression results from the matrix element of the torsion-angle-dependent transition dipole

$$\mu_{\mathrm{eg}} = \int_0^{2\pi} \psi_{\mathrm{e}}(\tau)\mu(\tau)\psi_{\mathrm{g}}(\tau)d\tau$$

between the respective torsional eigenfunctions $\psi_{\mathrm{g}}(\tau)$ for the electronic ground and $\psi_{\mathrm{e}}(\tau)$ electronically excited state, also calculated in the Fourier-space.

3. Results and their interpretation

3.1. Ground state 1^1A

The DFT calculations of the ground state[1] 1^1A for variation of the torsion angle given by the dihedral angle 1-2-2′-1′ (see Fig. 2) yield the expected torsional potential curve (see Fig. 1). The minima are not achieved for coplanar but only periplanar syn- and anti-conformations. This is caused by the steric hindering between the hydrogen atoms in ortho-position and the extended non-bonding orbitals of the sulfur, respectively. Thus, there exist five stationary points on the potential surface, two minima at torsion angles $\theta \sim 30°$ and 160° and three saddle-points (SP) at 0°, 90° and 180°. The respective geometries are quantified in Table 1. Notably, the diameter of the thienyl rings d_{25} as well as the inter-ring distance $d_{22'}$ are practically constant under torsion. The change of ~0.12 Å in the overall length of the molecule measured by $d_{55'}$ results only from the kinked geometry of the syn-conformer.

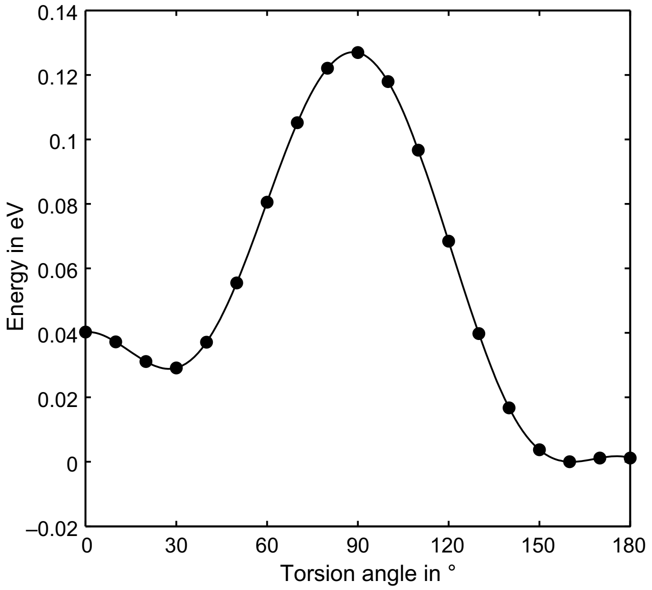

Fig. 1. Torsional potential curve for the relaxed ground state (1^1A) of bithiophene.

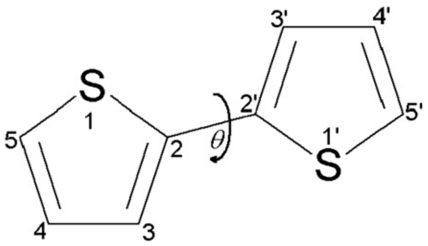

Fig. 2. Structure of bithiophene (shown in the anti-planar conformation) with numbering of the atoms. The torsion angle θ represents the dihedral angle between the two sulfurs around the inter-ring bond 2–2′.

The anti-periplanar minimum of the torsional curve at 160° is 0.03 eV lower in energy than the syn-periplanar minimum at 30°. Obviously, the repulsive interaction between the non-bonding orbitals of the sulfur and the hydrogen atoms is smaller than the combined sulfur–sulfur and hydrogen–hydrogen interactions. The energies of the three maxima are 0.04 eV at 0° (syn-coplanar), 0.13 eV at 90° (gauche), and negligible 1 meV at 180° (anti-coplanar) above the global anti-periplanar minimum. The high barrier at 90° hindered the thermal isomerization between the anti- and syn- conformer to an equilibrium ratio of approx. 1:3 at room temperature. Likewise, the torsion between the two syn-periplanar minima (±30°) is less but still significantly hindered, whereas the barrier at 180° between the two anti-periplanar conformers (±160°) is negligible. The latter value is quite uncertain – in the literature there exist very disperse results – most probably due to the difficulties to calculate the sulfur–hydrogen and sulfur–sulfur interaction, respectively. Note that the calculated hydrogen–hydrogen interaction should be reliable as has been proved for biphenyl [1].

Compared to the previous quantum-chemical studies [3–13], which give the minima at torsion angles between 142° and 152°

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[1] In what follows the electronic states will be assigned by the irreducible representation for the C_2 symmetry of the general bithiophene molecule, i.e. either A or B. These are prefixed by a superscript for the multiplicity and the number of occurrences of the respective representation as state in energetic order beginning from the fully relaxed ground state, which is consequently assigned as 1^1A. States calculated for deviating geometries are assigned by a subsequent superscript*.