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Invited Feature Article

Femtochemistry of selected di-substituted benzenes

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ABSTRACT

Ortho-di-substitution of benzenes provides the opportunity to study interactions between diverse functional groups in a defined environment. The substituents are forced to distances which allow chemical reactions to occur. In this feature article, we focus on photoreactive compounds containing nitro and carbonyl groups. The complex electronic structure of these molecules results in a rich photochemistry on the femto- and picosecond timescale. A combination of femtosecond spectroscopic techniques and quantum chemical calculations shows that all compounds studied undergo hydrogen transfers *via* both, singlet and triplet channels. In several cases these transfers are the starting point for further rearrangements. The experiments enabled us to elucidate the mechanisms of prominent photoreactions as the ones of *ortho*-nitrobenzaldehyde or of nitrobenzene derived photolabile protecting groups.

1. Introduction

Thanks to the development of femtosecond (fs) lasers [1,2] *some* chemical reactions may nowadays be studied on the ultimate time scale of chemistry. The periods of molecular vibrations ranging from ~10 to 200 fs define that time scale [3,4]. Most reactions studied to date by fs spectroscopy are photochemical ones. Such reactions may be triggered with the required temporal precision by short laser pulses. Uni-molecular photoreactions are commonly addressed since in bi-molecular ones diffusion will often mask the ultrafast reaction [5]. With these constraints in mind we sought for a class of molecules which allowed us studying elementary organic reactions by means of fs spectroscopy. This brought our attention to photoreactive *ortho*-disubstituted benzenes which are the topic of this Feature article. In these compounds, atoms of the two substituents are often at distances commensurate with a reaction (see Fig. 1). The benzene scaffold is very rigid ensuring a limited number of conformers. Most importantly, with suitable substituents many of these benzene derivatives undergo photoreactions with high quantum yields [6]. This distinguishes them from their *meta*- and *para*-derivatives which are commonly more photostable, see e.g. [7]. Contrasting the *meta*- and *para*-isomers with the *ortho* one may help extracting genuine spectroscopic hallmarks of the photoreaction.

Among these compounds we have focused on *ortho*-substituted nitrobenzenes. Their photo-reactivity is of value in synthetic chemistry since a very important class of photolabile protecting groups derives from them [8]. Most of the fs-data we have collected in this context are on the photochemistry of *ortho*-nitrobenzaldehyde (oNBA). The reasons for that selection will become apparent below. These results will be the central narrative of this article. In the light of the oNBA results, the photochemistry of other *ortho*-substituted nitrobenzenzes as well as *ortho*-substituted acylbenzenes will be discussed. Emphasis will be laid on experimental results—though some accompanying quantum chemical studies will be mentioned. In the course of our studies it became evident that the combination of different fs-techniques is crucial for a detailed understanding (cf. Fig. 2). The respective techniques will be introduced along with the data resulting from them.

2. General photophysical properties

Before turning to fs spectroscopy some relevant photophysical properties general to these compounds will be listed. Concerning their absorption spectra the mono-substituted benzenes resemble the di-substituted ones (cf. Fig. 3). So for this survey these mono-substituted ones will be focused on, with an emphasis on nitrobenzene (NB). In solution its UV/Vis absorption spectrum is bare of any vibronic structure. Also the gas phase spectrum [9] lacks pronounced progressions. The transition lowest in energy is centered around 340 nm (29,000 cm^{-1}) and exhibits a small peak absorption coefficient ϵ of 140 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ [9]. A much stronger transition is located around 250 nm (40,000 cm^{-1}) with a peak

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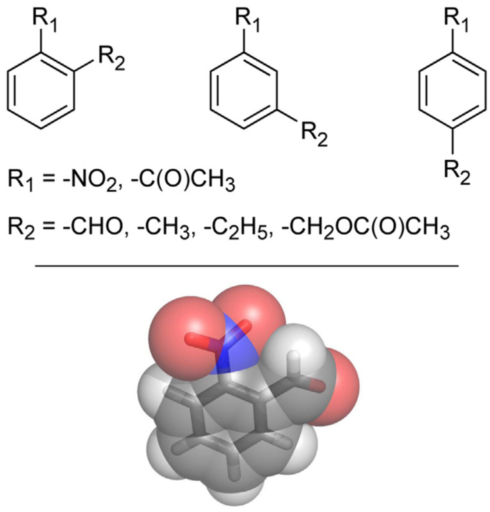
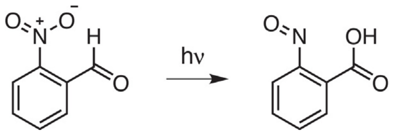


Fig. 1. Scheme of the molecules covered in this article (top). Structure of oNBA as derived from X-ray [65] and neutron diffraction data [18] (bottom). The surfaces represent van-der-Waals radii highlighting the proximity of the aldehyde hydrogen and the nitro group.

coefficient of 8500 M^{-1} cm^{-1}. This transition has a marked positive solvatochromism, i.e. it shifts to lower frequencies with increasing solvent polarity. In a recent comprehensive study the photophysical properties of NB have been scrutinized with numerous quantum chemical methods [10]. According to the authors of this study the quantum chemistry of NB is particularly challenging due to the multi-reference and double excitation character of the transitions (see also Ref. [11]). The computations attribute the weak band around 340 nm to two $n\pi^*$ transitions strongly localized at the nitro group. The stronger band at ~250 nm stems from $\pi\pi^*$ transitions involving the substituent and the aromatic ring. The involvement of the ring explains some similarities with the absorption spectrum of benzene (see Fig. 3). The solvatochromic behavior can be related to a partial transfer of negative charge from the benzene ring to the nitro group.



Scheme 1. Scheme of the photoreaction of oNBA to *ortho*-nitrosobenzoic acid.

The characteristics of these transitions imprint on the processes ensuing photo excitation. NB and other benzenes bearing substituents with lone pairs commonly feature very small fluorescence quantum yields. For NB the present authors are not aware of any value reported. The small yields can be attributed to internal conversion (IC) processes from the bright singlet $\pi\pi^*$ excitation to "dark" $n\pi^*$ states. Following El-Sayed [6,12] one also expects rapid intersystem crossing (ISC) since states differing in electron configuration are involved. Indeed, for NB, triplet quantum yields close to unity were reported [13,14]. While such high yields may also be observed for other benzene derivatives, e.g. benzophenone [15], a peculiarity of NB is its short lived triplet state. Its triplet excitation decays with a time constant on the order of 500 ps [14,16]. The mechanism of this rapid decay is still under scrutiny. A summary of the present knowledge may be found in ref. [10]. The localized nature of the $n\pi^*$ excitation (see Fig. 3) has also photochemical consequences. The excitation generates a hole in the non-bonding orbitals of the oxygen atoms. Because of this hole the oxygen atom develops a strong propensity to abstract hydrogen atoms [17]. For NBs bearing *ortho*-substituents with hydrogen atoms such a transfer may occur intramolecularly. For oNBA in particular neutron diffraction data [18] show that the hydrogen atom points to the nitro group and has van-der-Waals-contact with it. As outlined now, such hydrogen abstractions indeed occur and are the starting point for photochemical transformations of *ortho*-substituted NBs.

3. A case study: *ortho*-nitrobenzaldehyde

Under illumination oNBA transforms into *ortho*-nitrosobenzoic acid [19,20] (cf. Scheme 1). This "old" reaction—it was first reported on as early as 1901 [19]—has several beneficial properties for the

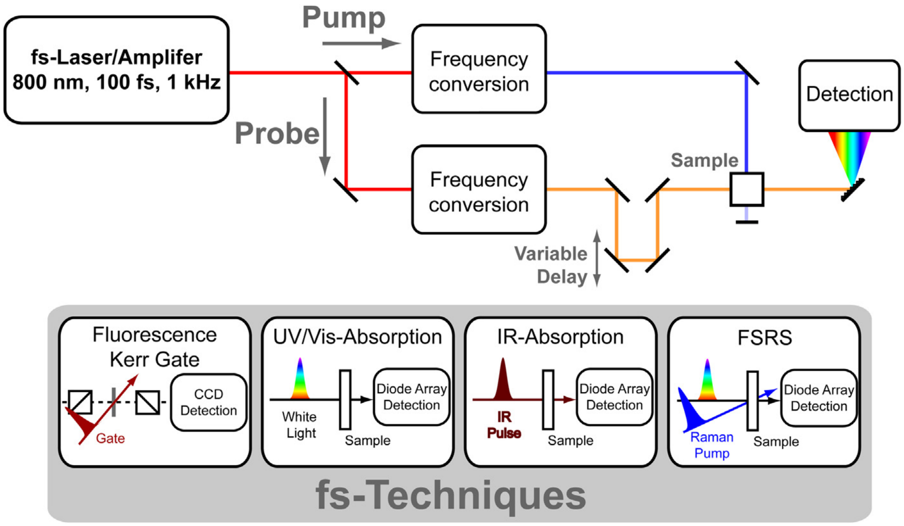


Fig. 2. fs techniques employed in the studies covered here. In all set-ups fs pulses for pumping and probing are derived from a Ti:sapphire based laser/amplifier system. Non-linear frequency converters shift the wavelengths of the pulses into the required regions. A variable delay defines the instant of probing with respect to the excitation. After crossing the pump beam in the sample (except for the fluorescence experiment) the probe beam is spectrally dispersed and then detected. This provides spectra as a function of delay time. In all experiments UV or Vis pump pulses were employed. With four different techniques the resulting spectroscopic changes were interrogated: With the fluorescence Kerr gate focus is laid on the primary excitation. UV/Vis absorption yields an overview of the processes occurring. IR and Raman (FSRS) probing highlight structural changes.