Double-Bond versus Triple-Bond Bridges: Does it Matter for the Charge-Transfer Absorption by Donor–Acceptor Chromophores?


Much work has focused on elucidating the different abilities of alkene and alkyne units to transmit donor–acceptor conjugation. One approach is to compare the characteristic charge-transfer (CT) absorption band maxima.[1] The CT band relies on both donor and acceptor strengths, that is, the energy of the separate HOMO of the donor and the separate LUMO of the acceptor, as well as on the electronic coupling between the two orbitals conveyed by the spacer. In the strong coupling regime, the resulting HOMO and LUMO orbitals are more separated in energy (blue-shifted absorption). In the weak coupling regime, each end of the molecule is unperturbed and the smallest HOMO–LUMO gap is obtained.

Figure 1 shows a variety of alkene and alkyne extended donor–acceptor chromophores and their CT absorptions in solution. Comparison of stilbene and tolane derivatives 1a and 1b as well as 2a and 2b[2] shows that exchange of a double bond for a triple bond results in a blue-shifted CT absorption. In contrast, the absorption maxima of tetrathiafulvalene (TTF) compounds 3a[3] and 3b[4] indicate that the electronic coupling between the donor (TTF) and acceptor ends is lowest when the spacer is an alkyne.[5] Yet, it is imperative to take solvent effects into account when comparing CT absorptions,[6] and particularly so for charged donor–acceptor chromophores (vide infra). In addition, conformational flexibility of the chromophore in question plays an important role for the overlap of \( \pi \) orbitals.

We have recently studied the intrinsic optical properties and solvatochromism of a series of \( p \)-nitrophenolates by state-of-the-art gas-phase experiments and quantum chemical calculations.[7] In the electronic transition, electron density is transferred from the phenolate oxygen to the nitro group. Compared to solution spectra, the isolated chromophores exhibited not only significantly red-shifted CT absorptions in the gas phase, but the relative positions in the series were also not identical to the sequence obtained in different solvents. Herein, we shed light on the difference between alkene and alkyne bridges by comparing two simple \( p \)-nitrophenolates 4a and 4b (Figure 1). We establish from gas-phase action spectroscopy that the coupling is strongest for the alkene spacer (4a).

The experimental setup consists of an electrostatic ion storage ring in combination with an electrospray ion source and a laser system (Figure 2).[8] The number of neutrals formed at one side of the ring is measured as a function of time, and from the increased number of neutrals formed after photoexcitation, we obtain a relative number for the absorption cross section, known as action spectroscopy. The detector is positioned on the opposite side of the ring as to where the photoexcitation takes place. Hence we measure neutrals formed by delayed dissociation, 30 \( \mu s \) after photoexcitation in the first instance and then after successive circulations in the ring. In a separate experiment in which the ring was used as a mass spectrometer,[9] the dissociation channels were found to be loss of NO and to a minor extent loss of NO\(_2\) (Supporting Information). For comparison, loss of NO from nitrobenzene is also a low-energy dissociation channel.[10]
Time spectra of 4a and 4b after photoexcitation at 690 and 710 nm, respectively, are shown in Figure 3. The spectra are similar for the two ions. The data can be accounted for by three exponentials. The slowest decay with a time constant of 100 ms is due to collision-induced dissociation as the ions collide with residual gas in the ring, where the pressure is about $10^{-10}$ mbar. This lifetime was also obtained from a separate measurement without laser excitation. The need for two sub-millisecond time constants for photodissociation (90 μs and 500 μs). The dashed blue curve in the upper panel is the result from the statistical model. The two curves overlap completely.

The dissociation results from stepwise absorption of two photons as the yield of neutrals increases to the second order with the number of photons in the laser pulse (see Figure 4). We emphasize that it is not a coherent two-photon absorption process where two photons are absorbed at the same time, as the laser pulses are several nanoseconds long. Instead, one photon is absorbed followed by internal conversion to the electronic ground state, absorption of a second photon, internal conversion and finally ionic dissociation on the microsecond to millisecond timescale (Figure 3). The energy of one 690 nm photon is 1.8 eV, which is less than the transition state for NO loss of 2.8 eV as predicted by B3LYP/TZVPP calculations (Experimental Section and Supporting Information). This supports the finding that the decay is due to the absorption of two photons. The photoyield therefore depends on the absorption cross section of the room-temperature ions (first absorption) and that of these vibrationally excited ions (second absorption). The absorption cross section may depend on the internal energy of the ions in which case the two absorption cross sections are not identical.

From fits to the time spectra it was possible to extrapolate back to time zero, defined as the time when the laser was fired. This allowed us to obtain the total number of photoexcited ions for each wavelength used (relative, not absolute, numbers) and subsequently deduce the absorption from this information.\textsuperscript{11} The number of photoexcited ions is proportional to the area under the fitted curve, not including the collision-induced dissociation seen as the base level reached after a couple of milliseconds. This area (time constant multiplied by the pre-exponential factor) was divided by the neutrals yield directly before photoexcitation to correct for changes in the ion-beam intensity and by the square of the number of photons in the laser pulse.\textsuperscript{1}

\textsuperscript{1} The spectrum of 4a reported in ref. [7] arises from an erroneous one-photon analysis and as a result the shape is different. The band maximum is red-shifted from 660 nm to 685 nm with the use of two-photon analysis and a narrower band is obtained.
The gas-phase absorption spectra are shown in Figure 5. One point represents the absorption cross section of room-temperature ions multiplied by that of ions that have absorbed one photon. Two Gaussian functions are fitted to the data. The lowest energy absorption maximum is at 685 nm and 695 nm for 4a and 4b, respectively, and the band width is around 80 nm. Hence the alkyne bridge results in a red-shift in the CT absorption as compared to the alkene bridge. In other words the coupling between the donor and acceptor groups is decreased for the alkyne bridge relative to the alkene one.

Theoretical results obtained with the CC2 coupled-cluster method for the planar structure are presented in Figure 5 by bars. The calculated vertical excitation energies (613 and 639 nm for 4a and 4b, respectively) are 0.16–0.22 eV higher than the experimental band maxima, but the red-shift from 4a to 4b is correctly predicted. Again a difference between theory and experiment could be due to a change in absorption cross section after absorption of the first photon since the experimental absorption spectrum depends on two cross sections while the calculation only accounts for the absorption of the first photon.

In acetonitrile (MeCN) solution, both absorption maxima are blue-shifted to 542 and 497 nm for the sodium salts of 4a and 4b, respectively (see Figure 6). In methanol (MeOH), the sodium salt of 4a exhibits an absorption maximum at 435 nm,[7] while the sodium salt of 4b absorbs at 408 nm. Thus, in both solvents the absorption maximum of 4a lies lower in energy than that of 4b in contrast to the situation in vacuo. The larger solvent blue-shift of 4b is most likely due to the larger change in dipole moment (18.3 D) compared to that of 4a (12.6 D), as predicted by the CC2 calculations (see Figure 7 for the molecular orbitals). The hypsochromic solvent shift is the result of an excitation-induced CT that works against the electric field of the solvent dipoles.

In conclusion, gas-phase absorption spectra of two p-nitrophenolate ions were measured to reveal the importance of the bridge between the donor and acceptor group being an alkenene or alkynene unit. We find that the coupling between the donor and the acceptor group is lowest for the tolane compound as it absorbs further to the red ($\lambda_{\text{max}} = 695 \text{ nm}$) than the stilbene compound ($\lambda_{\text{max}} = 685 \text{ nm}$). Coupled-cluster calculations also reveal a clear red-shift (26 nm) of the vertical excitation energy from 4a to 4b. From solution studies, one would have drawn the opposite and wrong conclusion regarding the ability of the two spacers to convey the electronic communication in nitrophenolates. Our findings can likely be generalized to neutral solutes in the case where the dipole moment is re-
duced or reverted upon excitation. Finally, the central stilbene and tolane units belong to the series of oligo(phenylenevinylene)s (OPVs) and oligo(phenyleneethynylene)s (OPEs), respectively, which are conjugated oligomers that have been exploited widely as wires for molecular electronics. The stronger electronic coupling observed for 4a relative to 4b is in line with the higher conductance of OPVs relative to OPEs.

Experimental and Computational Methods

Experiments were performed at the electrostatic ion storage ring in Aarhus, ELISA. The setup is described in detail elsewhere. Ions were produced by electrospray ionisation, stored in a 22-pole pretrap and accelerated as a bunch to 22 keV energies. Ions with the mass-over-charge of interest were selected by a magnet and injected into the ring where they circulated until they changed their kinetic-energy-to-charge ratio by dissociation. After 35 ms, the ions were irradiated by a nanosecond light pulse from a tunable EKSPLA laser. This is an Nd:YAG laser where the third harmonic (355 nm) pumps an optical parametric oscillator (OPO). The repetition rate of the experiment was 10 Hz. Lifetimes were obtained from measurements of the yield of neutrals hitting the microchannel plate (MCP) detector located at the end of the straight section opposite to the side where photoexcitation takes place.

The compounds corresponding to 4a and 4b were prepared according to ref. [15].

Computational Methods: CC2/aug-cc-pVTZ calculations were performed on MP2/TZVPP optimized geometries using TURBOMOLE (tm61). The first-order transition state for the NO cleavage reaction for 4a has been optimized with B3LYP/TZVPP, checked for triplet singularity and its energy corrected by the zero-point vibrational energy from the full Hessian. For the Arhenius analysis, un-scaled vibrational frequencies from B3LYP/TZVPP were used.

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