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## Spectroscopic and DFT investigation on the photo-chemical properties of a push-pull chromophore: 4-Dimethylamino-4'-nitrostilbene



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### ABSTRACT

4-Dimethylamino-4'-nitrostilbene (DANS), a  $\pi$ -conjugated push-pull molecule, has been investigated by means of a combined spectroscopic and computational approach. When the Raman excitation is close to the visible electronic transition of DANS, vibrational bands not belonging to DANS appear in the spectra, increasing with the laser power. These bands are observed at room temperature in the solid phase, but not at low temperature or in solution, and we interpret them as due to a thermally-activated photoreaction occurring under laser irradiation in the visible spectral region. Density-functional calculations correctly reproducing the electronic and vibrational spectra of DANS, describe the charge-transfer process, indicate that an azo-derivative is the product of the photoreaction of DANS and provide a reasonable interpretation of this process.

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### 1. Introduction

"Push-pull" chromophores are characterized by an electron-donating group and an electron-accepting group linked by a conjugated  $\pi$  system [1–9]. They generally exhibit large first and second hyperpolarizabilities and can be usefully employed in non-linear optical (NLO) applications, for example as efficient second-harmonic generators and fast waveguide electro-optical modulators. In the case of push-pull molecules, two resonance electronic structures help to explain their molecular behavior, a neutral form and a zwitterionic form [10]. A two-state model is often proposed, where the neutral form is predominant in the ground state and the zwitterion, instead, in the lowest excited state [11]. As a consequence of the charge-transfer occurring in the excited state, the molecule undergoes a large change in dipole moment and a strong solvatochromism is observed, as for 4-nitroaniline [12–14], 4-dimethylamino-4'-nitrostilbene (DANS) [15], and 4-nitroanisole [16]. Among these, DANS, whose resonance forms are shown in Fig. 1, presents peculiar fluorescence and photophysical behaviors, very sensitive to the polarity of the solvent [17–21].

These interesting properties are exploited in organic light-emitting diodes (OLEDs) for screen displays and solid-state lighting, where the organic molecule is used as a photoemitter and whose color is tuned by the environment (usually a polymeric matrix) where it is embedded.

Furthermore, because of its high two-photon activity [22–24], DANS molecules are good probes for bio-imaging and radiation therapy applications [25,26]. For these reasons, in recent years DANS was the object of numerous studies based on different computational approaches [27–31]. However, like other push-pull molecules, DANS can undergo photochemical processes, which can modify their opto-electronic properties [32–34] and limits their potential applications. The synthesis of photoactive materials with good thermal, chemical and photochemical stabilities [35,36] requires a proper understanding of the relationship between structure and optical response, along with knowledge of the possible photoproducts that may be generated once the molecule is excited with UV-vis electromagnetic waves. Therefore, in the present study, we have used experimental techniques (UV-vis absorption, FT-IR spectroscopy and Raman scattering) and density functional theory (DFT) calculations to investigate the spectroscopic properties of DANS in both solution and solid state, along with its behavior under irradiation with different laser lines.

### 2. Experimental Section

#### 2.1. Raman Spectra

Raman spectra of DANS as powder sample and in  $\text{CH}_2\text{Cl}_2$  solution ( $10^{-3}$  M concentration) were recorded by excitation with the 457.9 nm, 488.0 nm and 514.5 nm lines of an  $\text{Ar}^+$  laser, by using a Jobin-Yvon HG2S monochromator equipped with a cooled RCA-C31034A photomultiplier and a data acquisition facility. Power density measurements were performed with a power meter instrument (model 362; Scientech, Boulder, CO, USA) giving ~5% accuracy in the

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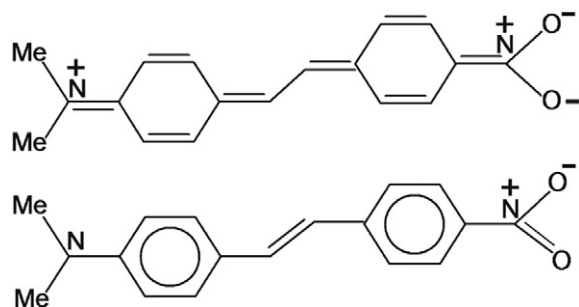


Fig. 1. Resonance structures of DANs (lower: benzenoid; upper: quinonoid).

300–1000 nm spectral range. Raman spectra of solid DANs were also recorded by using a micro-Raman spectrometer RM2000 Renishaw equipped with a diode laser emitting at 785 nm or with an Ar<sup>+</sup> laser emitting at 514.5 nm, a Leica optical microscope and a single grating monochromator. Sample irradiation was accomplished by using the 50 × microscope objective of a Leica Microscope DMLM. The beam power was ~3 mW, and the laser spot size was adjusted between 1 and 3 μm. The backscattered Raman signal was filtered by a double holographic Notch filter system and detected by an air-cooled CCD (2.5 cm<sup>-1</sup> per pixel). All spectra were calibrated with respect to a silicon wafer at 520 cm<sup>-1</sup>.

In the low-temperature micro-Raman measurements we used the THMS 600 device (Linkam Scientific Instruments, U.K.), which allowed obtaining spectra of a microscopic sample under a cold gas flow coming from a liquid nitrogen dewar. By acting on the gaseous nitrogen flow it was possible to vary the sample temperature in the range from +20 °C to -180 °C.

## 2.2. Infrared Spectra

Infrared spectra of solid DANs in KBr pellet were obtained in the 4000–450 cm<sup>-1</sup> region by a Perkin-Elmer FT-IR RX/1 spectrometer.

## 2.3. UV–visible Absorption Spectra

The absorption spectra of DANs dissolved in CH<sub>2</sub>Cl<sub>2</sub> solution or deposited as thin solid film on quartz plate (Hellma, GmbH & Co KG, Germany) were observed in the 200–800 nm spectral region by means of a Cary 5 Varian spectrophotometer. The absorption band shape of DANs in solution was independent of concentration in these experiments.

## 3. Computational Details

All the calculations were carried out using the GAUSSIAN 09 package [37]. Optimized geometries were obtained at the DFT level of theory with the Becke 3-parameter hybrid exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP) [38,39], along with the 6-311G(d,p) basis set. All the parameters were let free to relax and all the calculations converged toward optimized geometries corresponding to energy minima, as revealed by the lack of negative values in the subsequent frequency calculation. A scaling factor of 0.98 for the calculated harmonic wavenumbers was employed, as usually performed in calculations at this level of theory [40–43].

The DFT calculations of DANs were performed for the *trans* form with respect to the olefinic C=C bond, as well as for the *cis* form. The DFT calculations for the azo-derivative were performed by considering a *trans* arrangement with respect to the central N=N bond.

Time-dependent density functional theory (TD-DFT) calculations [44] were performed for DANs with the same functional and basis set on the optimized geometry in order to obtain a correct assignment of the observed bands in the UV–visible absorption spectra. The simulated

excitation spectrum was obtained by considering twenty S<sub>n</sub> ← S<sub>0</sub> excitations.

We computed the descriptors of charge-transfer with the spreadsheet provided in the Supplementary material of Ref. [45]. Molecular figures have been drawn with the Gaussview [46] and Jmol [47] softwares.

## 4. Results and Discussion

### 4.1. Structure and Electronic Spectra of DANs

DANs is a push-pull molecule due to an electronic charge-transfer occurring from amino to nitro group through the π-conjugated system. Fig. 1 shows the resonance structures of DANs, one benzenoid and another quinonoid, where negative charges are localized on the oxygen atoms of the nitro group.

The electronic spectrum (Fig. 2) shows essentially two bands: one in the UV region at about 305 nm, attributable to π → π\* transition, and another one in the visible region with maximum at 433 nm, related to the excitation of the nitro group. The latter band, which moves depending on the solvent [15], is shifted to higher wavelengths in the solid state, with a maximum at 438 nm and a pronounced tail extending beyond 600 nm.

Although not reported in the literature, the molecular structure of DANs can be considered planar on the basis of the DFT approach (but for H atoms of the methyl groups) that we have used here for the molecule in the *trans* form. The optimized structure, along with calculated energy and structural parameters, is shown in Fig. S1 (Supplementary material), whereas the ElectroStatic Potential (ESP) surface of DANs in the ground state is reported in Fig. S2 (Supplementary material).

By observing the contour plots of the computed frontier orbitals (Fig. 3), we notice that the HOMO has a benzenoid character, while the LUMO has a quinonoid one. In particular, for the HOMO the central C=C bond has olefinic character, whereas for the LUMO a nodal plane

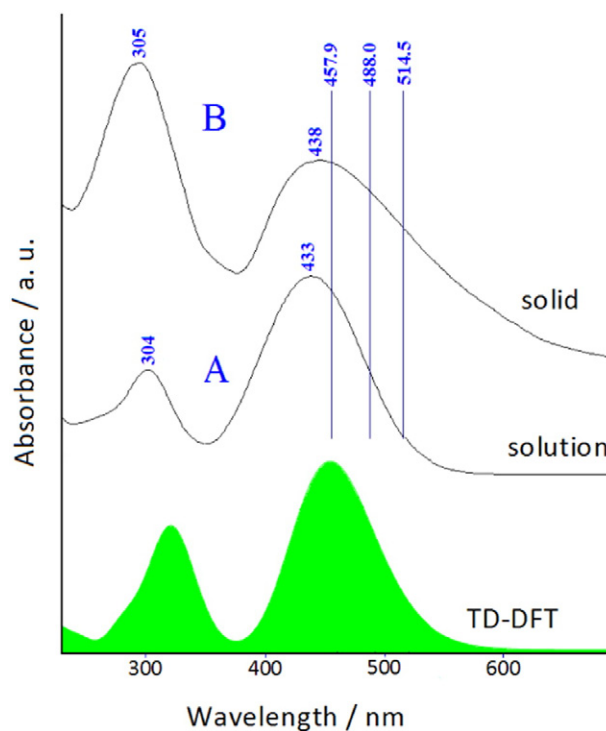


Fig. 2. UV–vis absorption spectra of DANs in CH<sub>2</sub>Cl<sub>2</sub> solution (A) and in the solid phase (B). The spectral positions of the visible laser lines used for the Raman excitation are shown. The simulated spectrum obtained by TD-DFT calculations is also reported in green for sake of comparison.

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