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In the search for experimental and quantumchemical evidence for zwitterionic nature of (2*E*)-3-[4-(dimethylamino)phenyl]-2-nitroprop-2-enenitrile – An extreme example of donor–π–acceptor push–pull molecule

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ABSTRACT

To explain an extremely low reactivity of (2E)-3-[4-(dimethylamino)phenyl]-2-nitroprop-2-enenitrile (**1**) in regard to other similar derivatives, the molecular structure of the title compound has been studied by experimental and theoretical methods. The crystal structure analysis provided the evidence, that the title compound exists in a solid state as a stable *E*-isomer in a zwitterionic form. Based on NMR, IR, UV/VIS spectroscopic and DFT calculations data, this structure has been also proposed for **1** dissolved in organic solvents.

1. Introduction

In recent years [1–5], we have thoroughly studied topics related to the synthesis and reactivity of (2E)-3-aryl-2-nitroprop-2-enenitriles. In particular, we have shown that these compounds belong to the group of particularly reactive dienophiles and they react very rapidly with cyclopentadiene, even at 0 °C [1,4]. These reactions lead to mixtures of stereoisomeric nitronorbornenes. Additionally, we have performed kinetic studies at room temperature for a series of related compounds with substituents with σ_R constants being in the range of −0.27 to 0.45 [3]. Approximating the obtained *Hammet* relationship, we have concluded that slightly less π-deficient (2E)-3-[4-(dimethylamino)phenyl]-2-nitroprop-2-enenitrile (**1**) ($\sigma_R = -0.83$ [6]) should react under similar conditions with a rate constant of *ca.* $1.7 \cdot 10^{-3}$ dm^3 mol^{-1} s^{-1}. In order to verify this assumption, we have performed a number of test reactions. The progress of the reaction was monitored using HPLC and ^1H NMR techniques. Surprisingly, it turned out that neither in these conditions nor at higher temperatures (80 °C, 110 °C), including solvent-free conditions, the Diels–Alder reaction of compound **1** with cyclopentadiene does not proceed. According to *Perekalin* [7] this compound may possess a zwitterionic nature (structure II at Fig. 1). The authors base this statement on the shape of the UV/VIS spectrum recorded in an ethanolic solution.

Additionally, the molecular structure of the title compound fulfills the requirements for being a π-conjugated "push–pull" molecule [8], where the $-N(CH_3)_2$ and $-NO_2$ functional groups arranged linearly may act as an electron-donor and an electron-acceptor, respectively, transferring the charge through the styrene π system [9]. Such zwitterionic nature of **1** could explain the surprisingly low reactivity of this compound.

The aforementioned facts prompted us to study the structure of the title compound in detail. We have decided (i) to thoroughly analyze NMR, IR and UV/VIS spectra of the title compound, (ii) to perform DFT simulations of the UV/VIS spectrum and interpret electronic transitions, (iii) to study the molecular structure of **1** by

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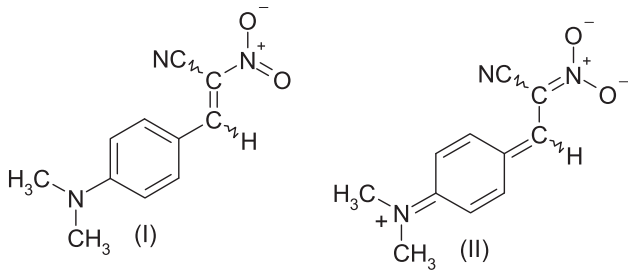

Fig. 1. Possible "alkene-like" (I) and zwitterionic (II) forms of (2E)-3-[4-(dimethylamino)phenyl]-2-nitroprop-2-enenitrile (**1**).

the X-ray diffraction experiment to elucidate the presence of the suggested conjugated zwitterionic system in the solid state, (iv) to analyze the molecular structures of related *E* and *Z* isomers based on *β*-nitrostyrenes and cinnaminic acid derivatives, (v) to search for the structural evidences for the possibility of conjugation in such systems. It should also be noted that the geometric isomerism of the aforementioned compounds has not been studied previously. On the other hand, the possibility of photoinduced *E*/*Z*-isomerization of such compounds has been suggested by *Pedireddi* [10] as an explanation for anomalous products formation in a solid state dimerization of 2-aryl-1-nitroethenes.

2. Experimental

2.1. Analytical techniques

Melting points were determined on a Boetius apparatus and are uncorrected. Elemental analyses were performed on a Perkin-Elmer PE-2400 CHN apparatus. IR spectra were recorded on a Bio-Rad spectrophotometer in CCl_4 solution. UV/VIS spectra were recorded on a Nanocolor Macherei-Nager spectrophotometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker AMX 500 spectrometer. Liquid chromatography (HPLC) was done using a Knauer apparatus equipped with a UV–VIS detector. For monitoring of the reaction progress, LiChrospher 18-RP 5 μm column (4 × 240 mm) and 75% methanol as the eluent at flow rate 1.0 cm^3/min were used. In HPLC/MS experiments was used Shimadzu LCMS-IT-TOF instrument with ES ionization (heat bock and CDL temperature 200 °C, nebulising gas flow 1.5 mL/min), connected to Shimadzu Prominence chromatograph two pumps LC-20AD equipped with Phenomenex Kinetex 2.6 μm C18 100A column (65% acetonitrile was used as the eluent).

2.2. Materials

Commercially available (Sigma–Aldrich) reagents and solvents were used. All solvents have been tested by means of gas chromatography just before use. Nitroacetonitrile was prepared according to procedure described previously in detail [11].

2.3. Preparation of (2E)-3-[4-(dimethylamino)phenyl]-2-nitroprop-2-enenitrile

0.100 Mol of 4-dimethylamine benzaldehyde was dissolved in 2 cm^3 of ethanol. Next, 0.1 g of 4 Å molecular sieves, 0.11 mol of nitroacetonitrile and catalytic amount of *n*-propylamine was added. Reaction mixture was stirred for 4 h at room temperature. Product was separated by filtration and recrystallized from ethanol to form violet crystals of m.p.: 189 °C (ref. 182–183 °C [12]) in 89% yield.

2.4. Spectral data

^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.20 (s, 6H, NC<u>H</u>$_3$), 6.76 (bd, 2H, J = 9.5 Hz, Ar), 7.93 (bd, 2H, J = 8.5 Hz, Ar), 8.49 (s, 1H, =C–<u>H</u>); ^{1}H NMR (500 MHz, acetone-d_6) δ: 3.25 (s, 6H, NC<u>H</u>$_3$), 6.95 (bd, 2H, J = 9.1 Hz, Ar), 8.02 (d, 2H, J = 9.1 Hz, Ar), 8.56 (s, 1H, =C–<u>H</u>); ^{1}H NMR (500 MHz, dmso-d_6) δ: 3.17 (s, 6H, NC<u>H</u>$_3$), 6.94 (bd, 2H, J = 9.5 Hz, Ar), 8.00 (d, 2H, J = 8.8 Hz, Ar), 8.64 (s, 1H, =C–<u>H</u>); ^{13}C NMR (126 MHz, acetone-d_6) δ: 40.43, 113.43, 114.47, 115.68, 136.73, 148.72, 156.65; ^{13}C NMR (126 MHz, dmso-d_6) δ: 39.95, 112.77, 114.07, 114.13, 114.38, 135.93, 147.97, 155.50; 13C NMR (126 MHz, $CDCl_3$) δ: 40.25, 112.25, 113.38, 114.97, 135.86, 147.79, 155.20; IR (CCl_4, cm^{-1}) ν_{max} = 1737(s), 1575(m), 1373(m); UV/VIS (MeOH, nm) λ_{max} = 275 (log ε = 3.90), 481 (log ε = 4.70); Elemental analysis: calc. (%): C 60.85; H 5.11, N 19.36, found (%): C 60.82; H 5.11; N 19.37; HR-MS: for $C_{11}H_{11}N_3O_2$ $(MH)^+$ calc. 218.0924 m/z, found 218.0924 m/z.

2.5. Quantumchemical calculations

The quantum-chemical calculations within DFT were performed using Gaussian09 software. The starting geometry configuration of (2E)-3-[4-(dimethylamino)phenyl]-2-nitroprop-2-enenitrile in gas phase was determined by optimization of its ground state in the cc-pVDZ basis set. Then the Polarizable Continuum Model (PCM) was applied with methanol as a solvent. In order to estimate the accuracies of the DFT results, higher basis sets with triple and quadruple zeta were employed. Figure in Supplementary Material presents the molecular total energy $E(n)$ for different cc-pVnZ basis sets, where n = D, T, Q. It should converge to the complete basis set E(CBS). Using the extrapolation procedure described in Refs. [13], the E(CBS) was derived. The difference E(D)-E(T) is almost 2.5 times higher than E(T)-E(CBS). Thus the cc-pVTZ basis set is sufficient for this sort of computation. Of course, the cc-pVQZ basis set brings closer to the CBS results but it makes the calculation significantly more expensive.

Another evaluation of calculation accuracies is comparison of its results with experimental data. As shown below in Table 5, the bonds lengths of the title molecule in a crystalline state measured experimentally agree well with the computed values despite the latter are derived for the PCM with methanol solvent. Moreover, analysis of the RMS reveals that employment of the cc-pVQZ basis set gives only a minor improvement over the cc-pVTZ basis set. However, all n = D, T, and Q are used in this work depending on a specific problem.

2.6. X-ray crystal structure determination

The X-ray diffraction intensities for **1** were collected at room temperature on SuperNova X-ray diffractometer equipped with Atlas S2 CCD detector using the mirror-monochromatized CuK_α radiation (λ = 1.54184 Å). All data were collected using the ω scan

Table 1
Comparison of selected physical properties of (2E)-3-[4-(R)phenyl]-2-nitroprop-2-enenitriles.

	R	σ_p^+	UV: λ_{max} [nm]	^{1}H NMR: $\delta_{H(vin)}$ [ppm]	IR: ν_{NO_2} [cm^{-1}]
1	$(H_3C)_2N$	−1.70	275, 481[a]	8.49	1388, 1575
2	H_3CO	−0.78	244, 367[a]	8.61	1318, 1560
3	F	−0.07	230, 330[a]	8.67	1327, 1537
4	H	0.00	227, 322[a]	8.70	1328, 1530
5	Cl	0.11	234, 331[a]	8.63	1325, 1536
6	H_3COOC	0.49	229, 321[a]	8.70	1332, 1542

[a] More intense maximum.