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The Structure of Two 1-(Nitrophenyl)- Δ^2 -pyrazolines: a Crystallographic and Theoretical Study

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The crystal and molecular structures of two nitrophenylpyrazolines have been determined. The geometries have been used as starting geometries for density functional theory (DFT) calculations. The differences in conformation between both molecules and between the solid state and gas phase are explained in terms of steric effects. An attractive intramolecular $N \cdot \cdot N$ interaction between the nitro group and the pyrazoline N2 nitrogens has been found. Absolute shieldings have been calculated (GIAO) and compared with experimental ¹H and ¹³C chemical shifts.

Manuscript received: 29 May 2004. Final version: 2 September 2004.

Introduction

There are five major sources of information on the chemistry of pyrazoles and their derivatives,^[1-5] in all of them the synthesis and reactivity of Δ^2 -pyrazolines (1*H*-4,5dihydropyrazoles) is extensively discussed. Not so their structural and spectroscopic aspects, which are only detailed in the last two references.^[4,5] However, these compounds have important properties as organic light-emitting diodes^[6] and fluorescent probes,^[7,8] and have other applications as intelligent materials, a field particularly explored by Prasanna de Silva et al.^[9–15] 1-Nitrophenyl- Δ^2 -pyrazolines are promising in these fields, being brightly coloured, but still unexplored. A search for these compounds shows that the great majority of such compounds belong to the *p*-nitrophenyl series 1 (Scheme 1).^{$[16-\bar{1}8]$} The reason is that these compounds can be obtained by cyclization of the *p*-nitrophenylhydrazones of α,β -unsaturated carbonyl compounds and by 1,3-dipolar cycloaddition of p-nitrophenylnitrilimines on olefins (including fullerenes).^[19,20] The 2',4'-dinitrophenyl derivatives 2 are much less abundant because the cyclization of the 2,4-dinitrophenylhydrazones of α , β -unsaturated carbonyl compounds generally fails (for an exception see the 5-hydroxy/5-trifluoromethyl intermediates).^[21–24] Finally, the 2',4',6'-trinitrophenyl derivatives **3** have only been reported in our work: compounds **1–3** are usually obtained by *N*-arylation of $1H-\Delta^2$ -pyrazolines with *p*-fluoronitrobenzene, 1-fluoro-2,4-dinitrobenzene, and 1-chloro-2,4,6-trinitrobenzene (picryl chloride).^[25–39] Reports of crystal-structure determinations of nitrophenylpyrazolines are limited to the highly substituted derivative **4**.^[40]

Results and Discussion

In this paper we will describe two compounds, one of type **2** and another of type **3**, namely 1-(2',4'-dinitrophenyl)-2-pyrazoline **5** and *trans*-1-(2',4',6'-trinitrophenyl)-3,4,5-trimethyl- Δ^2 -pyrazoline **6** (Scheme 2).

We have already published some information about these two compounds. The synthesis,^[27] reactivity,^[29,34] ¹³C NMR^[35] and ¹H NMR spectra,^[38] and $pK_a^{[39]}$ of compound **5** have been reported. The ¹³C NMR^[35] and ¹H NMR^[37] spectra of compound **6** have also been reported, and the synthesis of **6** is reported here.



Scheme 1.



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Solid-State Structures

Crystal data and refinement details are summarized in Table 1. The molecules are represented in Fig. 1 (top). Although there is potentially free rotation between the phenyl and heterocyclic rings during crystallization of 5, the molecule tends to be flat in the solid with the angles between the mean planes of the rings at 17.0(4) and $8.6(4)^{\circ}$ for the two independent molecules in the asymmetric unit. The molecules are packed in a herringbone pattern on the 0 1 1 projection. The packing diagram shows molecules having phenyl-phenyl distances of 3.5–3.8 Å, which suggests π -stacking. Note that the *ortho*nitro group is situated close to the pyrazoline N2 atom as represented in 5. In the solid state, the methyl groups on the heterocyclic rings appear in 6 to exert enough steric influence to twist the phenyl and heterocyclic rings from each other, thereby increasing the angle between ring mean planes to 38.2°. The enhanced steric influence afforded by the methyl groups on the ring can also be observed from the increase in puckering of the heterocyclic ring from a 0.064(5) Å average mean plane deviation in 5 to the considerably more puckered 0.099(4) Å mean plane deviation in 6. The pyrazoline ring in this last compound adopts a $C_{\rm s}$ conformation. In the case of 1-(2',4'-dinitrophenyl)- Δ^2 -pyrazolin-5-ones, the X-ray structure shows that the 2'-nitro group prefers the proximity of the 5-C=O group than that of the N2 atom.^[41]

Density Functional Theory Calculations

Geometries

We have optimized the geometries at the B3LYP/6– $311++G^{**}$ level. Although we have not carried out a complete exploration of the energy hypersurface, these geometries are minima (no imaginary frequencies). To compare the four situations depicted in Fig. 1, we have summarized the most relevant geometrical parameters in Table 2, but it is possible to visually notice the great similarity between the experimental and calculated geometries.

In more detail, the calculated geometries confirm the fact that in 1-(2',4'-dinitrophenyl)pyrazolines **2**, the *ortho*-nitro group places itself close to the pyrazole N2, a particularly novel result. We assign this fact (also observed, by ¹H NMR spectroscopy in solution, for the corresponding pyrazoles^[42] but not reported for pyrazolines) to an attractive interaction between the positively charged N atom of the nitro group and the lone pair of electrons of N2. The calculated N2··· N(*o*-NO₂) distance is a little longer than the crystallographic one, perhaps because of crystal packing forces. The distance is shorter for **6** than for **5**. An examination of the calculated geometries of these two compounds shows that the 6-nitro group pushes the pyrazoline ring towards the 2-nitro group (**5**: N2–N1–C1' 120.6°, N1–C1'–C2' 123.3°; **6**: N2–N1–C1' 117.8°, N1–C1'–C2' 121.3°) shortening the N···N distance.

Table 1. Summary of crystal data and refinement details for 5 and 6 Quantity minimized = $R(wF^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^2)^2\}^{1/2}$: $R(F) = \Sigma\Delta/\Sigma(F_o), \Delta = |(F_o - F_c)|$: $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$: $P = [2F_c^2 + \max(F_o, 0)]/3$

Parameter	5	6 C ₁₂ H ₁₃ N ₅ O ₆	
Empirical formula	C9H8N4O4		
Formula weight	236.19	323.27	
Colour	orange	block orange, plate	
Crystal dimensions [mm ³]	$0.10 \times 0.10 \times 0.10$	$0.10 \times 0.10 \times 0.04$	
Space group	$\overline{P}1$ (no. 2)	P_{21}/c (no. 14)	
Z	4	4	
a [Å]	8.0211(14)	12.761(6)	
b [Å]	10.3927(19)	8.704(2)	
<i>c</i> [Å]	13.296(3)	13.848(6)	
α [°]	76.261(8)	90	
β[°]	86.133(14)	112.97(2)	
γ [°]	75.246(9)	90	
Collection ranges	$-10 \le h \le 10; -12 \le k \le 12;$	$-16 \le h \le 15; -11 \le k \le 10;$	
	$-17 \le l \le 17$	$-18 \le l \le 17$	
Temperature [K]	298(2)	120(2)	
Volume [Å ³]	1041.1(3)	1416.2(10)	
$D_{\text{calc}} [\text{mg m}^{-3}]$	1.507	1.516	
Radiation	Mo _{Kα} (λ 0.71073 Å)	Mo _{Kα} (λ 0.71073 Å)	
Absorption coeff. μ [mm ⁻¹]	0.122	0.124	
Absorption correction	SADABS	SADABS	
$T_{\rm max}/T_{\rm min}$	0.9879/0.9879	0.9951/0.9877	
<i>F</i> (000)	488	672	
θ range for data collection [°]	2.08-28.00	2.83-28.08	
Observed reflections	5210	7161	
Independent reflections	4826 (R _{int} 0.0534)	3335 (<i>R</i> _{int} 0.0365)	
Data/restraints/parameters	4826/0/307	3335/0/208	
Maximum shift/error	0.000	0.000	
Goodness-of-fit on F^2	1.042	1.056	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 0.0662, wR_2 0.1719$	$R_1 \ 0.0662, \ wR_2 \ 0.1719$ $R_1 \ 0.0529, \ wR_2 \ 0.1227$	
Largest diff. peak and hole [e $Å^{-3}$]	0.288 and -0.244	0.371 and -0.299	

The analysis of the electron density using the atoms in molecules (AIM) methodology shows a bond critical point connecting the N2 of the pyrazoline ring and the nitrogen atom of the *ortho*-nitro group for the two systems studied here. The presence of bond critical points is characteristic of attractive interactions between the two atoms that generate it, and in this case it can be explained based on the interaction of the lone pair of N2 and the positive charge of the nitrogen atom of the NO₂ group.

The puckering of the five-membered rings, similar to that of cyclopentene (envelope C_s conformation), principally affects the C5 carbon opposite to the N2–C3 double bond. It can be described using the N2–C3–C4–C5 torsion angle. Our



Fig. 1. X-Ray and optimized structures. Top-left, X-ray structure of 5 (two independent molecules); top-right, X-ray structure of 6; bottom-left, optimized structure of 5; bottom-right, optimized structure of 6.

calculations reproduce the experimental data well for compound 5 (-12° versus -11°). In the case of compound 6 the puckering determined by crystallography (15°) appears to be related to the crystal packing and not to the presence of the 3-, 4-, and 5-methyl groups on the pyrazoline ring. We reached this conclusion because, in the calculated geometry that represents the conformation in the gas phase, the puckering is only 6.8°. The twist angle between both rings, as defined by the N2–N1–C1–C2 angle, is similar in both compounds and is similar in the solid state and in the gas phase.

The nitro groups are almost planar (the sum of the angles about the N atom, $\Sigma\theta$, close to 360°). The *para*-nitro group (4'-NO₂) is almost coplanar with the phenyl ring (167–178°). On the contrary, the *ortho*-nitro groups (2'-NO₂ and 6'-NO₂) are near perpendicular.

The Possible Attractive Intramolecular $N \cdots N$ Interaction between the Nitro and Pvrazoline Nitrogens

One of the most interesting observations of the present paper is the existence of an interaction between the nitro group nitrogen, which is acting as an acceptor to the pyrazoline N2 lone pair, an interaction that we will discuss using the calculated geometries of 5 and 6, where $d_{N...N}$ is 2.78 and 2.69 Å, and the sum of the van der Waals radii is 3.16 Å (Kitaigorodsky) and 3.00 Å (Pauling).^[43] Most weak interactions involving nitro groups are hydrogen-bond interactions between proton donors (including acidic CHs)^[44] and one of the negatively charged O atoms of the nitro group $[X-H \cdots O(NO)-R]$. However, the electronic structure of the nitro group presents a formal positive charge on the nitrogen that can interact with a Lewis base, for instance, a lone pair. This interaction should weaken the C2'-NO₂ bond increasing the C-N bond length.^[45] In compound 5 the 2'-nitro group has a $d_{\rm CN}$ of 1.479 Å while the 4'-nitro group has a $d_{\rm CN}$ of 1.464 Å; the stronger interaction present in compound **6** has a corresponding $d_{\rm CN}(2')$ of 1.483 Å [$d_{\rm CN}(4')$ 1.467 Å and $d_{\rm CN}(6')$ 1.470 Å]. Another possible criterion is that the interaction should modify the planarity of the nitro group, resulting in a slight pyramidalization towards the N atom. In molecules 5 and 6, for all the nitro groups not involved in N···N interactions, the sum of the three angles, $\Sigma \theta$, amount to 360.0°, whereas $\Sigma \theta$ of the 2'-nitro groups is 359.8°. The phenomenon described here bears some relationship with the structure-correlation principle of Dunitz and Bürgi.^[46] Note, however, that the approach of an amine to the carbon atom

 Table 2.
 Characteristic geometrical parameters of 5 and 6

 5a and 5b refer to the two independent molecules found in the unit cell

Geometry	5a (X-Ray)	5b (X-Ray)	5 (DFT)	6 (X-Ray)	6 (DFT)
Puckering (N2–C3–C4–C5) [°]	-9.7	-11.9	-10.9	15.0	6.8
Inter-ring torsion (N2–N1–C1′–C2′) [°]	23.5	14.9	23.4	26.1	29.1
Distance N2···N(o -NO ₂) [Å]	2.70	2.74	2.78	2.62	2.69
Torsion of 2-NO ₂ (C1'-C2'-NO) [$^{\circ}$]	54.2/-129.5	74.3/-106.8	49.6/-134.5	65.2/-117.8	49.1/-135.4
Torsion of 4-NO ₂ (C3'–C4'–NO) $[^{\circ}]$	-11.1/169.8	12.4/-166.7	-1.5/178.6	-7.7/172.3	-1.8/178.2
Torsion of 6-NO ₂ (C5'–C6'–NO) [°]	_	—	—	25.1/-150.7	40.7/-136.4



Fig. 2. The calculated molecular structure of the $C_3H_5N_2O_2^-$ anion.

of a carbonyl group is the first step of a nucleophilic addition, while the approach to a nitrogen atom of a nitro group cannot lead to any product (the only possible attack is on the carbon with the NO₂ as a leaving group). A search in the Crystal Structure Database (version 5.25, update July 2004),^[47] shows several nitroaromatic derivatives with short N···N distances (approx. 2.7 Å) the second nitrogen atom belonging to an amino, imino, azo, or one heterocycle (see Scheme 3 for some examples).

The most interesting case is DIWWEL, studied by Egli et al.^[48] The structure of 1-dimethylamino-8-nitronaphthalene has been observed in seven environments. The shortest $N \cdot \cdot N$ distance is 2.643 Å (DIWWEL01) with a sum of the three angles $\Sigma \theta$ of 359.9° (in other structures the sum is 359.6°), evidence, according to these authors, of 'an attraction between the two groups'. The same conclusion is valid for compounds **5** and **6**. If one wants larger interactions, the N atom should bear a negative charge as in the imaginary molecule represented in Fig. 2.

For this molecule (B3LYP/6–311++G** calculations), a $d_{\text{N}...\text{N}}$ of 2.567 Å and a $\Sigma\theta$ of 356.3° were calculated.

Absolute Shieldings

We have calculated (GIAO on B3LYP/6–311++G^{**} geometries) the ¹H and ¹³C absolute shieldings (σ , ppm, unreported) of compounds **5** and **6** [Eqns (1) and (2)]. The

correlations with the experimental data^[20,23] are excellent:

$$\delta_{\rm H}(\exp) = (31.2 \pm 0.7) - (0.94 \pm 0.027)\sigma^{1}{\rm H}, \qquad (1)$$
$$n = 12, r^{2} = 0.993$$

$$\delta_{\rm C}(\exp) = (175.1 \pm 1.3) - (0.963 \pm 0.014)\sigma^{13}{\rm C},$$
 (2)
 $n = 19, r^2 = 0.997$

The intercepts are relatively close to the σ values for tetramethylsilane (TMS) calculated at the same level: ¹H (31.97 ppm) and ¹³C (184.75 ppm). When only sp² carbons are correlated, like in Eqn (2), TMS is far away and the intercept does not correspond to the calculated value. In two recent publications, we have found intercepts of 175.8 ± 0.9 and 176.7 ± 1.7 ppm for ¹³C NMR correlations.^[49,50]

Conclusions

The determination of the structures of compounds **5** and **6** fills a gap in the knowledge of 1-nitroarylpyrazolines, a series of dyes that, conveniently modified, could have useful properties in non-linear optics.^[51,52] The AIM analysis revealed that the *ortho*-nitro substituent interacts with the lone pair of the pyrazoline N2 atom thus explaining the preferred *syn* conformation. This type of donor–acceptor interaction can potentially have a large impact on the conformation of flexible molecules and may also play a role in controlling crystal packing (for the intermolecular type of interaction).

Experimental

Synthesis of trans-1-(2',4',6'-Trinitrophenyl)-3,4,5-trimethyl-2-pyrazoline **6**

From 3-methylpent-3-en-2-one^[53] and hydrazine, 3,4,5-trimethyl-2pyrazoline was prepared.^[54] Compound **6** was obtained by treating 3,4,5-trimethyl-2-pyrazoline^[53] with picryl chloride in a 1:1 molar ratio in boiling ethanol.^[27] The compound was crystallized from ethanol/benzene. Yield 87%, mp 118–120°C (Found: C 44.3, H 4.1, N 21.1. C₁₂H₁₃N₅O₆ requires C 44.6, H 4.1, N 21.3%).

Crystallographic Structural Studies of 5 and 6

Compounds 5 and 6 were crystallized by slow cooling of saturated solutions in hot bromobenzene. Suitable crystals were selected, sectioned as necessary, mounted on glass fibres with epoxy adhesive for 5, and mounted with Paratone oil and flash-cooled to the data collection temperature for 6. Unit cell parameters were obtained from 60 data frames, 0.3°, from three different sections of the Ewald sphere. No symmetry higher than triclinic was observed for 5 and solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable refinement. Systematic absences in the diffraction data and unit cell parameters for 6 were uniquely consistent with the reported space group $P2_1/c$. SADABS absorption corrections were applied based on redundant data.^[55] Two crystallographically unique but chemically equivalent molecules were located in the asymmetric unit of 5. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Structure factors are contained in the SHELXTL 6.12-program library.^[50] The CIF is available from the Cambridge Crystallographic Data Centre under the deposition numbers CCDC 226261 and 226262 for compounds 5 and 6, respectively.

Computational Details

The geometries of compounds **5** and **6** were initially optimized with the B3LYP method^[56] using the 6-31G* basis set.^[57] The minimum

nature of all structures was confirmed by frequency calculations.^[58] In addition, B3LYP/6–311++G**^[59] optimizations were carried out and the structures thus obtained [also minima]^[58] were used to calculate the absolute shieldings, σ , at the same computational level with the GIAO approximation.^[60] The complexes represented in Fig. 1 correspond to the structure optimized at the B3LYP/6–311++G** level. All the calculations were performed using *Gaussian 98*.^[61] The electron density of the compounds has been analyzed by means of the AIM methodology.^[62]

Acknowledgments

Financial support was provided by the Spanish DGI/MCYT (Projects no. BQU-2003-01251 and SAF-2003-08003-C02-02).

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