The extraordinary richness of the reaction between diazomethane and tetracyanoethylene: can computational calculations shed light on old papers?†

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In the quest of the structure of the intermediate between $\Delta^1$- and $\Delta^2$-pyrazolines, the reactivity of these molecules tetrasubstituted by cyano groups in adjacent positions (3,3,4,4 or 4,4,5,5) has been explored in their neutral and protonated forms. Many reactions reported in the literature for pyrazolines have been studied and quantified (energies and transition states). Thirty-three structures of pyrazolines, their open-ring counterparts and their complexes are described. Acid–base equilibria, rotations, electrocyclic reactions and sigmatropic transpositions are reported.

1. Introduction

The reaction of diazomethane 2 with tetracyanoethylene 1, both very common compounds, has only been studied two times. In 1962, Bastuís and Castells reported the reactions of Fig. 1 (their numbering of formulae is different). They indicated that 3 can be explosive and this probably prevented other authors from repeating its preparation.

$\Delta^1$-pyrazoline 3 (4,5-dihydro-5$H$-pyrazole-3,3,4,4-tetracarbonitrile) was isolated and it spontaneously evolved nitrogen to yield 1,1,2,2-tetracyanocyclopropane 4 that was already known having been prepared by other methods. Compound 3 was washed with benzene to eliminate all traces of 1 and was slowly dissolved in dry ether to yield a compound to which structure 5 (2,2,3,3-tetracyano-1,5-diaza-bicyclo[2.1.0]pentane) was assigned. Compound 5 when treated for about 90 min with a 5% solution of 1 in dry ether afforded $\Delta^2$-pyrazoline 6. The isomerization of 6 to 5 was performed using wet ether or dry ether containing traces of hydrogen chloride. Both substances can be kept for several weeks without alteration. According to Bastuís and Castells, the $6\rightarrow5$ isomerization involves the pyrazolinium cation $6bH^+$. The role of TCNE (1) in the $5\rightarrow6$ isomerization was assigned to a 1:5 complex.

Huisgen et al. repeated the reaction. They cited Banús and Castells but they isolated only 4 and 6. Leaving aside 4 (also $6bH^+$ was not characterized), we have summarized in Table 1 all the available information on the compounds in Fig. 1.

Calatroni and Gandolfi reported a series of reactions that are related to the work of Banús and Castells (Fig. 2). $\Delta^1$-pyrazoline I reacted in two ways with TCNE (1) to afford a charge-transfer complex II and adduct III that was not isolated nor identified. They assumed that the reaction $1\rightarrow III$ is fast and reversible. Besides, TCNE promotes the isomerization $I\rightarrow IV$ in agreement with Castells’ results. A reaction product V was postulated corresponding to the reaction of IV with TCNE.

Calatroni and Gandolfi indicated in their paper that they wanted to determine the crystal structure of II (yellow crystals) but they probably failed because no structure like II was reported in the CSD. The only one that bears resemblance to II is FEJDUT (VI), see Fig. 3.
We decided to study theoretically structures 3, 5 and 6 and their corresponding protonated cations (Fig. 4) as well as some concerted reactions related to Woodward–Hoffmann rules.\textsuperscript{8–10}

2. Computational details

The geometries of pyrazolines (Pz) and pyrazolinium cations (PzH\textsuperscript{+}) have been fully optimized using the functional B3LYP\textsuperscript{11} and the 6-311++G(d,p) basis set\textsuperscript{12} in the spin restricted formalism as implemented in the Gaussian 16 package (the coordinates of all the optimized geometries are gathered in the ESI\textsuperscript{†}).\textsuperscript{13} The minimum energy and transition state structures of all compounds were characterized using frequency analysis. The solvent effects have been evaluated by re-optimizing the structures at the B3LYP/6-311++G(d,p) level and using the self-consistency reaction field (SCRF) method\textsuperscript{14} based on the polarized continuum model (PCM) of Tomasi and co-workers\textsuperscript{15} in ethanol, diethylether and benzene as solvents using the standard parameters provided by the Gaussian-09 program. For the infrared spectra, the frequencies have been scaled by a factor of 0.9679.\textsuperscript{16} Absolute chemical shieldings have been calculated with the GIAO approximation\textsuperscript{17} and then transformed into chemical shifts using empirical equations.\textsuperscript{18} The static intrinsic reaction coordinates (IRCs)\textsuperscript{19} were analyzed in two cases.

3. Results and discussion

3.1. 4,5-Dihydro-5\textit{H}-pyrazole-3,3,4,4-tetrcarbonitrile (3)

Diazomethane, a 1,3-dipole with octet stabilization,\textsuperscript{10} reacts with CC double and triple bonds to afford pyrazolines and...
Table 2  Relative energies in kJ mol\(^{-1}\) with regard to 6 (neutral) and 6\(BH^+\) (protonated)

|   | Neutral | 5a (inside) | 5b (outside) | 6   |
|---|---------|------------|-------------|-----|
| Cations | 3a\(H^+\) | 3b\(H^+\) | 5a\(H^+\) | 5b\(H^+\) | 6\(H^+\) | 6\(H^+\) |
|   | 36.9    | 40.5      | 164.4      | 154.3 | 15.3  | 0.0   |

3.3. 4,5-Dihydro-1H-pyrazole-4,4,5,5-tetracarbonitrile (6)

\(\Delta^1\)-pyrazoline 6 is the most stable of the three isomers (Table 2). The 3 \rightarrow 6 tautomerization involves a 1,3 CH to NH prototropy. A direct proton transfer has a high barrier that in similar five-membered rings prevents this mechanism, while the following one involves assistance by solvent molecules (one or two) such as water or alcohols with a low barrier.\(^{22}\) The calculated TS between 3 and 7 is 289.7 kJ mol\(^{-1}\) and between 7 and 8, it is 277.8 kJ mol\(^{-1}\).

The experimental IR spectrum (KBr) and the calculated bands (gas phase) agree exceptionally well assuming that there is an intercept. The corresponding linear regression line is:

\[
\text{Exp.} = (126 \pm 37) + (0.93 \pm 0.1) \text{Calc.}, \ n = 7, R^2 = 0.999, \ R\text{MS residual} = 32 \text{ cm}^{-1}
\] (1)

Table 3  IR (scaled frequencies in cm\(^{-1}\)) and NMR calculated properties (chemical shift, \(\delta\), in ppm) of compounds 3, 5a, 6 and 7

| Compound | \(\delta\) (\text{CH}) | \(\delta\) (\text{CN}) | \(\delta\) (\text{N}1) | \(\delta\) (\text{N}2) | \(\delta\) (\text{N}N CN) | \(\delta\) (\text{N}N CN) |
|----------|-----------------------|-----------------------|---------------------|----------------------|------------------------|------------------------|
| 3        | 5.04 & 5.73           | 40.8                  | 91.3                | 105.4                | –99.4 & –101.0          | –86.6 & –90.7          |
| 3a       | 91.5                  | 43.4                  | 236.8               | 3419                 | 236.8                  | 297.0                 |
| 3b       | 86.5                  | 59.8                  | 107.8 & 106.8       | 1304                 | 107.2 & 107.6           | 1532b                 |
| 5a       | 3.95 & NH 2.57        | 63.2                  | 106.0 & 108.2       | 2273–2295            | 107.6 & 108.1           |
| 5b       | 58.2                  | 59.8                  | 106.8               | 3419                 | –29.5                  |
| 6        | 6.41 & NH 5.78        | 53.1                  | 105.7 & 106.8       | 2273–2295            | 107.6 & 108.1           |
| 7        | 5.93 & NH 9.72        | 50.8                  | 105.7 & 106.8       | 3419                 | –149.1                 |

Although the compound is a \(5H\)-3,3,4,4-tetracarbonitrile, we have numbered it, for consistency with the other compounds, as \(3H\)-4,4,5,5-tetracarbonitrile.\(^{b}\) This vibration involves the 1,3-(N\(\equiv\)N\(\equiv\)C) dipole.

We have removed Castells' bands at 1592 and 1595 cm\(^{-1}\) assigned to NH bending because according to eqn (1) they should appear at 1269 and 1417 cm\(^{-1}\). On the other hand, if the 1592 cm\(^{-1}\) band is assigned to N\(\equiv\)N\(\equiv\)C of 7, the agreement is good (fitted value 1544 cm\(^{-1}\)). In conclusion, on IR grounds, structure 5b should be rejected while structure 7 is acceptable.

The available \(^{13}\)C NMR data of compound 6\(^{a}\) agree with the calculated values according to the linear regression,

\[
\text{Exp.} = (173.5 \pm 3.4) - (0.91 \pm 0.04) \text{Calc.}, \ n = 7, R^2 = 0.991, \ R\text{MS residual} = 2.9 \text{ ppm (2)}
\]

The most different signals of the three compounds are the \(^{15}\)N chemical shifts of the ring nitrogen atoms: +91.3 and +105.4 ppm for 3; –236.8 and –29.5 for 6; –285.8 and –297.0 for 5b.

3.4. A first attempt to find a more stable structure for intermediate 5

We have considered that the intermediate instead of being diaziridene 5b could be zwitterion 7 (Fig. 6).

Compound 7 is much more stable than 5b, 88.3 vs. 151.0 kJ mol\(^{-1}\), but still too high for allowing the 6 \rightarrow 5 backward reaction. Solvent effects (amongst those used by Castells\(^{3}\)) calculated using the PCM model decrease the difference by a small amount: benzene, 79.7; diethylether, 75.4; and ethanol, 70.4 kJ mol\(^{-1}\).

Calculation of the IR spectrum of compound 7 leads to scaled bands at 3419 cm\(^{-1}\) (vNH) and 1523 cm\(^{-1}\) (N\(\equiv\)N\(\equiv\)C).
Using eqn (1), these values in KBr should be 3319 and 1520 cm⁻¹. Castells et al. did not report a C=\(\text{N}\) band but 3319 cm⁻¹ is consistent with the experimental value of 3295 cm⁻¹.

### 3.5. Acid–base equilibria, rotations, electrocyclic reactions and sigmatropic transpositions

Two reviews provide an overview of the electrocyclic reactions and sigmatropic reactions involving pyrazolines.⁵⁻⁷⁹ We have already reported the \(1 + 2 \rightarrow 3\) reaction with a TS of 73.8 kJ mol⁻¹ with regard to 3 (IRC, Fig. 7). Other reactions that we have studied theoretically are reported in Fig. 8 and 11 together with acid–base equilibria (protonation) and with rotations about single bonds. Note that the loss of dinitrogen to afford 4 is a very exergonic reaction.

Regarding Fig. 8, as we have already commented, the proposed structure of intermediate 7 lies 88.3 kJ mol⁻¹ higher than 6 (71.2 kJ mol⁻¹ above 3). A 1,2 (C to N) transfer of hydrogen has a barrier of 289.7 kJ mol⁻¹; the subsequent 1,2 (C to N) transfer of hydrogen to afford 6 has a barrier of 289.7 kJ mol⁻¹. These very high barriers do not correspond to real pathways because proton transfers assisted by solvent molecules have much lower barriers (see previous discussion).

Ring opening of 7 to 8a should occur thermally in a disrotatory way.⁵⁻⁷⁹ However, the geometry of 8a (Fig. 9) allows only a conrotatory mechanism with a barrier of 71.9 kJ mol⁻¹ with regard to 7. A rotation about the single NC bond affords the more stable 8b while prototropy results in the less stable azine 8c. Note that according to the Woodward–Hoffmann rules,⁸⁻¹⁰ a conrotatory mechanism is thermally forbidden.

We then considered that the complex 1:5 (Fig. 1) could be the cycloaddition product of 7 (an azomethine imine) with 1 but the resulting 9 is a bicyclic compound very destabilized by the eight cyano groups (Fig. 8).

\(\Delta^2\text{-Pyrazoline (4,5-dihydro-1H-pyrazole-4,4,5,5-tetracarbonitrile)}\) 6 can result from the reaction of tetracyanoethylene 1 with diazen-1-ium-1-ylidenemethanamide (10), a 1,3-dipole with octet stabilization (a nitrile imine).²³⁻²⁶ The cycloreversion barrier of 166 kJ mol⁻¹ is much higher than that of diazomethane.

Isomerization \(6 \rightarrow 12a\) [(2,2,3,3)-tetracyanocyclopropyl-diazene, 67.8 kJ mol⁻¹] corresponds to a [1,3]-sigmatropic transposition that has been reported in other compounds.²³ In particular, Rosenkranz and Schmid described the photochemical transformation of 5-phenyl-\(\Delta^2\)-pyrazolines into compounds similar to 12a (1-methylazo-2-phenyl-cyclopropanes); on thermal treatment, these compounds are reconverted into the corresponding pyrazolines. Compound 12b, an isomer of 12a, also possible from a similar mechanism, lies much higher in energy.

Loss of HCN from 6 affords 15. According to Rodríguez Morán, when they carried out the reaction of 1 + 2 to afford 6,¹ release of hydrogen cyanide was observed.²⁷

The last reaction we have studied is the cycloaddition of diazomethane 2 on \(\Delta^2\)-pyrazoline 6. It is known that \(\Delta^2\)-pyrazolines react with 2 to afford 1,2-diazabicyclo[3.1.0]hexanes, related to 14.²⁸ These compounds should result from the loss of dinitrogen of either 13a or 13b. According to the literature, the cycloaddition of diazomethane on imines (or Schiff bases) results in 1,2,3-triazolines related to 13a.²⁹ In our case, the reverse addition leads to a more stable compound, 1,3,4-triazoline 13b instead of 1,2,3-triazoline 13a; this is probably related to the fourth N atom, i.e. our compounds are hydrazones, not imines. The loss of dinitrogen to form 14 is strongly favored (−151.4 kJ mol⁻¹).

We then decided to carry out calculations parallel to those of Calatroni and Gandolfi.⁵ They are reported in Fig. 10.

Compound 16 is the complex of 1 and 3 (compared with the 1:5 complex of Fig. 1 and with complex II of Fig. 3); it is located 7.1 kJ mol⁻¹ above 6 and at −10.0 kJ mol⁻¹ from 3. The zwiterion 17 (compare with III of Fig. 3) is not stable and reverts to 16 both in the gas phase and in ethanol (PCM); this sheds doubt on the hypothetical III structure.⁵ Structure 19 lies 66.0 kJ mol⁻¹ above 6, also an indication that structure V in Fig. 3 was probably never formed. Charge-transfer complex 18a is not stable and evolves to the hydrogen-bonded complex 18b; it is located at −20.1 kJ mol⁻¹ from 6. The stabilization results from the hydrogen-bond and from a CN/CN stacking between both molecules.
Fig. 8  Reactions involving neutral molecules (all values in kJ mol\(^{-1}\) with regard to the minimum 6) except 5. TSs in cursive.

Fig. 9  The open ring compounds 8a and 8b their cations 8aH\(^+\) and 8bH\(^+\) and compounds 9 and 15.
It is also interesting to study the reactivity of the conjugated acids of structures of Fig. 8 because Castells et al. indicated that 5/6 equilibration was acid catalyzed (Fig. 11). Usually, Δ²-pyrazolines protonate on N1 (type a) but probably due to the presence of the four cyano groups, in this case, the protonation takes place preferably on N2 (6bH⁺), which corresponds to the hypothesis of Castells et al. However, the most important finding is that 5H⁺ (even the most stable 5bH⁺, Table 2, 154.3 kJ mol⁻¹) has an energy that makes it impossible to isomerize 6H⁺ into 5bH⁺. The cations have relative energies similar to those of the neutral molecules, 6 < 3 < 5. Although the synthesis of Δ²-pyrazolines protonated on N1, 6aH⁺, from 1 and 10H⁺, is unknown, both the stability and the barrier made it a feasible possibility.

One of the reactions of Δ²-pyrazolines protonated on N1 is to open into compounds related to 20b; this has been proven...
isomerize $^5$ can be transformed into $^5$ a stretching NH at 3295 cm$^{-1}/C_0$ the 1H NMR data. This added to the non-reproducibility of the preparation of $^5$, made it impossible to ascertain its structure. Charge transfer complexes are colored (yellow/red) but no indication of the color is reported.$^1$

On the other hand, a plethora of structures and reactions surrounding the chemistry of tetracyanoethylene (1) has been explored covering different aspects of the chemistry of pyrazolines$^{39}$ that would prove useful in related studies because several of them were not experimentally known.

### Conflicts of interest

There are no conflicts to declare.

### Appendix

According to SciFinder,$^{40}$ in the paper of Bastús and Castells,$^1$ there is the compound (a co-crystal?) represented in Fig. 12 (CAS RN 786697-55-0). Actually, there is nothing of that sort, even the dihydropyridazinone (3,4-diazabicyclo[4.2.0]oct-4-en-2-one) part is unknown.

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