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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 Δ^1- and Δ^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, Bastús and Castells reported the reactions of Fig. 1 (their numbering of formulae is different).[1] They indicated that **3** can be explosive and this probably prevented other authors from repeating its preparation.

Δ^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.[2] 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 Δ^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 Bastús and Castells, the **6** to **5** isomerization involves the pyrazolinium cation **6bH**$^+$.[1] The role of TCNE (**1**) in the **5** → **6** isomerization was assigned to a **1**:**5** complex.

Huisgen *et al.* repeated the reaction.[3,4] 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.

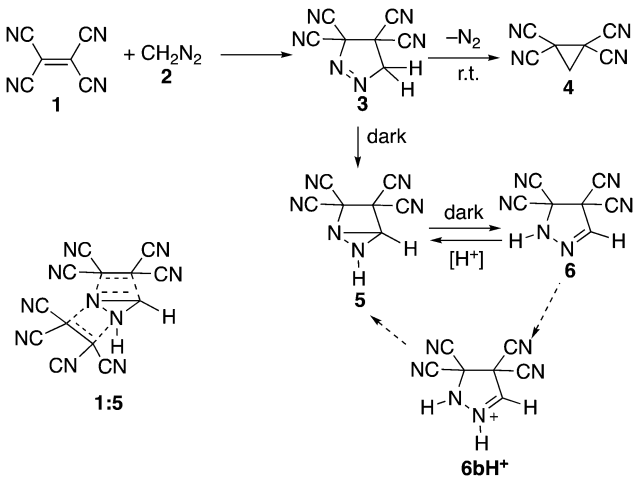

Fig. 1 Reaction of diazomethane with tetracyanoethylene according to Bastús and Castells.[1]

Calatroni and Gandolfi reported a series of reactions that are related to the work of Banús and Castells (Fig. 2).[5] Δ^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 **I** ⇌ **III** is fast and reversible. Besides, TCNE promotes the isomerization **I** → **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.[6] The only one that bears resemblance to **II** is FEJDUT (**VI**), see Fig. 3.[7]

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† Electronic supplementary information (ESI) available: Cartesian coordinates for all the compounds studied at the B3LYP/6-311++G(d,p) computational level. See DOI: 10.1039/c9nj00824a

Table 1 Experimental data on compounds **3**, **5** and **6**

Authors	Compound	3	5	6
Castells *et al.*[1]	m.p. (°C)	133 (dec.)	120 (dec.)	126 (dec.)
	IR KBr (cm^{-1})	N═N band at 1595, no C═N band	νNH at 3295 δNH at 1592 C═N band?	νNH at 3333 δNH at 1595 C═N at 1618
Huisgen *et al.*[3,4]	m.p. (°C)			125–127
	IR KBr (cm^{-1})			νNH at 3333 C≡N at 2260 C═N at 1617
	^{1}H NMR (acetone-d_6) ppm			H3: 7.65 NH: 9.40 (broad)
	^{13}C NMR (acetone-d_6) ppm			C3: 132.9, C4: 52.8, C5: 62.7 108.0, 110.0 (CN)

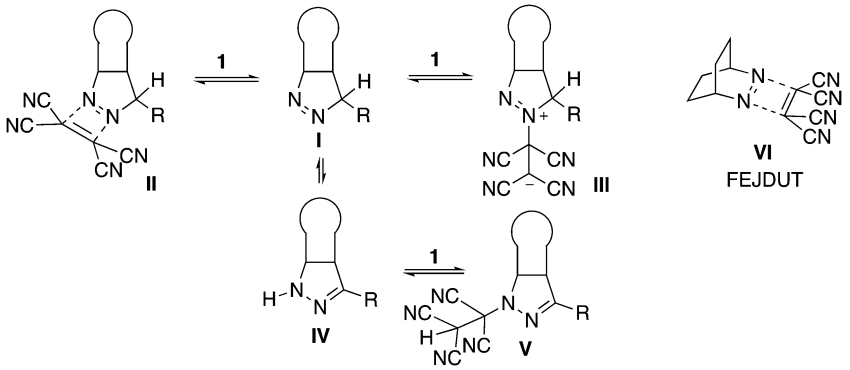

Fig. 2 Reactivity of Δ^1-pyrazolines with TCNE. The fused rings are either substituted cyclobutanes or bicyclo[2.2.2]octanes.

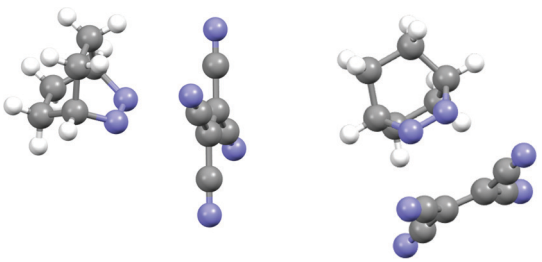

Fig. 3 Two views of the X-ray molecular structure of FEJDUT.

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.[8–10]

2. Computational details

The geometries of pyrazolines (Pz) and pyrazolinium cations (PzH^+) have been fully optimized using the functional B3LYP[11] and the 6-311++G(d,p) basis set[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†).[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[14] based on the polarized continuum model (PCM) of Tomasi and co-workers[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.[16] Absolute chemical shieldings have been calculated with the GIAO approximation[17] and then transformed into chemical shifts using empirical equations.[18] The static intrinsic reaction coordinates (IRCs)[19] were analyzed in two cases.

3. Results and discussion

3.1. 4,5-Dihydro-5*H*-pyrazole-3,3,4,4-tetracarbonitrile (3)

Diazomethane, a 1,3-dipole with octet stabilization,[10] reacts with CC double and triple bonds to afford pyrazolines and

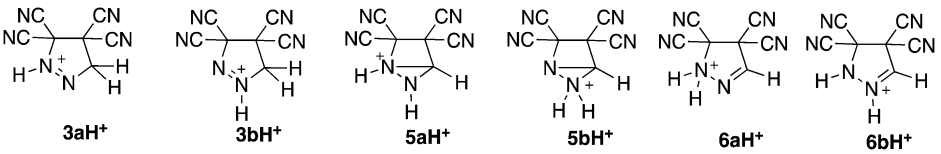

Fig. 4 Conjugated acids of the three compounds.

Table 2 Relative energies in kJ mol^{-1} with regard to **6** (neutral) and **6bH$^+$** (protonated)

Neutral	**3**	**5a** (inside)	**5b** (outside)	**6**
	17.1	165.8	151.0	0.0

Cations	**3aH$^+$**	**3bH$^+$**	**5aH$^+$**	**5bH$^+$**	**6aH$^+$**	**6bH$^+$**
	36.9	40.5	164.4	154.3	15.3	0.0

pyrazoles.[20] For the reaction **1** + **2** → **3**, Δ^1-pyrazoline **3** lies 17.1 kJ mol^{-1} higher than the potential surface minimum, the Δ^2-pyrazoline **6** (Table 2), and the barrier with regard to **3** is 73.8 kJ mol^{-1}. For the reaction between diazomethane and different olefins, Ess and Houk calculated barriers between 57 and 70 kJ mol^{-1}.[21] Calculated IR, the NMR properties of compound **5** are reported in Table 3.

3.2. 2,2,3,3-Tetracyano-1,5-diaza-bicyclo[2.1.0]pentane (5)

This compound has two conformations depending on the position of the NH bond, towards or out of the ring (Fig. 5). Compounds **5** lie 165.8 (**5a**) and 151.0 (**5b**) kJ mol^{-1} over the potential surface minimum and Δ^2-pyrazoline **6** (Table 2). Calculated IR and NMR properties of compound **3** are reported in Table 3.

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

Δ^2-pyrazoline **6** is the most stable of the three isomers (Table 2). The **3** → **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 calculate 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:

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

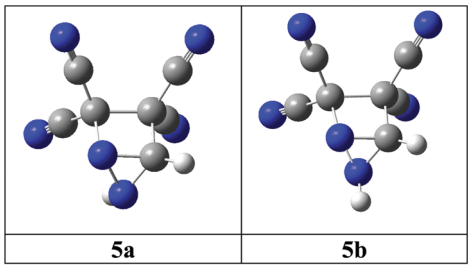

Fig. 5 Structure of **5a** and **5b**.

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═N═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**[3] agree with the calculated values according to the linear regression,

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

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 diaziridine **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** → **5** backward reaction. Solvent effects (amongst them those used by Castells[1]) 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} (νNH) and 1523 cm^{-1} [(N═N═C)$^{\pm}$].

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

Compound	**3**[a]	**5b**	**6**	**7**
Stretching N═N	1626	—	—	—
Stretching νNH	—	3382	3451	3419
Bending δNH	—	1228	1387	1304
Stretching C═N	—	—	1614	1523[b]
Stretching C≡N	2281–2291	2286–2293	2276–2294	2273–2295
^{1}H	CH_2: 5.04 & 5.73	CH: 3.95 & NH 2.57	CH: 6.41 & NH 5.78	CH: 5.93 & NH 9.72
^{13}C, C3	CH_2: 91.5	CH: 58.2	CH: 130.9	109.9
^{13}C, C4	$C(CN)_2$: 40.8	$C(CN)_2$: 43.4	$C(CN)_2$: 53.1	$C(CN)_2$: 50.8
^{13}C, C5	$C(CN)_2$: 86.5	$C(CN)_2$: 59.8	$C(CN)_2$: 63.2	$C(CN)_2$: 110.6
^{13}C, CN at C4	107.8 & 108.7	106.0 & 108.2	105.7 & 106.8	107.2 & 107.6
^{13}C, CN at C5	104.9 & 106.8	107.0 & 107.8	107.4 & 109.5	107.6 & 108.1
^{15}N, N1	91.3	N: −285.8	−236.8	N: −149.1
^{15}N, N2	105.4	NH: −297.0	−29.5	NH: −122.5
^{15}N, CN at C4	−99.4 & −101.0	−95.6 & −96.9	−95.4 & −97.9	−93.2 & −99.3
^{15}N, CN at C5	−86.6 & −90.7	−92.3 & −93.2	−97.4 & −98.7	−99.9 & −100.5

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

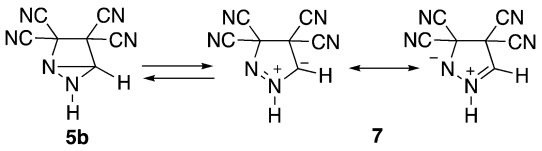

Fig. 6 The equilibrium between **5a** and **7**.

Using eqn (1), these values in KBr should be 3319 and 1520 cm^{-1}. Castells *et al.* did not report a C=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.[23,24] We have already reported the **1** + **2** → **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.[23,24] 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).

Δ^2-Pyrazoline (4,5-dihydro-1*H*-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** → **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-Δ^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**,[3] release of hydrogen cyanide was observed.[27]

The last reaction we have studied is the cycloaddition of diazomethane **2** on Δ^2-pyrazoline **6**. It is known that Δ^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 zwitterion **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.

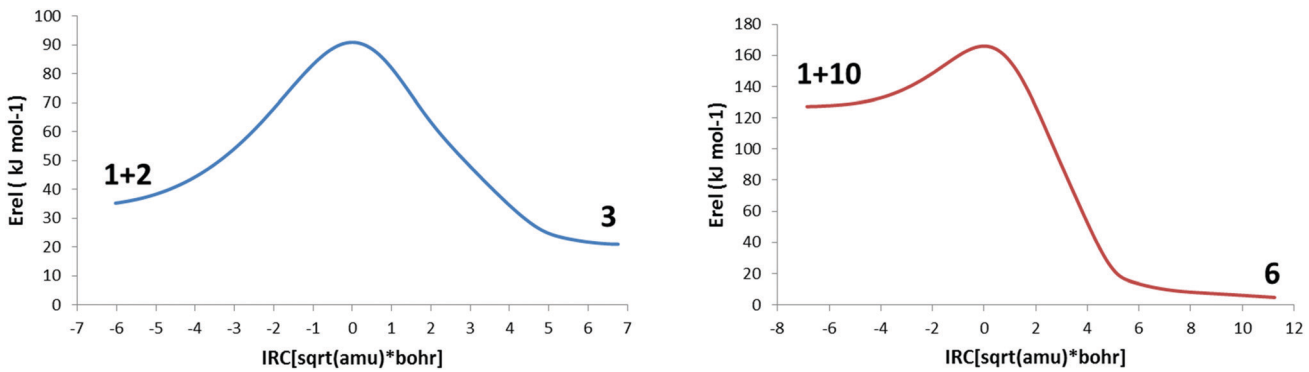

Fig. 7 IRC of the **1** + **2** → **3** and **1** + **10** → **6** reactions.

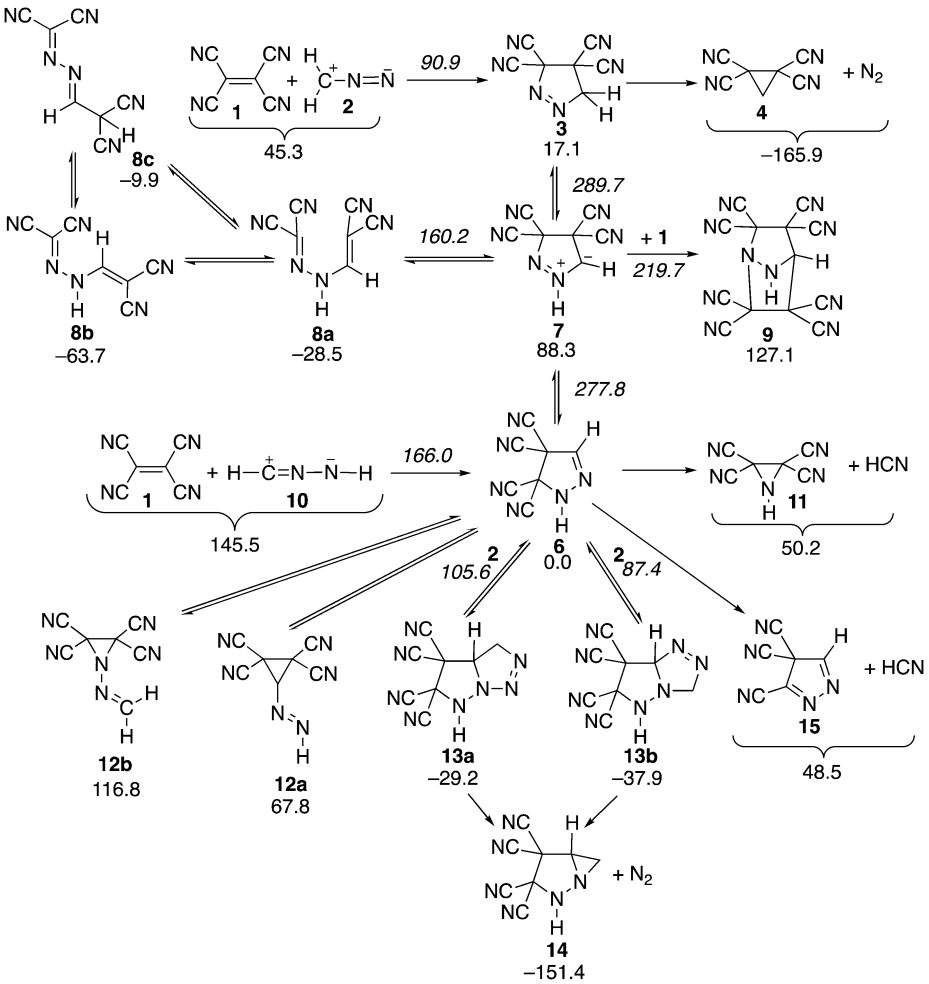

Fig. 8 Reactions involving neutral molecules (all values in kJ mol^{-1} with regard to the minimum **6**) except **5**. TSs in cursives.

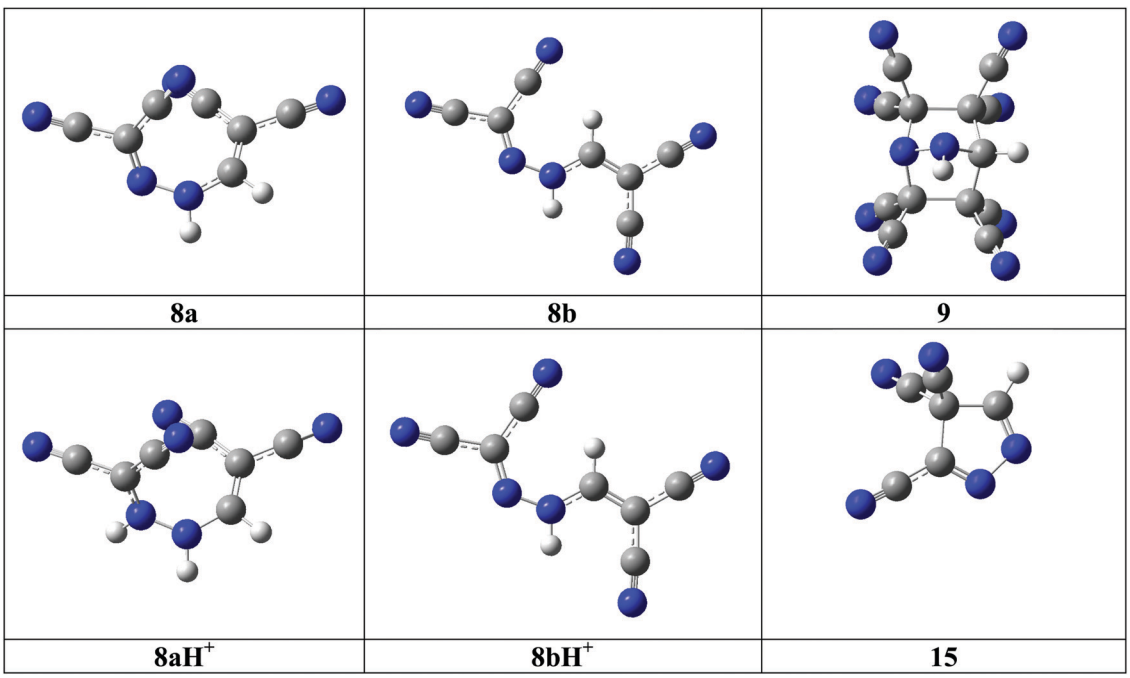

Fig. 9 The open ring compounds **8a** and **8b** their cations **8aH**$^+$ and **8bH**$^+$ and compounds **9** and **15**.

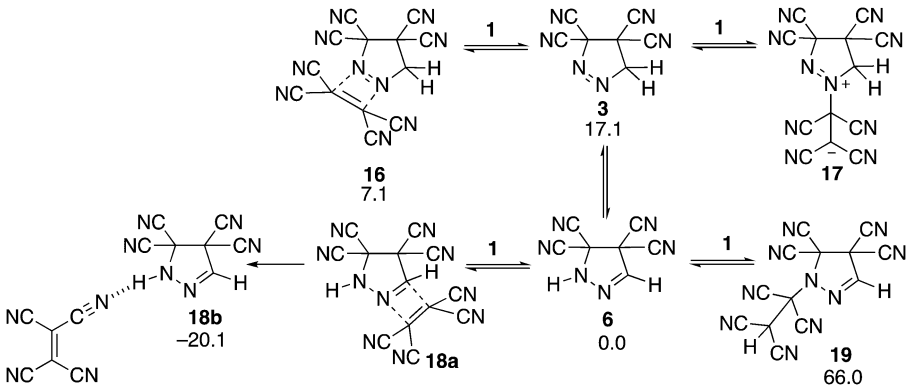

Fig. 10 Reactions and interactions between pyrazolines and TCNE.

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).[1]

Usually, Δ^2-pyrazolines protonate on N1 (type a)[30] 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 Δ^2-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 Δ^2-pyrazolines protonated on N1 is to open into compounds related to **20b**; this has been proven

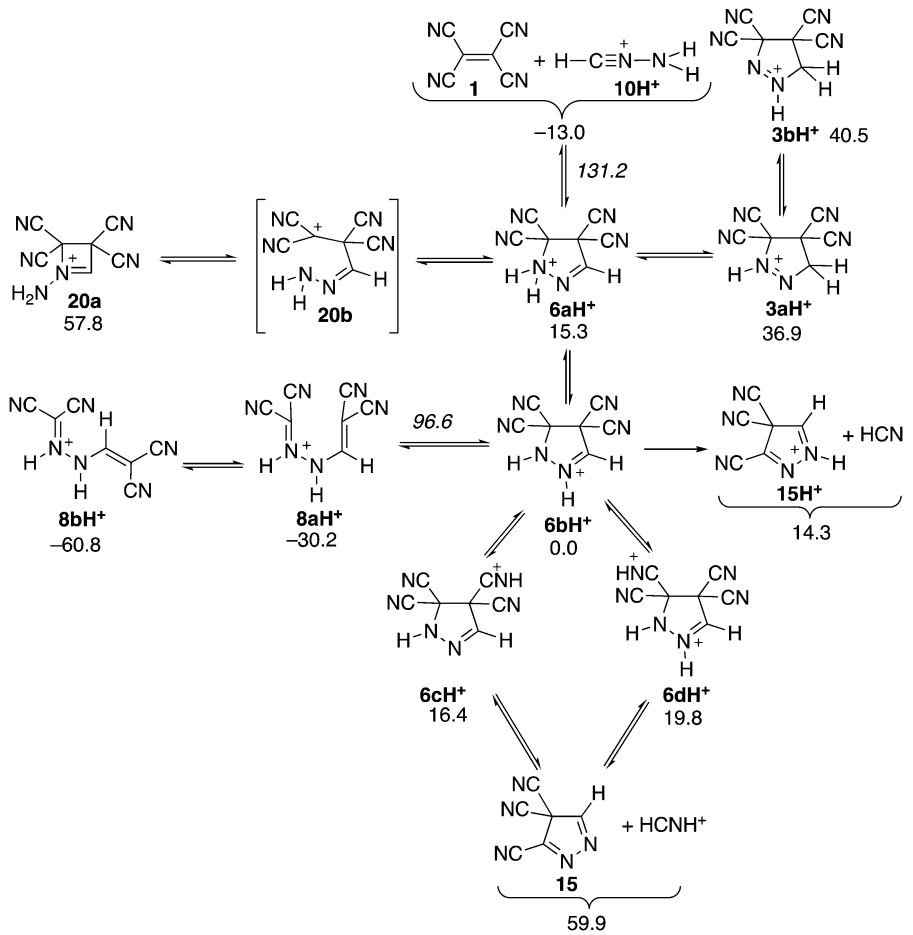

Fig. 11 Reactions involving protonated molecules except **5aH**$^+$ and **5bH**$^+$ (all values in kJ mol^{-1} with regard to the minimum **6bH**$^+$). TSs in cursives.

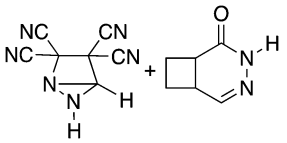

Fig. 12 The mysterious compound.

experimentally.[30b] However, in the present case, the optimization led to a quaternary azetinium (2,3-dihydroazetium) cation **20a**, still too high in energy.

The loss of HCN from **6bH**$^+$ generates a protonated isopyrazole **15H**$^+$ (1*H*-isopyrazolium) that is slightly less stable. Protonation of the cyano groups leads to cations **6cH**$^+$ (CN at position 4) and **6dH**$^+$ (CN at position 5) of similar energies to **6aH**$^+$, *i.e.* the CN groups are similar to the amino group of a pyrazoline. This is a surprising result because the PA of CH_3CN is 787 kJ mol^{-1} and that of CH_3NH_2 is 899 kJ mol^{-1},[31] but the role of the four CN groups and the Δ^2-pyrazoline structure may modify the proton affinity; it is known that cyano derivatives can be superbases.[32] From the most stable of these cations, loss of protonated hydrogen cyanide results in the formation of **15** with an energy of 59.9 kJ mol^{-1}.

4. Conclusions

Castells intermediate **5** (Fig. 1)[1] is characterized by IR in KBr by a stretching NH at 3295 cm^{-1} and a bending NH at 1592 cm^{-1} as well as by the absence of a C=N band although these last bands appear in Δ^2-pyrazolines at 1555–1570,[33] 1557,[34] 1560,[35] 1580–1592,[36] 1600[37] and 1618–1622 cm^{-1}.[38] Therefore, the compound has a NH group, *i.e.*, it is not a Δ^1-pyrazoline, but the presence or absence of a C=N band is dubious.

The reactivity of intermediate assumed to be **5** is that it never affords **3** but it is in equilibrium with **6**. Light and TCNE isomerize **5** to **6**; water, HCl and time isomerize **6** to **5**.[1] If pure **6** can be transformed into **5**, this latter must be an isomer not containing TCNE.

Of all the compounds that we have studied, which is the best candidate? Our calculations of IR spectra and its high energy show that **5** can be definitely excluded. That the intermediate could be a salt was possible when HCl was used but not with wet ether. If, by an experimental error, TCNE still remained in the reaction medium, **16** is a good candidate due to its energy and absence of barrier.

Finally, the best candidates because they are consistent with the IR data are **7**, as already discussed, and **8b**. The linear equation relating both variables is:

$$\text{Exp.} = (115 \pm 31) + (0.93 \pm 0.1)\,\text{Calc.},\ n = 7,\ R^2 = 0.999,\ \text{RMS residual} = 27\ \text{cm}^{-1} \quad (3)$$

The problem is that the available information is too scarce, there is not even the complete IR spectrum of **5** let alone the ^{1}H NMR data. This added to the non-reproducibility of the preparation of **5**[3,27] 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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