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The calculated enthalpies of the nine pyrazole anions, cations, and radicals: a comparison with experiment

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Dedicated to Professor Miha Tišler on the occasion of his 80th birthday in recognition of his contribution to chemistry

Abstract—Enthalpies of 12 pyrazole species including neutral, anions, cations, and radicals have been calculated at the G3B3 level. The main conclusions are: (i) there are ten equilibria between species of which six have been measured experimentally and the agreement is excellent; (ii) two structures, cyclic and chain, have been found for the pyrazolium-radical **8** that are able to explain the electrochemistry of pyrazolium salts; (iii) the aromaticity, calculated as the NICS indexes, is related to the unexpected stability of the pyrazole anion **3**.

1. Introduction

Radicals play major role in many reactions, for instance, SET, direct electron transfer, and $S_{RN}1$,[1–3] spectroscopies such as PES,[4] ESR (EPR),[5] mass spectrometry (both positive and negative ions),[6] and electrochemistry.[7] Radicals are related, through electron and proton transfers, to neutral molecules, anions, and cations. On the other hand, we have been interested in pyrazoles for a long time.[8] It was thus natural that we wanted to explore the potential surface of the entities reported in Scheme 1 from an energy point of view.

First of all, we will summarize the information available on the nine compounds, not chronologically but in the order they appear in Scheme 1. The pyrazole cation **1** has been studied only once.[9] According to Pasto et al. the energy minimum corresponds to a closed-shell singlet with four π electrons in a $(1b_1)^2,(2b_1)^2$ configuration. This structure shows very long CN distances and a short NN distance. A second minimum with $(1b_1)^2,(1a_1)^2$ configuration with also four π electrons presents short CN distances and a long NN distance.

The 1-pyrazolyl radical **2** of Scheme 1 is, by far, the most studied radical. The question of its structure (σ-type with a $^2B_2$ state or π-type with $^2A_2$ or $^2B_1$ states) was first discussed by Janssen et al. on experimental grounds (Scheme 2),[10] and simultaneously by van der Meer and Mulder using the ab initio STO-3G basis set.[11] The result is that the most stable structure is the π-$^2B_1$, followed by the π-$^2A_2$ (34.7 kJ mol^{-1}) and the σ-$^2B_2$ (60.7 kJ mol^{-1}). The calculation level was increased to Davidson-corrected CISD/6-31G* by Bofill et al.[12] resulting in the 1-pyrazolyl radical in a different profile with the $^2B_1$ π-type being the minimum and differences of 48.1 (local minimum) and 73.6 kJ mol^{-1} (crossing) with the $^2B_2$ σ-type. It has been independently reported that the pyrazolyl radical **2** is one of the rare cases where there are three electronic states with conical intersections in the ground state.[13]

Fortunately, a very recent paper of Lineberger et al.[14] report not only calculations on **2** at the B3LYP/6-311++G(d,p) level but also important experimental data on equilibria involving **2**, **3**, and **5**, that will be very useful to test our calculations. At the same level, Flammang et al.[15] calculated the adiabatic ionization energies (IE) of the radical cation **4** that agree very well with the experimental values.

2. Computational methods

The structures have been initially optimized at the hybrid DFT/HF, B3LYP,[16] computational level and the 6-31G* basis set[17] as implemented in the Gaussian 03 package.[18] Frequency calculations have been carried out to confirm that the structures obtained correspond to energy minima. Other electronic configurations have been explored at this computational level. Further, G3//B3LYP (usually reported in the literature as G3B3) calculations[19] have been carried out in the structures selected in the first step. The reported energy values correspond to enthalpies at 298.15 K, which include zero point energy (ZPE) and thermal corrections. The most stable compound is **8** (open) (−226.570952 hartree). We will report only the structures of lower energy except in those cases where there are two structures of similar energy.

Keywords: Pyrazoles; Radicals; Aromaticity; Ab initio; NICS.

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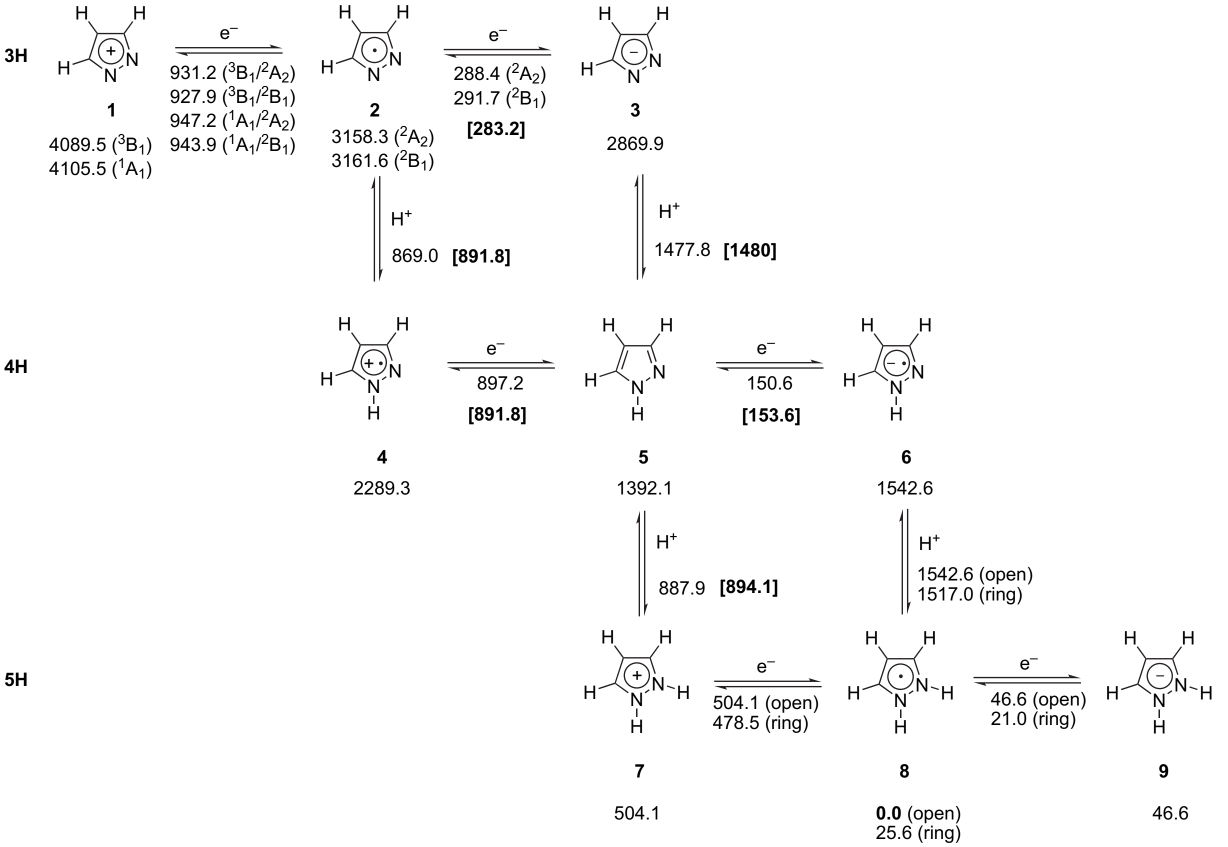
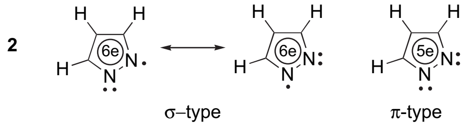


Scheme 1. The nine pyrazole derivatives under study.



Scheme 2. σ- and π-type structures of 1-pyrazolyl radical.

3. Results and discussion

3.1. Geometries

We have reported in Table 1 the main characteristics of the 12 studied compounds.

We have calculated the average bond distances (sum of the five distances/5) that reflects the size of the pyrazole ring. Leaving aside the open compound **8** (1.697 Å), these average distances belong to two groups: long distances, between 1.452 Å **9** and 1.412 Å **8** ring including **6** (1.419 Å) and **1s** (1.413 Å) and short distances, between 1.384 Å **4** and 1.365 Å **7**, the remaining compounds. We have also calculated the ratio of C–N (N2–C3/C5–N1) and C–C distances (C3–C4/C4–C5). In most cases these ratios are 1 (due to symmetry) except for four compounds: **4** (1.011 and 0.971), **5** (0.981 and 1.024), **6** (0.923 and 0.969) and **9** (0.981 and 0.958).

3.2. Energies

There are 10 equilibria in Scheme 1: the values under the formulae are the energies in kJ mol^{-1} with regard to the absolute minimum, compound **8**. The numbers close to the double arrows correspond to the equilibria and are differences between the former values. There are experimental enthalpies corresponding to six out of ten equilibria: **2/3** 283.2 kJ mol^{-1},[14] **2/4** 891.8 kJ mol^{-1},[15,16] **3/5** 1480 kJ mol^{-1},[20] **4/5** 891.8 kJ mol^{-1},[15] **5/6** 153.6 kJ mol^{-1},[14] and **5/7** 894.1 kJ mol^{-1}.[20]

Table 1. Geometries of the calculated structures at the B3LYP/6-31G* computational level. The electronic configuration and molecular symmetry are also given

	Electronic configuration	Molecular symmetry	N1–N2	N2–C3	C3–C4	C4–C5	C5–N1
1	$^3B_1$	C_{2v}	1.19	1.45	1.39	1.39	1.45
1	$^1A_1$	C_{2v}	1.23	1.54	1.38	1.38	1.54
2	$^2A_2$	C_{2v}	1.28	1.43	1.39	1.39	1.43
2	$^2B_1$	C_{2v}	1.47	1.30	1.38	1.38	1.30
3	$^1A_1$	C_{2v}	1.37	1.35	1.40	1.40	1.35
4	$^2A''$	C_s	1.42	1.32	1.42	1.46	1.30
5	$^1A'$	C_s	1.35	1.33	1.41	1.38	1.36
6	^2A	C_1	1.45	1.35	1.39	1.44	1.46
7	$^1A_1$	C_{2v}	1.35	1.35	1.39	1.39	1.34
8 ring	^2A	C_2	1.45	1.42	1.38	1.38	1.42
8 open	^2B	C_2	3.02	1.23	1.43	1.43	1.30
9	^1A	C_1	1.48	1.48	1.37	1.43	1.50

These data and the values of Scheme 1 are highly correlated (Eq. 1):

$$\Delta H^0_{298}\text{exp.} = (1.005 \pm 0.005)\Delta H^0_{298}\text{ calcd}, \quad n = 6, \quad r^2 = 0.99989 \qquad (1)$$

This gives strong confidence to the remaining four values. We have tried an empirical model to correlate the relative energies to some structural properties. Eq. 2 corresponds to the best model (the fact that the compound is a radical or not has no significant influence on the enthalpy); in the case of compounds **1**, **2**, and **8**, where there are two values (two structures) this model describes both structures as being identical.

$$\begin{aligned}\Delta\Delta H^0_{298}\,\text{calcd} = {} & (7909\pm105)-(1590\pm25)\,\text{no. of H} \\ & +(1188\pm134)\,\text{charge}+(346\pm43)\,\text{charge}^2 \\ & -(195\pm34)\,\text{no. of H}^{*}\text{charge},\quad n=12, \\ & r^2=0.9986 \qquad (2)\end{aligned}$$

No. of H is the number of hydrogen atoms (3, 4, or 5, see Scheme 1); charge is the charge −1 (anion), 0 (neutral), and +1 (cation). The largest residuals do not affect compounds **1**, **2**, and **8**, therefore treating both structures together has no significant influence on the model. To compare the coefficients, it is necessary to scale (−1, 0, +1) all the independent variables, this results in Eq. 3.

$$\begin{aligned}\Delta\Delta H^0_{298}\,\text{calcd} = {} & (1548\pm33)-(1590\pm25)\,\text{no. of H} \\ & +(407\pm28)\,\text{charge}+(346\pm43)\,\text{charge}^2 \\ & -(195\pm33)\,\text{no. of H}^{*}\text{charge},\ n=12, \\ & r^2=0.9986 \qquad (3)\end{aligned}$$

While the intercept has no physical meaning, the number of hydrogen atoms is the most important factor, to the point that it roughly explains most of the variance (Eq. 4).

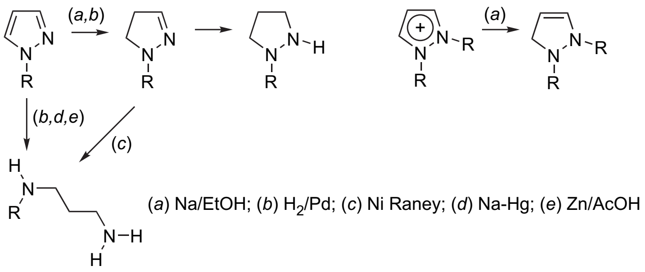
$$\begin{aligned}\Delta\Delta H^0_{298}\,\text{calcd} = {} & (1793\pm129)-(1668\pm149)\,\text{no. of H}, \\ & n=12,\ r^2=0.926 \qquad (4)\end{aligned}$$

Since the number of carbon and nitrogen atoms are the same for all compounds, Eq. 4 indicates that $\Delta\Delta H^0_{298}$ calcd is an almost additive property.

In the 4H and 5H series the stability follows the neutral> anion>>cation but in the 3H series the order is different being anion>neutral>cation. May be anion **3** is overstabilized.

3.3. Structure and properties of radicals 8

Two minima have been found for **8**: a ring structure (25.6 kJ mol^{-1}) and an open structure (more stable, 0.0 kJ mol^{-1}). An examination of the literature in what concerns the reduction by Na/EtOH, Na–Hg, and H$_2$/Pd and electrochemistry of pyrazoles (related to **5** but *N*-substituted) and pyrazolium salts (related to **7** but *N*,*N*-disubstituted)[8,21,22] shows (Scheme 3) that these compounds are reduced to pyrazolines, pyrazolidines, and 1,3-diamines.



Scheme 3. The reduction of pyrazoles, pyrazolines, and pyrazolium salts.

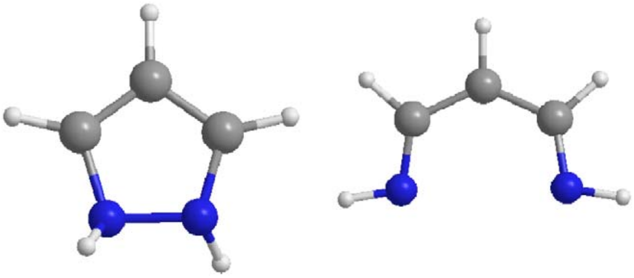


Figure 1. Structure of pyrazolium radicals **8**: both are minima and have a C_2 symmetry.

It is reasonable to assume that the radicals of Figure 1 are involved in some of these processes. Note from Scheme 1, that it should be easier to reduce the cation **7** than the neutral pyrazole **5**. Reciprocally, the reduction of **1** is calculated to be more difficult. This could be related to the fact that there are less H atoms to distribute the generated positive charge.

3.4. Aromaticity

In order to get some insight on the molecular properties of the structures of Scheme 1 we have calculated their NICS(0) and NICS(1) values.[23–25] The NICS(0) is calculated in the plane of the ring while the NICS(1) is calculated 1 Å above the ring plane. Note that we use[24,25] in Table 2 a sign conversion opposite to that of Schleyer et al.[23]

Although both NICS values are different they are roughly proportional [NICS(1)=(2.4±0.6)+(0.61±0.06) NICS(0), n = 12, r^2 = 0.92] so we will discuss only the NICS(1) values. Taking 11.2 ppm as the reference value, the true aromatic compounds are **3**, **5**, and **7**, the vertical column of non-radicals in Scheme 1. Slightly aromatic compounds are **6**, **8** (ring), and **9** (the bottom right side of Scheme 1) and medium (**1**(^{3}B$_1$), **2**(^{2}A$_2$), **2**(^{2}B$_1$), and **4**) to strongly antiaromatic (**1s**) compounds occupy the top left side of Scheme 1. The anomalies we have reported in the energetic discussion could be related to the large aromaticity of pyrazolate

Table 2. NICS values (ppm)

Molecule	NICS(0)	NICS(1)
1 (^{3}B$_1$)	−5.0	−1.8
1 (^{1}A$_1$)	−16.4	−7.7
2 (^{2}A$_2$)	−8.6	−1.3
2 (^{2}B$_1$)	−12.4	−3.7
3	14.1	13.3
4	−10.2	−2.8
5	15.0	12.4
6	5.5	3.6
7	15.4	11.6
8 Ring	5.8	3.2
9	3.2	1.2
Benzene	9.7	11.2

anion, **3**, which is common to other five-membered anions like cyclopentadienyl.[26]

4. Conclusions

The theoretical calculation of the enthalpies of the structures involved in proton and electron transfer of pyrazole yield good results if carried out at sufficient level (G3B3). They explain the observed equilibria and allow a confident prediction of the still missing data. Aromaticity seems to play a significant role on the stability of the different structures.

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