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1,2-Proton shifts in pyrazole and related systems: a computational study of [1,5]-sigmatropic migrations of hydrogen and related phenomena †

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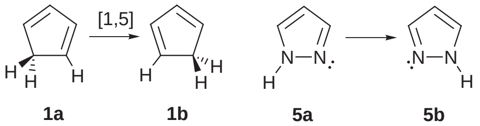
Three different approaches are used to discuss the possible analogy between the [1,5] hydrogen shift in cyclopentadiene and the prototropy in 1*H*-pyrazole. In the first, a series of NH→HN hydrogen shifts in cyclic conjugated molecules are considered demonstrating that the case of pyrazole is not intrinsically different from the other systems which are unrelated to [1,5] H shifts. The second approach compares pyrazole and cyclopentadiene with their open-ring structures, pentadiene and aminoazadiene, proving that the N–N bond is essential to describe pyrazole while the C(sp^3)–C(sp^2) bond in cyclopentadiene can be considered as a perturbation. Finally, the third approach is a study of cyclopentadienide and pyrazolide anions as hydrogen-bond acceptors, the first one being a π-acceptor while the second one is a σ-acceptor through the nitrogen lone pair. The conclusion is that N(sp^2)–N(sp^2) migrations of hydrogen in aromatic azoles are outside the Woodward–Hoffmann domain of application.

Introduction

One of the most sound foundations of the Woodward–Hoffmann rules are the [1,*j*]-sigmatropic migrations.[1a–7a] Among these migrations, the [1,5]-sigmatropic rearrangement of cyclopentadiene **1** (σ^2s + π^4s) is particularly relevant for the present work.[1b–7b] The possibility that the intramolecular migration of a proton between the nitrogen atoms of pyrazole, **5**, and related systems (pyrazolinones, tetrazoles) could represent another example of [1,5]-sigmatropic reactions has been considered by different authors.[8–10]

Although obviously very different, several authors have assumed that pyrazole and cyclopentadiene can be assimilated [quoting as justification refs. 1 and 11(*a*)]. Consequently the process **5a**→**5b** is described (Scheme 1) as a sigmatropic process, which is by no means a trivial matter.[11b] Thus, Wentrup *et al.*[9] wrote that 'the transition structure for the *symmetry-allowed* hydrogen shift (ref. 11) from 1*H* to 2*H*-tetrazole . . .'. Of the same opinion are Schäfer *et al.*[10] who, discussing the intramolecular proton transfer between 3-hydroxy- and 5-hydroxypyrazole, wrote 'The FMO (ref. 1) theory predicts that, for thermal reactions, *[1,5] suprafacial hydrogen shifts are symmetry allowed*'. Nevertheless, all authors note that the calculated barriers for processes like **5a**→**5b**, are surprisingly high. Thus, Catalán *et al.*[8] reported a barrier of 51 kcal mol^{-1} (INDO) for pyrazole, Wentrup *et al.*[9] a barrier of 49.5 kcal mol^{-1} [QCISD(T)/6-311+G**] for tetrazole and Schäfer *et al.*[10] a barrier of about 50 kcal mol^{-1} (MP2/6-31G**) for hydroxypyrazole.‡ These last authors comment that 'It is unclear why the energy barrier for the rearrangement of G (pyrazolinone) to B1 (3-hydroxypyrazole) is comparable to that for rearrangement of A (5-hydroxypyrazole) to B1, even though the former involves a [1,3] hydrogen shift that is forbidden by orbital symmetry for a thermal reaction'.



Scheme 1

This work presents a study of the intramolecular proton transfer in pyrazole **5** using three approaches: i) comparing the case of pyrazole with other NH→HN migrations; ii) comparing pyrazole and cyclopentadiene with the corresponding open compounds; iii) comparing the HB (hydrogen-bond) properties of cyclopentadienide and pyrazolide anions. In each section we will discuss first the geometries (ground and transition states) and then the energies.

Theoretical methods

The geometry of all the systems has been optimized with the Gaussian-94 program[12] using the standard 6-31G*[13] basis sets and the hybrid Hartree–Fock-density functional method (Becke3LYP).[14] Symmetry conditions have been used whenever possible, and specially for the calculation of the transition states.

The nature of the stationary points of all the calculated systems has been established by verifying the number of imaginary frequencies. In the case of minimum structures, all the frequencies should be positive and in the transition states, only one of them should be imaginary.

The topological properties of the electronic charge density and the atomic charges have been characterized using the atoms in molecules methodology (AIM)[15] with the AIMPAC program package.[16]

Results and discussion

NH→HN Intramolecular proton transfers

To approach this study, we have selected five conjugated hetero-

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† Geometries of all the GS's and TS's are available as supplementary data (SUPPL. NO. 57436, pp. 5) from the British Library. For details of the Supplementary Publications Scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available *via* the RSC Web page (http://www.rsc.org/authors).

‡ 1 cal = 4.184 J.

Table 1 Classification of the compounds under study

Compound	Ring size	Neutral/ Cationic	Aromatic/ Antiaromatic	N–N bond
3	3	N	AA	single
4	4	C	AA	double
5	5	N	A	aromatic
6	6	C	A	aromatic
7	7	N	AA	single

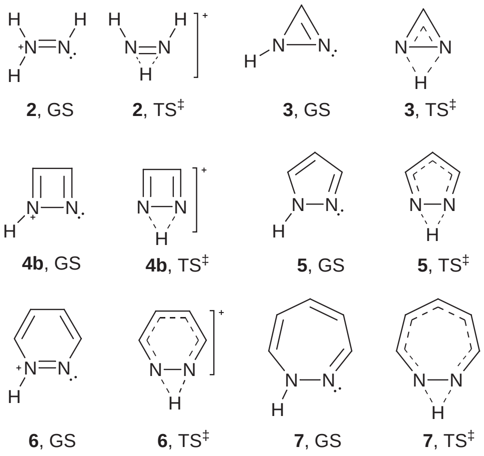
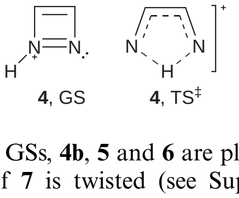


Fig. 1 Molecules used for the first approach.

cycles, including pyrazole **5** (Fig. 1), which have in common the fact that the structure resulting after the proton transfer is the same as the starting molecule (identical ground states, GS; this proton tautomerism is called autotrope or degenerate)[17] and, consequently, that the transition states, TS‡, are always of, at least, C_s symmetry. Another common feature they share is that the second nitrogen atom is always of sp^2 hybridization, like in pyrazole. Finally, diazenyl cation **2** was selected as the simplest model compound.

The compounds of Fig. 1 can be classified according to three criteria: ring size, neutral *vs.* cationic, and aromatic *vs.* antiaromatic (Table 1), which seemed to us relevant for the problem under study. A fourth criterion, which was not initially suspected, the nature of the bond between the nitrogen atoms, is also reported in Table 1. Therefore, there are three neutral and two cations and two aromatic and three antiaromatic compounds. This even distribution (optimality of the experimental design)[18] will allow us to discuss the influence of the three criteria in Table 1 on the structure, properties and energy of the transition states.

When we started this work, we selected the other valence isomer of 1,2-diazete, that having a double bond between the nitrogen atoms, structure **4** less stable than **4b** (17.6 kcal mol^{-1}, similar values were reported previously for the neutral molecules).[19–21] For **4**, the transition state corresponds to a planar open-ring structure (see below); this result led us to study the isomer **4b** represented in Fig. 1.



Concerning the GSs, **4b**, **5** and **6** are planar while the seven-membered ring of **7** is twisted (see Supplementary Information). 1,2-Diazirine, **3** (also called isodiazirine), has a peculiar property that had already been noted:[22–25] the N–N bond length is surprisingly long (1.679 Å, Table 2). A Bader's analysis on this compound shows that there is no bond critical point between the nitrogen atoms, the structure being similar to that of an imino-nitrene, an unknown 1,3-dipole without octet stabilization (note, however, that the NCN internal angle is 78.2°).

Since the properties of the N–N bonds in the compounds of Fig. 1 are important to understand their behavior, we have found it useful to compare the N–N and C–C bonds of a series of related compounds (Table 2).

Pauling's bond orders *n* have been calculated using the linear relationships (1) and (2) [in Table 2 the values used to define them are printed in bold]:[27]

$$\ln n_{CC} = (5.18 \pm 0.06) - (3.38 \pm 0.05)\, R_{CC}\,(\text{Å}),\ n = 3,\quad r^2 = 1.000 \qquad (1)$$

$$\ln n_{NN} = (4.25 \pm 0.07) - (2.86 \pm 0.05)\, R_{NN}\,(\text{Å}),\ n = 3,\quad r^2 = 1.000 \qquad (2)$$

Eqn. (1) predicts for benzene $n = 1.58$, *ca.* 1.5 for a bond intermediate between the single and double bond (a value of $n = 1.67$ has been reported for benzene).[28] Hexazine and triaziridine have bond orders much like benzene and cyclopropane, therefore, for the five standard bond types (triple, double, single, aromatic and bent), CC and NN are similar which justifies the following discussion. Cation **3** shows a typical NN double bond, the diazirine **3** has a very weak bond (much weaker than in cyclobutadiene) which corresponds to the absence of bond critical point, diazetyl cations **4** and **4b** are comparable with butadiene, pyrazole **5** and pyridazine cation **6** have typical aromatic NN bonds while the antiaromatic diazepine **7** has a single NN bond.

These transition states can be characterized by five properties: i) The geometry of the NHN triangle in the TS‡ with regard to the plane defined by the heterocycle. ii) ΔE, the difference in energy between the TS‡ and the GS. iii) The density at the bond critical points (ρ_{bcp}) of the N–H bond in the GS *vs.* that of the N · · · H bonds in the TS‡ (and its Laplacian, $\nabla^2\rho_{bcp}$). iv) The topology of the TS‡. v) Δq, the difference in charge of the NH proton between TS‡ and GS.

The geometrical data are reported in Table 3 together with some literature results. Note that the HXY and NHN angles for pyrazole are similar to those reported for tetrazole and hydroxypyrazole.[9,10]

Regarding the NN bond length there are two cases where the comparison between the neutral molecules and the TS are not possible: i) the 1,2-diazirine **3** because the neutral molecule 'lacks' the NN bond and ii) the diazetyl cation **4** because in the transition state there is no NN bond (N**H**N angle of 112.9°). For the remaining four compounds, the ΔR_{NN} (Å) = 0.018 (**2**), 0.054 (**4**), 0.013 (**5**), 0.029 (**6**) and 0.128 (**7**), that is, the NN bond length increases in the TS‡ and depends on the charge and, to a lesser extent, on the ring size but not on the aromaticity. The **H · · · X** distance, the elevation **HXY** angle and the ring size are strongly related [for instance, eqn. (3)] for compounds **3**, **4b** and

$$\mathbf{HXY}\,(°) = (20 \pm 2) + (8.5 \pm 0.5)\,\text{size},\ n = 3,\ r^2 = 0.996 \qquad (3)$$

5. Compounds **6** and **7** have planar transition states (neglecting the deformation of the seven-membered ring). A possible explanation§ for the different behavior of compound **5** (pyrazole, out-of-plane TS, ΔE + ZPE = 47.3 kcal mol^{-1}¶) and **6** (pyridazinium cation, planar TS, ΔE + ZPE = 60.1 kcal mol^{-1}) is that the energy cost for bending the H 40° out of plane for **6** (13.9 kcal mol^{-1}) is higher than for **5** (6.2 kcal mol^{-1}). This difference (7.7 kcal mol^{-1}) could prevent the suprafacial TS in the case of **6**.

The data collected in Tables 2–4 show the logarithmic

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§ We are indebted to a referee for drawing our attention to this explanation.

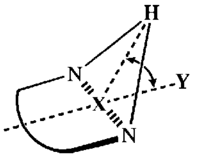
¶ ZPE = zero point energy.

Table 2 Comparative properties of CC and NN bonds according to the AIM methodology together with Pauling's bond orders (n)

Compound	R/Å	ρ_{bcp}	$\nabla^2\rho_{bcp}$	n	Compound	R/Å	ρ_{bcp}	$\nabla^2\rho_{bcp}$	n
Acetylene	1.205	0.4027	−1.1726	3	Dinitrogen	1.106	0.6640	−2.2727	**3**
Ethylene	1.331	0.3455	−1.0092	2	Diazene	1.241	0.4768	−1.1616	**2**
Ethane	1.531	0.2419	−0.5461	1	Hydrazine	1.489	0.2727	−0.4359	**1**
Benzene	1.397	0.3112	−0.8463	1.58	Hexazine (C_{6v})	1.323	0.4017	−0.8473	1.60
Cyclopropane	1.509	0.2490	−0.4268	1.08	Triaziridine (*cis*)[a]	1.466	0.2791	−0.3504	1.06
					Diazenyl cation **2**	1.229	0.4857	−1.2221	2.09
					2-Diazirine **3**	1.679	—	—	0.58
Cyclobutadiene (C=C)	1.335	0.3470	−0.9944	1.95	1,2-Diazetyl cation **4**	1.242	0.4839	−1.2154	2.02
Cyclobutadiene (C–C)	1.578	0.2196	−0.4446	0.86	1,2-Diazetyl cation **4b**	1.586	0.2184	−0.2045	0.75
Cyclopentadiene **1**	1.507	0.2558	−0.5966	1.09	Pyrazole **5**	1.350	0.3667	−0.6889	1.48
(Csp^3–Csp^2 bond)					Pyridazine cation **6**	1.326	0.3874	−0.7909	1.59
					1,2-Diazepine **7**	1.447	0.2962	−0.4818	1.12

[a] The *cis* isomer (C_{3v}) is less stable than the alternate isomer (C_s) by 11–13 kcal mol^{-1} at the 6-31G* and DZP levels (see ref. 26).

Table 3 Geometry of the transition states TS‡



TS‡	R_{NN}/Å	Distance H···**X**/Å[a]	**HXY**/°	NHN/°
Diazenyl cation **2**	1.247	1.099	0.0	59.2
2-Diazirine **3**	1.299	1.376	46.2	64.7
1,2-Diazetyl cation **4**	2.088	0.692	0.0	112.9
1,2-Diazetyl cation **4b**	1.296	1.124	53.9	59.9
Pyrazole **5**	1.464	1.011	63.4	71.8
Pyridazine cation **6**	1.355	1.064	0.0	65.0
1,2-Diazepine **7**[b]	1.575	0.950	0.0	79.3
Tetrazole[c] [MP2][9]	1.449	1.254[d]	57.2	70.6
Hydroxypyrazole [MP2][10]	1.480	1.235[d]	55	74

[a] **X** is the N···N centroid. [b] The seven-membered ring is not planar (the middle of C_4C_5–**X**–**Y** is a straight line). [c] 1H→2H proton transfer. [d] Average values (non symmetric TS‡s).

Table 4 Some characteristic of the ground (GS) and transition states (TS‡) corresponding to Fig. 1, first N···H critical points, then energies

Compound	State	Distance/ Å	ρ_{bcp}(N···H)	$\nabla^2\rho_{bcp}$-(N···H)	Charge of the H (Δq)	E_{total}/ Hartree	ΔE/ kcal mol^{-1}	ZPE/ kcal mol^{-1}	ΔE + ZPE/ kcal mol^{-1}
Diazenyl cation **2**	GS	1.032	0.3166	−1.6603	0.538	−110.94553		26.6	
	TS‡	1.263	0.1475[a]	−0.0079	0.675 (0.137)	−110.83171	71.4	21.2	66.0
2-Diazirine **3**	GS	1.031	0.3263	−1.5989	0.350	−148.68159		20.5	
	TS‡	1.521	0.0949[a]	0.1759	0.153 (−0.197)	−148.51492	104.6	14.6	98.7[c]
1,2-Diazetyl cation **4**	GS	1.031	0.3123	−1.6228	0.537	−187.04996		31.8	
	TS‡	1.297	0.1553[a]	−0.0020	0.523 (−0.014)	−186.94716	64.5	27.9	60.7
1,2-Diazetyl cation **4b**	GS	1.024	0.3126	−1.6213	0.548	−187.07800		32.0	
	TS‡	1.253	0.1645[b]	−0.2064	0.414 (−0.134)	−187.01121	41.9	28.3	38.2
Pyrazole **5**	GS	1.009	0.3354	−1.7203	0.451	−226.19860		44.8	
	TS‡	1.248	0.1689[b]	−0.0303	0.438 (−0.013)	−226.11716	51.2	40.9	47.3
Pyridazine cation **6**	GS	1.021	0.3279	−1.7158	0.505	−264.65333		57.0	
	TS‡	1.261	0.1473[b]	−0.0327	0.633 (0.128)	−264.54958	65.1	52.0	60.1
1,2-Diazepine **7**	GS	1.014	0.3394	−1.7113	0.381	−303.55660		65.8	
	TS‡	1.234	0.1549[a]	0.2692	0.507 (0.126)	−303.45601	63.1	61.2	58.5

Nature of the bcp: [a] catastrophic, [b] bifurcated. [c] In cyclopropene (the carbon analog of **3**) the barrier to the [1,3] hydrogen shift has been calculated to be 90 kcal mol^{-1} at the CASSCF/6-31G* level (see ref. 29).

dependence of N···H and N···N distances on the corresponding ρ_{bpc} values, independently of the nature of the structures, GS or TS‡.[27]

$$dN\cdots N\,(\text{Å}) = (0.61 \pm 0.02) - (0.74 \pm 0.03)\ln \rho_{bpc}\,(NN),\quad n = 17,\ r^2 = 0.98 \qquad (4)$$

$$dN\cdots H\,(\text{Å}) = (0.63 \pm 0.02) - (0.35 \pm 0.02)\ln \rho_{bpc}\,(NH),\quad n = 17,\ r^2 = 0.97 \qquad (5)$$

The barriers to the proton transfer reported in Table 4, also follow a linear relationship with ρ_{bcp}(N···H) for the TS‡.

$$\Delta E + \text{ZPE (kcal mol}^{-1}) = (170 \pm 15) - (740 \pm 98)\,\rho_{bcp}(N\cdots H),\ n = 7,\ r^2 = 0.92 \qquad (6)$$

The largest deviation is found for compound **4**. On the other hand, the ΔE + ZPE values for compounds **4b**, **5**, **6** and **7** do not show any clear relationship with the descriptors of Table 1

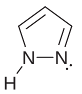
Table 5 Experimental and calculated barriers for [1,5]-intramolecular proton transfers (all values in kcal mol^{-1})

Compound	Cyclopenta-diene **1**	Pentadiene **8**	Pyrazole **5**	1-Amino-4-azadiene **9**
Exp.	24.3^a	35.4^a	—	—
Calc.	26.4^b–27.0^c	37.6^d	—	—
Calc.	—	38.0^e	—	—
Calc.^{f}	27.0	36.6	47.3	5.7^g

^{a} From ref. 30. ^{b} (MP2/6-31G* + ZPE scaled).[40] ^{c} (RMP4SDTQ/6-311G**).[41] ^{d} (MP2/6-31G*).[38] ^{e} (MP2/6-31G**).[35] ^{f} (DFT + ZPE), this work. ^{g} With regard to the *Z-sZ* isomer (−1.3 kcal mol^{-1} with regard to the *Z-sE* isomer).

including Pauling's bond orders of Table 2. Pyrazole has the lowest barrier of this group, 47.3 kcal mol^{-1}, which compares well with the values reported in the introduction (about 50 kcal mol^{-1}).

There is a column in Table 4 with the charges of the migrating hydrogen atom. This charge is +1 for the proton, 0 for the atomic hydrogen and −1 for the hydride, therefore, all the H atoms linked to nitrogen have a 'protic' character. The Δq values ($q_{GS} - q_{TS^{\ddagger}}$) for compounds **4b**, **5**, **6** and **7** correspond to a transfer of electrons from the ring to the H (−0.134 and −0.013) in the case of the four and five-membered rings and a transfer from the H to the ring in the case of the largest rings (+0.127). In any case, there is no relationship with the aromatic (**5** and **6**) *vs.* the antiaromatic character (**4b** and **7**). In the case of pyrazole, the transfer is very small and the neutral molecule and the pyrazolide anion appear to be similarly aromatic while the antiaromaticity of the diazepine increases between the neutral molecule and the anion.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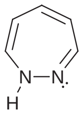
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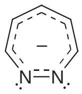

7$^-$

The electron density topological characteristic of the TSs (Table 4) will be discussed in the next section together with cyclopentadiene.

Pyrazole/cyclopentadiene *vs.* aminoazadiene/penta-1,3-diene

We reasoned that if the main difference between cyclopentadiene and pyrazole is the aromatic character of the latter, then breaking the C–C single bond in **1** and the N–N bond in **5** should have very different consequences on the intramolecular proton transfer. The corresponding open-chain compounds are the *Z*-isomers of pentadiene **8** and 1-amino-4-azadiene **9**.

There is abundant information about the **1**/**8** pair both experimental and theoretical (Table 5) (although we have used Roth's values,[30] several other authors have reported barriers to the proton transfer for **1**, **8** and related compounds).[31–33] One of the explanations that has been proposed to account for the barrier of **1** being lower than that of **8** is the fact that in **1** the H atom that migrates is 'protonic' (associated with the aromatic cyclopentadienide anion) while in **8** it migrates as a slightly negative charged entity (hydric).[34]

Our hybrid density functional theory (DFT) calculations for the **1**/**8** pair yield energy values comparable with the MP2 and RMP4SDTQ ones[40,41] (for previous DFT calculations on **8** see Stanton).[35] This gives confidence to our calculations for the **5**/**9** pair. The fact that B3LYP can be used to calculate the transition states in the case of cyclopentadiene was already noted by Jiao and Schleyer[41] (note that their RMP4SDTQ/6-311G** calculations lead to a value of 27.0 kcal mol^{-1}, identical with our value, Table 5).

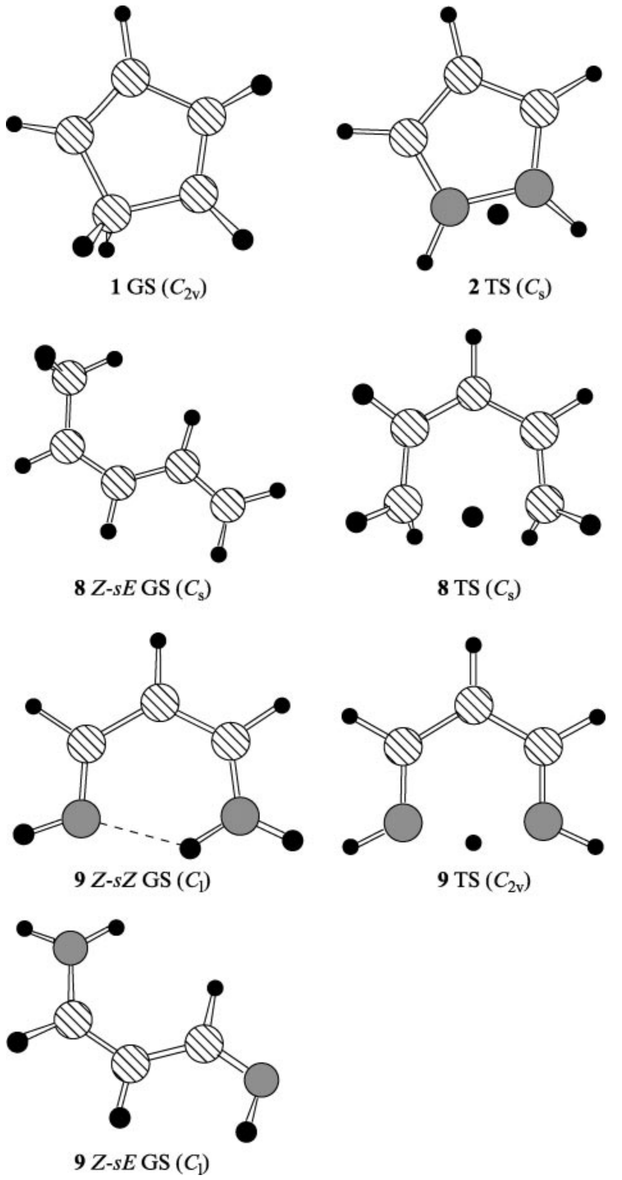


Fig. 2 Geometries of the ground and transition states of the molecules used for the second approach.

First, note the enormous increase of the barrier in going from **1** to **5**. We have represented in Fig. 2, the ground and transition states for compounds **1**, **8** and **9** (the case of pyrazole **5** has been discussed previously). In the case of **8** we have used, as all previous authors,[34–39] the *Z-sE* conformation; in the case of **9**, however, in addition to the *Z-sE* conformation, there is a *Z-sZ* conformation of much lower energy ($\Delta\Delta H = 7.0$ kcal mol^{-1}). Therefore, in Table 5 we have reported two values for compound **9** although only the positive value has a meaning. Bachrach has discussed the topology of HBs in the TS‡ for the cases of pyrrole and cyclopentadiene, bifurcated and catastrophic, respectively.[40]

In the case of pentadiene **1** [q_H (CH$_2$) = 0.042] and its transition state ($q_H = 0.163$), the migrating hydrogen becomes much more protonic ($\Delta q = 0.121$) as reported previously by Houk *et al.*[34] This has been explained by the fact that the cyclopentadienide anion is aromatic,[34] while in the case of pyrazole there is no gain in aromaticity from the neutral pyrazole to its anion ($\Delta q = -0.013$, *i.e.* a very small loss of charge).

As far as the bond path networks in the transition state are concerned, we have found the two situations reported in Table 4: bifurcated and catastrophic (also called T-shaped).[40] In the case of cyclopentadiene (Fig. 3), the situation corresponds to the latter case. Bachrach reported that compounds with transition states of C_s symmetry (including that of cyclopentadiene) are always catastrophic.[40] Therefore, compounds **1** and **5** have opposite topologies, thus providing an additional indication of the differences between cyclopentadiene and pyrazole. Antiaromatic systems like **4** and **7** have catastrophic networks.

Cyclopentadienide and pyrazolide anions

This third approach was based on the premise that an HB complex represents an intermediate situation (not necessarily the transition state) of the protonation.[42] This explains the success of Dunitz and others to describe protonation paths using a series of hydrogen-bonded crystal structures.[43] In the case benzene···HF complex,[44] the HF molecule points towards the middle point of one of the C–C bonds according to our B3LYP/6-3-311++G** calculations (the same happens for the benzene···ICl complex).[45]

We have compared anions $\mathbf{1}^-$ and $\mathbf{5}^-$ in their interaction with hydrogen-bond donors such as $HC\equiv CH$, HCN, HNC, HF and HCl. In principle, several minima could be expected; in the case of the cyclopentadienide anion, on the π-system, on the middle point of a C–C bond (like benzene) or on a C vertex.[46] These different hydrogen-bonded complexes can afterwards evolve towards other situations (Fig. 4). In the case of HCl, the strongest acid in the gas phase, the proton is transferred to the anion and the final structure is $\mathbf{1}\cdots Cl^-$. For the other hydrogen-bond donors, the geometry (Table 6) evolves from the π-complex (H···C–H ≈ 120°) in the case of acetylene to the complex on the C vertex (H···C–H ≈ 90°) in the case of hydrogen fluoride following a reaction path which ends in the cyclopentadiene/chloride anion complex (H···C–H = 102.6°) already close to isolated cyclopentadiene (H–C–H = 105.8°). The different pairs of H···C (Å)/H···C–H (°) values are related and evolve in a smooth way (Fig. 5) although there is a discontinuity between $\mathbf{1}^-\cdots HF$ and $\mathbf{1}\cdots Cl^-$, as happens for other proton transfers along HBs.[47] The strongest interaction corresponds to hydrogen isocyanide (E_{I+BSSE}, where BSSE is the basis set superposition error), the case of hydrogen fluoride being abnormal with a shorter H···C distance but an interaction energy lower than with HCN and HNC. Calculating the interaction energy not from the isolated monomers in their minimum energy geometries (E_I) but from the monomers with their geometries in the complex, [$E_{I(def)}$],[48] does not change this fact although the complex with HF is relatively the most stabilized.

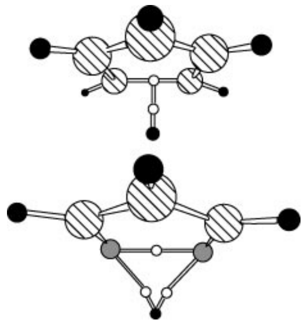
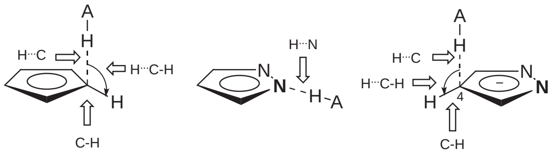


Fig. 3 Transition states corresponding to cyclopentadiene **1** and pyrazole **2**. White circles represent bond critical points (only for the CHC and NHN parts).



In the case of the pyrazolide anion $\mathbf{5}^-$, there are a series of situations similar to those of $\mathbf{1}^-$ (Fig. 4) and there is also the possibility that the hydrogen-bond donor 'attacks' the two in-plane lone pairs. The transfer is already observed in the case of HNC and only with the two weakest acids (acetylene and hydrogen cyanide) is it possible to obtain the HB complexes as stable minima. Both are of the σ-type but on a vertex not on the NN edge. To verify that pyrazolide anion behaves normally in the CCC periphery, we have calculated two complexes with C_4 symmetry (HNC and HF, in the case of HCl the transfer occurs and in the case of HCN the only minimum is that bound to the N atom, see previously). In these cases, pyrazolide anion behaves like the cyclopentadienide anion but the HNC complex of the former (H···C–H = 95.2°) resembles that of HF of both pyrazolate and cyclopentadienide. Here again the hydrogen fluoride has the shortest H···N distance but the weakest interaction energy, both E_I and $E_{I(def)}$.

Conclusions

Considering that in cyclic structures thermal migration of hydrogen is allowed only as a *suprafacial* process, then the

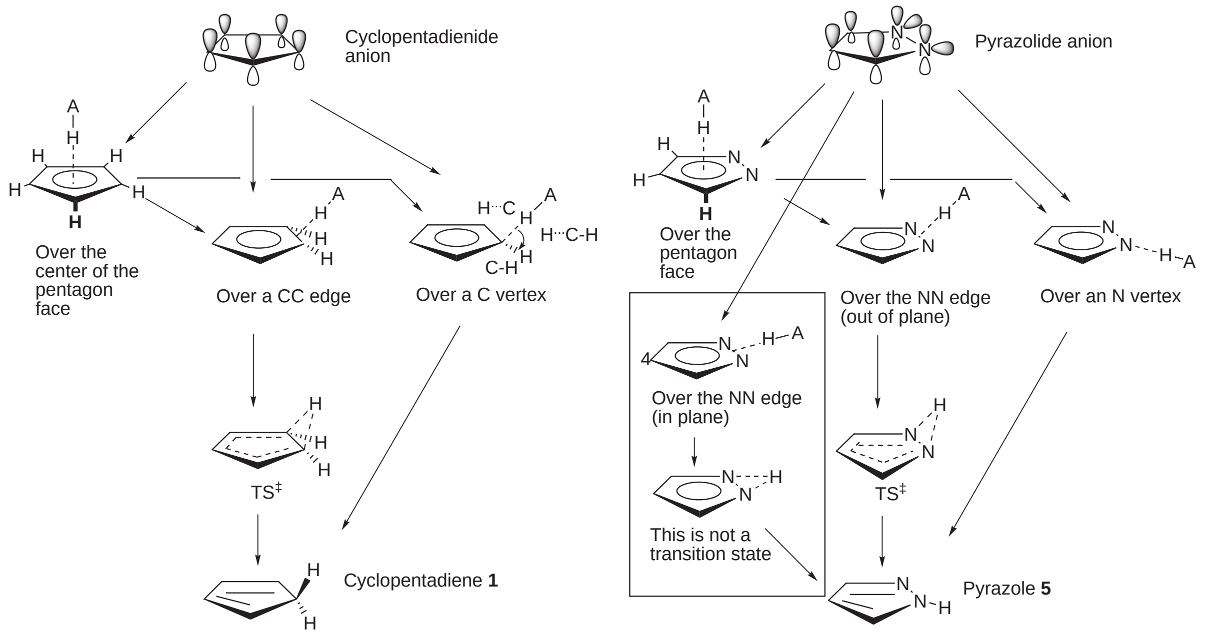


Fig. 4 Different hydrogen-bonded structures for cyclopentadienide and pyrazolide anions.

Table 6 Geometric (Å, °) and energetic (total in hartrees and relative in kcal mol^{-1}) characteristics of the hydrogen bonds with cyclopentadienide and pyrazolide anions

Cyclopentadienide[a]								
A–H	H···C	H···C–H	C–H	E_{total}	E_I	BSSE	$E_{I + BSSE}$	$E_{I(def)}$
HC≡CH[b]	2.428	117.2	1.089	−270.84453	−11.367	1.690	−9.677	−11.502
HCN[c]	2.160	113.1	1.088	−286.96025	−23.136	1.890	−21.246	−23.491
HNC[d]	1.958	104.8	1.088	−286.93773	−25.635	1.960	−23.675	−27.080
HF[e]	1.864	89.4	1.089	−293.95554	−21.716	2.880	−18.836	−23.222
HCl[f]	1.124	102.6	1.101					
Pyrazolide (NN edge)[g]								
A–H	H···N	N···H–A		E_{total}	E_I	BSSE	$E_{I + BSSE}$	$E_{I(def)}$
HC≡CH	1.910	180		−302.95158	−14.315	2.870	−11.445	−15.310
HCN	1.659	180		−319.06877	−27.000	3.260	−23.740	−30.868
Pyrazolide (C_4 vertex)[g]								
A–H	H···C	H···C–H	C–H	E_{total}	E_I	BSSE	$E_{I + BSSE}$	$E_{I(def)}$
HNC	1.983	95.24	1.086	−319.03229	−20.740	1.770	−18.970	−21.948
HF	1.902	87.46	1.086	−326.05292	−18.591	2.640	−15.951	−19.581
HCl[h]	1.145	102.24	1.098					

[a] H···C = C–H = 1.091 Å, H···C–H = 105.8°, $E = -193.50077$. [b] $E = -77.326$. [c] $E = -93.42262$. [d] $E = -93.39611$. [e] $E = -100.42017$. [f] Proton transferred. [g] $E = -225.60312$. [h] Proton transferred.

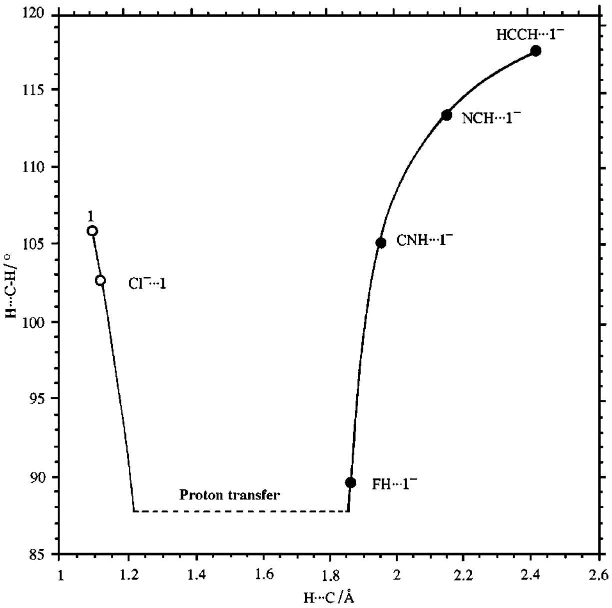


Fig. 5 Plot of H···C–H angles *vs.* H···C distances in cyclopentadiene and cyclopentadienide complexes.

[1,*j*] thermal sigmatropic shift is allowed in cyclopentadiene [1,5: *suprafacial*] but forbidden in cycloheptatriene [1,7: *antarafacial*].[1c,2c,4b,5b] The corresponding heterocycles, pyrazole **5** (formally [1,5]) and diazepine **7** (formally [1,7]), show both high barriers and although the first one (47.3 kcal mol^{-1}) is lower than the second one (58.5 kcal mol^{-1}) this relatively small decrease does not correspond to an allowed/forbidden relationship, even assuming that it is due to orbital symmetry differences.

The second approach has shown the differences between cyclopentadiene **1** and pyrazole **5**. The five membered ring is not essential in the first case, although the aromaticity of cyclopentadienide anion facilitates the H migration as a 'protic' entity, while it is essential to explain the high barrier in the case of pyrazole. This added to the different bond paths points to the dissimilarity between classical [1,5]-sigmatropic shifts and pyrazole prototropy.

The third approach has shown that, regarding hydrogen-bond donors, cyclopentadienide is a π-acceptor (in general η^5-over the face- but also η^1-on a C vertex-) while pyrazolide is a σ-acceptor (the same happens with metals).[49,50]

In conclusion, the Woodward–Hoffmann rules correspond to a clear-cut qualitative decision: processes are either 'allowed' or 'forbidden'. Proton transfer in pyrazole is formally a [1,5] hydrogen shift but only assuming a very extended definition of the Woodward–Hoffmann rules. Being at the borderline of the domain or even beyond, it is better defined as neither 'allowed' nor 'forbidden'.

Note finally that prototropy (annular tautomerism)[51] is very common in azoles and the barriers determined in solution[52–55] and in the solid state[56,57] for processes related to **5a** $\rightleftharpoons$ **5b** are in the range of 10–14 kcal mol^{-1}. Obviously in these cases, the transfer is not an intramolecular proton transfer but necessarily involves either solvent molecules (water, for instance)[8,58] or the formation of cyclic dimers, trimers or tetramers in the crystal.[59,60]

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References

1 R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Academic Press, Weinheim, 1970: (*a*) p. 114; (*b*) p. 123; (*c*) p. 126.
2 N. T. Anh, *Les Règles de Woodward–Hoffmann*, Ediscience, Paris, 1970: (*a*) p. 45; (*b*) p. 51; (*c*) p. 66.
3 T. L. Gilchrist and R. C. Storr, *Organic Reactions and Orbital Symmetry*, Cambridge University Press, Cambridge, 1972: (*a*) p. 204; (*b*) p. 210.
4 I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley, London, 1976: (*a*) p. 98; (*b*) p. 99.
5 R. G. Pearson, *Symmetry Rules for Chemical Reactions*, Wiley, New York, 1976: (*a*) p. 94; (*b*) p. 390.
6 W. J. Hehre, L. Radom, P. von R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986: (*a*) p. 501; (*b*) p. 503.
7 J. March, *Advanced Organic Chemistry* (*Fourth Edition*), Wiley, New York, 1992: (*a*) p. 1121; (*b*) p. 1124.
8 J. Catalán, J. L. G. de Paz, M. Sánchez-Cabezudo and J. Elguero, *Bull. Soc. Chim. Fr.*, 1986, 429.

9 M. W. Wong, R. Leung-Toung and C. Wentrup, *J. Am. Chem. Soc.*, 1993, **115**, 2465.

10 M. Cao, B. J. Teppen, D. M. Miller, J. Pranata and L. Schäfer, *J. Phys. Chem.*, 1994, **98**, 11353.

11 (*a*) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 1965, **87**, 395 and 2511; (*b*) R. Hoffmann, personal communication.

12 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian 94* (*Revision D.3*), Gaussian, Inc., Pittsburgh, PA, 1995.

13 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

14 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; C. Lee, W. Yang and R. G. Parr, *Phys. Rev.*, 1988, **37**, 785.

15 R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Oxford University, New York, 1990.

16 F. W. Biegler-König, R. F. W. Bader and T. H. J. Tang, *J. Comput. Chem.*, 1982, **3**, 317.

17 J. Elguero, C. Marzin, P. Linda and A. R. Katritzky, *The Tautomerism of Heterocycles*, Academic Press, New York, 1976; J. Elguero, *Pyrazoles and their Benzo Derivatives*, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 5, p. 167; J. Elguero, *Pyrazoles*, in *Comprehensive Heterocyclic Chemistry II*, ed. A. R. Katritzky, C. W. Rees and E. F. Scriven, Pergamon, Oxford, 1996, vol. 3, p. 1.

18 A. C. Atkinson and A. N. Donev, *Optimum Experimental Designs*, Oxford Science Publications, Clarendon Press, Oxford, 1992.

19 I. Alkorta, J. Elguero, I. Rozas and A. T. Balaban, *THEOCHEM*, 1990, **208**, 63.

20 J. C. Facelli, *THEOCHEM*, 1991, **236**, 119.

21 W. W. Schoeller and T. Busch, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 617.

22 C. Thomson and C. Glidewell, *J. Comput. Chem.*, 1983, **4**, 1.

23 C. Guimon, S. Khayar, F. Gracian, M. Begtrup and G. Pfister-Guillouzo, *Chem. Phys.*, 1989, **138**, 157.

24 B. Ya. Simkin, V. I. Minkin and M. N. Glukhovtsev, *Adv. Heterocycl. Chem.*, 1993, **56**, 303.

25 M. Alcamí, O. Mó and M. Yáñez, *J. Am. Chem. Soc.*, 1993, **115**, 11074.

26 D. H. Magers, E. A. Salter, R. J. Bartlett, C. Salter, B. A. Hess and L. J. Schaad, *J. Am. Chem. Soc.*, 1988, **110**, 3435.

27 I. Alkorta, S. Rozas and J. Elguero, *Struct. Chem.*, 1998, **9**, 243.

28 J. P. Paolini, *J. Comput. Chem.*, 1990, **11**, 1160.

29 F. Jensen, *Chem. Phys. Lett.*, 1989, **161**, 368.

30 W. R. Roth, *Tetrahedron Lett.*, 1964, 1009; W. R. Roth and J. König, *Liebigs Ann. Chem.*, 1966, **699**, 24; W. R. Roth, *Chimia*, 1966, **20**, 229.

31 S. McLean and P. Haynes, *Tetrahedron Lett.*, 1964, 2385.

32 K. Alder and H. J. Ache, *Chem. Ber.*, 1962, **95**, 503 and 511.

33 D. S. Glass, R. S. Boikess and S. Weinstein, *Tetrahedron Lett.*, 1966, 999.

34 S. D. Kahn, W. J. Hehre, N. G. Rondan and K. N. Houk, *J. Am. Chem. Soc.*, 1985, **107**, 8291.

35 R. V. Stanton and K. M. Merz, *J. Chem. Phys.*, 1994, **100**, 434.

36 B. A. Hess and L. J. Schaad, *J. Am. Chem. Soc.*, 1983, **105**, 7185.

37 B. A. Hess, L. J. Schaad and J. Pancir, *J. Am. Chem. Soc.*, 1985, **107**, 149.

38 F. Jensen and K. N. Houk, *J. Am. Chem. Soc.*, 1987, **109**, 3139.

39 Y. P. Liu, G. C. Lynch, T. N. Truong, D. H. Lu, D. G. Truhlar and B. C. Garrett, *J. Am. Chem. Soc.*, 1993, **115**, 2408.

40 S. M. Bachrach, *J. Org. Chem.*, 1993, **58**, 5414.

41 H. Jiao and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1995, **117**, 11529.

42 I. Alkorta, I. Rozas and J. Elguero, *Chem. Soc. Rev.*, 1998, **27**, 155.

43 J. D. Dunitz, *X-Ray Analysis and the Structure of Organic Molecules*, Cornell University Press, Ithaca, 1979, p. 337; H.-B. Burgi and J. D. Dunitz, *Structure Correlation*, VCH, Weinheim, 1994, vol. 1.

44 I. Rozas, I. Alkorta and J. Elguero, *J. Phys. Chem.*, A, 1997, **101**, 9457.

45 S. S. C. Ammal, S. P. Ananthavel, P. Venuvanalingam and M. S. Hegde, *J. Phys. Chem. A*, 1998, **102**, 532.

46 Recently, intramolecular hydrogen bonds between N–H and the vertex of pentasubstituted cyclopentadienide anions have been described: G. A. Dushenko, I. E. Mikhailov, O. E. Kompan, A. Zschunke, G. Reck, B. Schulz, C. Mugge and V. I. Minkin, *Mendeleev Commun.*, 1997, 127.

47 M. Ramos, I. Alkorta, J. Elguero, N. S. Golubev, G. S. Denisov, H. Benedict and H. H. Limbach, *J. Phys. Chem.*, *A*, 1997, **101**, 9791.

48 K. Szalewicz and B. Jeziorski, in *Molecular Interactions*, ed. S. Scheiner, Wiley, Chichester, 1997, p. 4.

49 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984, pp. 367–373.

50 G. La Monica and G. A. Ardizzoia, in *Progress in Inorganic Chemistry*, ed. K. D. Karlin, 1997, **46**, 151.

51 J. Elguero, C. Marzin, A. R. Katritzky and P. Linda, *The Tautomerism of Heterocycles*, Academic Press, New York, 1976, p. 266.

52 M. L. Roumestant, P. Viallefont, J. Elguero and R. Jacquier, *Tetrahedron Lett.*, 1969, 495.

53 M. T. Chenon, C. Coupry, D. M. Grant and R. J. Pugmire, *J. Org. Chem.*, 1977, **42**, 659.

54 R. M. Claramunt, J. Elguero, C. Marzin and J. Seita, *Anal. Quim.*, 1979, **75**, 701.

55 M. Perrin, A. Thozet, P. Cabildo, R. M. Claramunt, E. Valentí and J. Elguero, *Can. J. Chem.*, 1993, **71**, 1443.

56 F. Aguilar-Parrilla, G. Scherer, H. H. Limbach, C. Foces-Foces, F. H. Cano, J. A. S. Smith, C. Toiron and J. Elguero, *J. Am. Chem. Soc.*, 1992, **114**, 9657.

57 F. Aguilar-Parrilla, O. Klein, J. Elguero and H. H. Limbach, *Ber. Bunsenges. Phys. Chem.*, 1997, **101**, 889.

58 O. Bensaude, M. Chevrier and J. E. Dubois, *Tetrahedron*, 1978, **34**, 2259.

59 J. L. G. de Paz, J. Elguero, C. Foces-Foces, A. L. Llamas-Saiz, F. Aguilar-Parrilla, O. Klein and H. H. Limbach, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, 101.

60 R. M. Claramunt, M. D. Santa María, I. Forfar, F. Aguilar-Parrilla, M. Minguet-Bonvehí, O. Klein, H. H. Limbach, C. Foces-Foces, A. L. Llamas-Saiz and J. Elguero, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, 1867.

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