

Barriers to the Intramolecular N- to N-Transfer of Different Groups in Pyrazoles: Prototropy vs. Elementotropy

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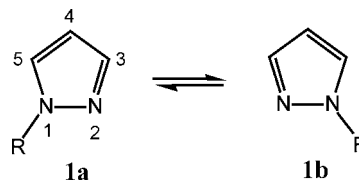
ABSTRACT: Barriers to the N- to N- transfer of different groups in pyrazole have been calculated at different levels (B3LYP and MP2 with 6-31G*, 6-311G*, and CEP-121 basis sets). Ten groups studied were H, BH₂, CH₃, CHO, AlH₂, SiH₃, GaH₂, GeH₃, SnH₃, and HgH. Two types of different transition states were found: The most common is a triangular situation with the group symmetrically linked to both N atoms. For metals M of the group 13 (B, Ga, Al) that situation is a second minimum while the TS corresponds to a rotation about the N–M bond plus a displacement of the migrating group to yield a nonsymmetric TS. A relationship between the barrier and the geometry has been found. © 2005 Wiley Periodicals, Inc. *Heteroatom Chem* 16:628–636, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20163

INTRODUCTION

Amongst the heterocyclic compounds, pyrazoles **1** are the best suited to study the transfer of the group attached to the nitrogen atom from one N to the other. This is due to the proximity of two kinds of nitrogen atoms, one “pyrrole-like” and the other “pyridine-like” [1,2]. Only other azoles, like triazoles

and tetrazole, share this property, but the situation is more complex and consequently are worse suited for fundamental studies.

The migration of any R group between both nitrogen atoms of pyrazole, i.e. the transformation **1a/1b**, can take place either intra- or intermolecularly:



When R = H, the transformation of **1a** into **1b** is an example of prototropic tautomerism. If, as represented above, both structures have the same energy (in general, when the substituents at positions 3 and 5 are identical) the process is called autotrope or degenerate [1,2]. We have collected in Table 1 all the available information up to now and reported in Scheme 1 the actual structure of the studied compounds.

These compounds can exist as dimers in the solid state, for instance, boron derivatives (pyrazaboles) [5c,16], aluminum derivatives [5c,17], and gallium derivatives [5c,18], but the monomers have been isolated and their dynamic behavior (fluxionality) studied in some cases.

The transfer of proton (prototropy, R = H) has been considerably studied mainly after it was discovered that the process could take place in the solid state (SSPT, solid-state proton transfer)

Dedicated to our friend Professor Vladimir I. Minkin on his 70th anniversary.

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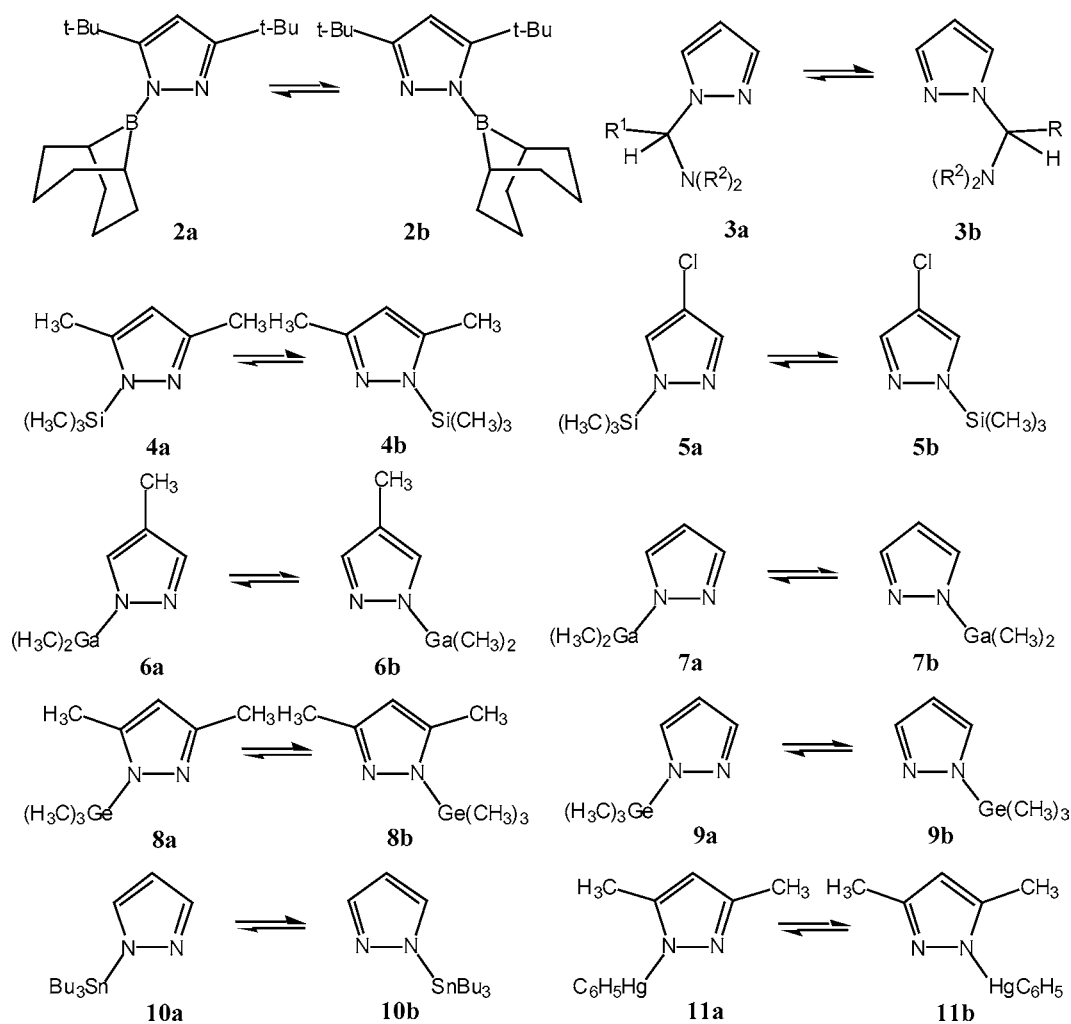
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TABLE 1 Experimental Data on Tautomeric Processes Involving the Migration of R (in kJ mol⁻¹)

<i>R</i>	<i>AN</i> ^a	Nature of the Process	Barrier	Notes and References
H	1	Intermolecular	–	The intramolecular process is forbidden [3]
BH ₂	5	Intramolecular	–	The compound has structure 2 [4,5a]
		Intramolecular	83.3	Calculated (MP2/6-31G*) for BH ₂ [5a,6]
CH ₃	6	Intermolecular	–	Intermolecular carbonotropies are only observed when there is a dissociation/recombination process [5a] with <i>N</i> -substituents like 3
CHO	6	Intermolecular	–	Intermolecular acylotropies involve two molecules [7]
AlH ₂	13	Intramolecular	–	No data on aluminotropies. For pyrazolato bridged dialuminum complexes, see [8]
SiH ₃	14	Intramolecular	95–100	The compounds have the structures from 4 to 6 , respectively [5b,9,10]
GaH ₂	31	Intramolecular	Very fast	The compound has the structure 6 [5a,11]
GeH ₃	32	Intramolecular	84–92	The compounds has the structure 7 and 8 , respectively [5b,12,13]
SnH ₃	50	Intramolecular	Very fast	The compound has the structure 9 [5b,9,14]
HgH	80	Intramolecular	42.3 ^b	The data correspond to compound 10 [15]

^aAtomic number.^bEstimated by the present authors from the spectra reported in [15].**SCHEME 1** The different N-substituted pyrazoles.

provided that several pyrazole molecules are linked together forming cyclic structures [19–23]. However, although NH-pyrazoles rapidly attain the equilibrium in the gas phase (the tautomeric equilibrium constant, K_T , changes monotonically with temperature), theoretical studies have shown that the transfer is not intramolecular but must involve collisions with other molecules or the walls on the instrument of measure [3,24,25].

The other substituents have been much less studied to the point that for some people tautomerism is synonymous with prototropy. However, the fact that they are rare does not mean that they are not interesting. In the case of intramolecular processes, the transformation $\mathbf{1a} \rightleftharpoons \mathbf{1b}$ provides a simple system amenable to high-level computations for studying the effect of the R nature in its migratory aptitude. It is expected that if some regularity or a simple explanation is found, these calculations could be useful in understanding the barrier involved in other group migrations, for instance, in sigmatropic reactions [26–30]. Even when the barriers are too high for the intramolecular transfer to occur, it is important to have an idea of the energy border that separates the intra- from the inter-molecular transfers.

Computational Details

The geometries of the structures have been optimized, using symmetry when possible, with the B3LYP/6-31G* [31,32], MP2/6-311G* [33,34], B3LYP/CEP-121 [35], and MP2/CEP-121 [35] as implemented in the Gaussian-03 package [36]. The minimum and transition state nature of the structures have been established by frequency calculation of the B3LYP/6-31G* and B3LYP/CEP-121 optimized geometries at the same computational level of the geometry optimization. In the case of the molecules with Sn and Hg, no full electron basis set was available and thus only the effective core potential basis

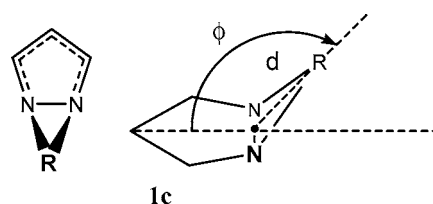
set, CEP-121, was used. The CEP-121 calculations for the remaining cases were carried out for comparative purposes with full electron ones. The electron density has been analyzed using the Atoms In Molecules (AIM) methodology [37] and the AIMPAC package [38].

RESULTS AND DISCUSSION

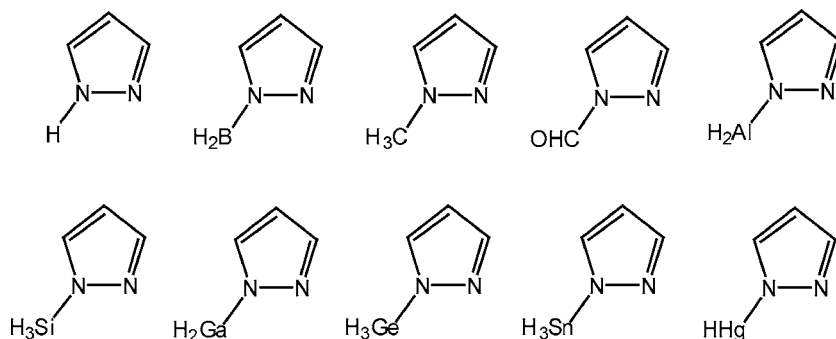
Having collected all the information available on these processes (Table 1), the purpose of the present paper is to carry out calculations on model compounds and to compare the results with the experimental data. Finally, if they are consistent, to examine the possible extension of these calculations to other systems. The calculations have been carried out on the simplest possible molecules as reported in Scheme 2.

We have found that the most obvious transition state that having a symmetry plane going through the C4 atom and the middle of the NN bond is not always a TS. Therefore, we have collected the calculated barriers and the geometrical parameters in Tables 2 and 3 for those cases where the TS is the symmetric diaza bicyclo[3.1.0] ring system, and in Tables 3 and 5 the other cases.

All the processes reported in Table 2 correspond to a TS $\mathbf{1c}$ (Scheme 3) where the R group lies outside the plane of the pyrazole ring; the angle ϕ ($^\circ$) and the



SCHEME 3 Migration of the R group: structure of the transition state $\mathbf{1c}$.



SCHEME 2 The calculated pyrazoles.

TABLE 2 Calculated Barriers (kJ mol⁻¹) of the Intramolecular Processes Involving the Migration of R

R	AN	B3LYP/6-31G*+ZPE	B3LYP/CEP-121+ZPE	MP2/6-311G*+ZPE ^a	MP2/CEP-121+ZPE ^b
H	1	197.7	215.6	199.7	203.0
CH ₃	6	275.8	274.1	276.2	267.7
CHO	6	172.7	184.8	155.2	168.2
SiH ₃	14	87.9	102.0	87.2	101.9
GeH ₃	32	81.8	95.5	74.1	93.6
SnH ₃	50	–	51.5	–	50.7
HgH	80	–	43.4	–	40.9

AN is the atomic number.

^aZPE taken from the B3LYP/6-31G* calculations.^bZPE taken from the B3LYP/CEP-121 calculations.**TABLE 3** Geometries of the Transition States **1c**

R	B3LYP/6-31G*		B3LYP/CEP-121		MP2/6-311G*		MP2/CEP-121	
	ϕ	<i>d</i>	θ	<i>d</i>	ϕ	<i>d</i>	θ	<i>d</i>
H	118.4	1.247	124.4	1.277	120.5	1.240	123.8	1.283
CH ₃	121.5	1.922	124.2	1.991	119.9	1.872	121.8	1.988
CHO	127.2	1.727	131.3	1.782	127.4	1.737	130.9	1.850
SiH ₃	144.7	1.945	155.0	2.033	145.5	1.942	151.6	2.065
GeH ₃	137.1	2.079	151.8	2.117	140.7	2.088	149.3	2.148
SnH ₃	–	–	165.4	2.245	–	–	162.8	2.277
HgH	–	–	162.5	2.301	–	–	150.3	2.287

Angles (ϕ) are in °, and distances (*d*) are in Å.**TABLE 4** Calculated Barriers (kJ mol⁻¹) of the Intramolecular Processes Involving the Migration of R with Regard to the First Minimum

R	AN	Min-2 1c B3LYP/ 6-31G*+ZPE	TS 1d B3LYP/ 6-31G*+ZPE	Min-2 1c B3LYP/ CEP-121+ZPE	TS 1d B3LYP/ CEP-121+ZPE
		BH ₂	5	70.2	76.2
AlH ₂	13	–36.9	5.1	–21.0	9.5
GaH ₂	31	–6.7	16.8	3.9	16.3
R	AN	Min-2 1c MP2/ 6-311G*+ZPE ^a	TS 1d MP2/ 6-311G*+ZPE ^a	Min-2 1c MP2/ CEP-121+ZPE ^b	TS 1d MP2/ CEP-121+ZPE ^b
		BH ₂	5	55.7	66.4
AlH ₂	13	–42.3	4.3	–18.2	10.4
GaH ₂	31	–6.4	9.4	8.6	18.3

^aZPE taken from the B3LYP/6-31G* calculations.^bZPE taken from the B3LYP/CEP-121 calculations.

distance *d* (Å) describe the position of the R group (Table 3).

The situation of the compounds reported in Tables 4 and 5 is more complex because two minima have been found (Scheme 4), one the initial structure **1a** or **1b**, i.e. the R group attached to one of the nitrogen atoms of the pyrazole ring (Min-1) and the other the R group attached to the two nitrogen atoms of the pyrazole ring (Min-2), i.e. similar to the previous TS **1c**. In the present case, the TS **1d**, situated be-

tween both minima, corresponds to a rotation and a displacement of the N-metal bond. Stable structures corresponding to **1c** have been described by Winter and coworkers in the case of pyrazolato titanium(IV) complexes [39].

An AIM analysis of the topology of all **1c** structures (B3LYP/6-31G*) shows the expected presence of a three-membered ring between the migrating group and both nitrogens never have a bifurcated type T topology.

TABLE 5 Geometries of the Second Minimum **1c** and the TS **1d** (θ is H–M–N–N Dihedral Angle in $^\circ$)

<i>R</i>	1c B3LYP/6-31G*		1d B3LYP/6-31G*		1c B3LYP/CEP-121		1d B3LYP/CEP-121	
	<i>d</i>	ϕ	<i>d</i>	θ	<i>d</i>	ϕ	<i>d</i>	θ
BH ₂	1.591	142.4	1.486	105.7	1.634	148.3	1.571	102.3
AlH ₂	1.926	180.0	1.842	45.0	1.964	180.0	1.863	53.2
GaH ₂	2.010	180.0	1.907	61.7	2.029	180.0	1.902	65.6
<i>R</i>	1c MP2/6-311G*		1d MP2/6-311G*		1c MP2/CEP-121		1d MP2/CEP-121	
	<i>d</i>	ϕ	<i>d</i>	θ	<i>d</i>	ϕ	<i>d</i>	θ
BH ₂	1.596	142.1	1.486	108.0	1.654	143.4	1.574	102.2
AlH ₂	1.928	180.0	1.847	43.4	1.992	180.0	1.881	54.8
GaH ₂	2.052	180.0	1.933	58.4	2.028	180.0	1.898	67.4

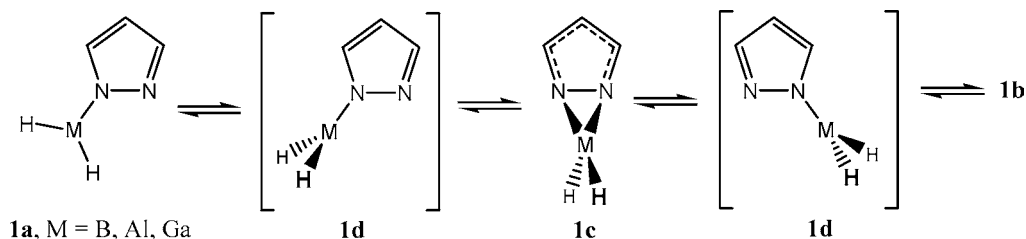
Distances (*d*) are in Å, and angles (ϕ) are in $^\circ$.

^aAlthough the metal M is not planar (sum of the angles about N < 360 $^\circ$), we have reported only the smaller value of θ .

TABLE 6 “Experimental Fitted and Predicted” Barriers

H (1c) 186.7	CH ₃ (1c) 244.3	CHO (1c) 155.6	SiH ₃ (1c) 96.5	GeH ₃ (1c) 89.1	SnH ₃ (1c) 50.9	HgH (1c) 42.1
BH ₂ (1c) 92.2	AlH ₂ (1c) –10.5	GaH ₂ (1c) 13.4	BH ₂ (1d) 92.2	AlH ₂ (1d) 15.0	GaH ₂ (1d) 22.0	

All values are in kJ mol^{–1}.

SCHEME 4 Migration of the R group: Structure of the transition state **1d**.

Barriers: Energy Aspects

To avoid a cumbersome discussion, we will report only the results obtained using the MP2 calculations noting that they are proportional to the B3LYP ones ($r^2 = 0.998$, where r^2 is the coefficient of determination).

The CEP-121 and 6-311G* values (only SnH₃ and HgH are missing) are related:

$$\text{MP2/6-311G}^* = -(21 \pm 6) + (1.07 \pm 0.05) \times \text{MP2/CEP-121}, n = 11, r^2 = 0.984 \quad (1)$$

Therefore, we decided to use the MP2/CEP-121 values since they are complete and compared them to the three experimental barriers (SiH₃ 97.5, GeH₃ 88.0, and HgH 42.3 kJ mol^{–1}):

$$\text{Exp} = (5.7 \pm 2.7) + (0.89 \pm 0.03)\text{MP2/CEP-121}, n = 3, r^2 = 0.999 \quad (2)$$

From this equation, a series of fitted and predicted values were obtained and that are reported in Table 6 as “experimental fitted and predicted” barriers in kilojoules per mole.

Remember that **1c** is a transition state for all substituents except those of the group 13 where it is a second minimum; the corresponding TS has the **1d** structure. We have represented in Fig. 1 two types of energy profiles for the **1a/1b** transformation. Figure 1(a) corresponds to the typical situation found in all the compounds of Table 2 (H, CH₃, CHO, SiH₃, GeH₃, SnH₃, and HgH) that we have exemplified with the case of the SiH₃ group. The remaining all three profiles correspond to Table 4: three cases can be seen in Fig. 1(b), where the case of the BH₂ group is depicted and energies of **1d** and **1c** are nearly degenerated. The compound minimum is a classical structure **1a**, and the transformation to **1b** can go directly through **1c** or first to **1d** and then to **1c**. The barrier,

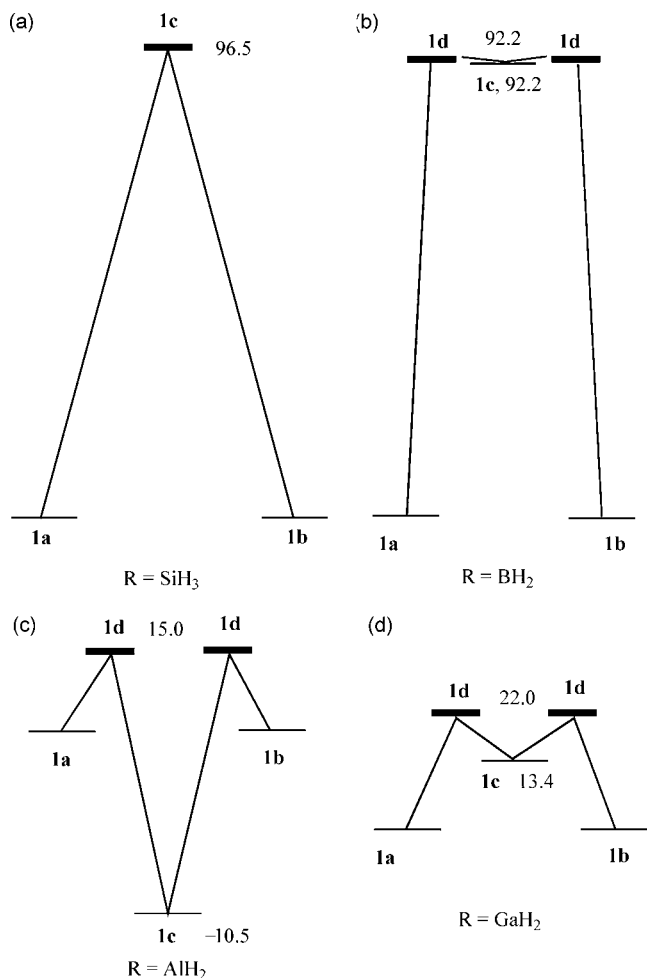


FIGURE 1 The different types of energy profiles from Table 6 data.

92.2 kJ mol⁻¹, is close to that reported by Schleyer et al. (83.3 kJ mol⁻¹) [5a,6], although the structures are not the same (that of [6] corresponds to torsion without displacement). In Fig. 1(c), the case of R = AlH₂ is shown; in this case, the energy minimum has the structure **1c**, the AlH₂ derivative should not be stable in its **1a** (**1b**) form and should exist as a

monomer having the structure **1c**. Finally, the GaH₂ derivative also has a classical minimum **1a** (**1b**) with a barrier of 22 kJ mol⁻¹; the secondary minimum **1c** is less stable than **1a**. In this way, Fig. 1 covers all possible types of energy profiles for the migration of R between both nitrogen atoms of pyrazoles.

Figure 2 reports the calculated barriers of Table 6 (for AlH₂, the 15 kJ mol⁻¹ barrier through **1d** has been represented) and the nature of the experimental processes. It is reasonable to assume that for calculated intramolecular barriers higher than 125 kJ mol⁻¹, the migration should follow an intermolecular path of lower energy if allowed.

Barriers: Geometry Aspects

What is the origin of these barriers? A first simple explanation will relate them to the N–R bond dissociation energies. Wiberg et al. [40] as well as some of us [41] have calculated the bond dissociation energies (BDE, kJ mol⁻¹) for simple H₂N–XH_n diatomic molecules. Here are Wiberg's values: H₂N–H 443.9, H₂N–CH₃ 345.2, H₂N–CHO 409.6, H₂N–BH₂ 589.9, H₂N–SiH₃ 427.7, and H₂N–AlH₂ 459.4 kJ mol⁻¹ [40]. There is no correlation between Table 6 values and these BDEs, neither with the atomic number.

We have then tried to examine whether there is some relationship with the geometry of the structures **1c** and **1d**, and we have found that the barriers are related to the cosines of the angles ϕ and θ (Fig. 3).

When the angle ϕ increases (the group R migrates closer to the pyrazole plane, $\phi = 180^\circ$), the “barrier,” i.e. the relative energy of **1c**, decreases. When the angle θ (H–M–N–N dihedral angle) increases, i.e. the relative energy of **1d**, the barrier increases. In **1a**, $\theta = 0^\circ$, thus an increase in θ means that the MH₂ group rotates more in BH₂ (102.2°, 92.2 kJ mol⁻¹) than in AlH₂ (54.8°, 15.0 kJ mol⁻¹) to attain the TS **1d**.

Finally, we have examined if the barriers of Table 6 bear any relationship with the 1,2-shifts ([1,5]-sigmatropic shifts) of the circumambulatory

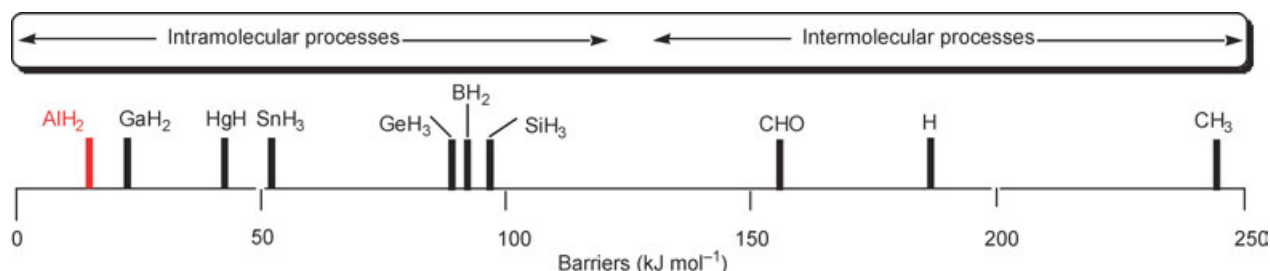


FIGURE 2 Range of energy barriers.

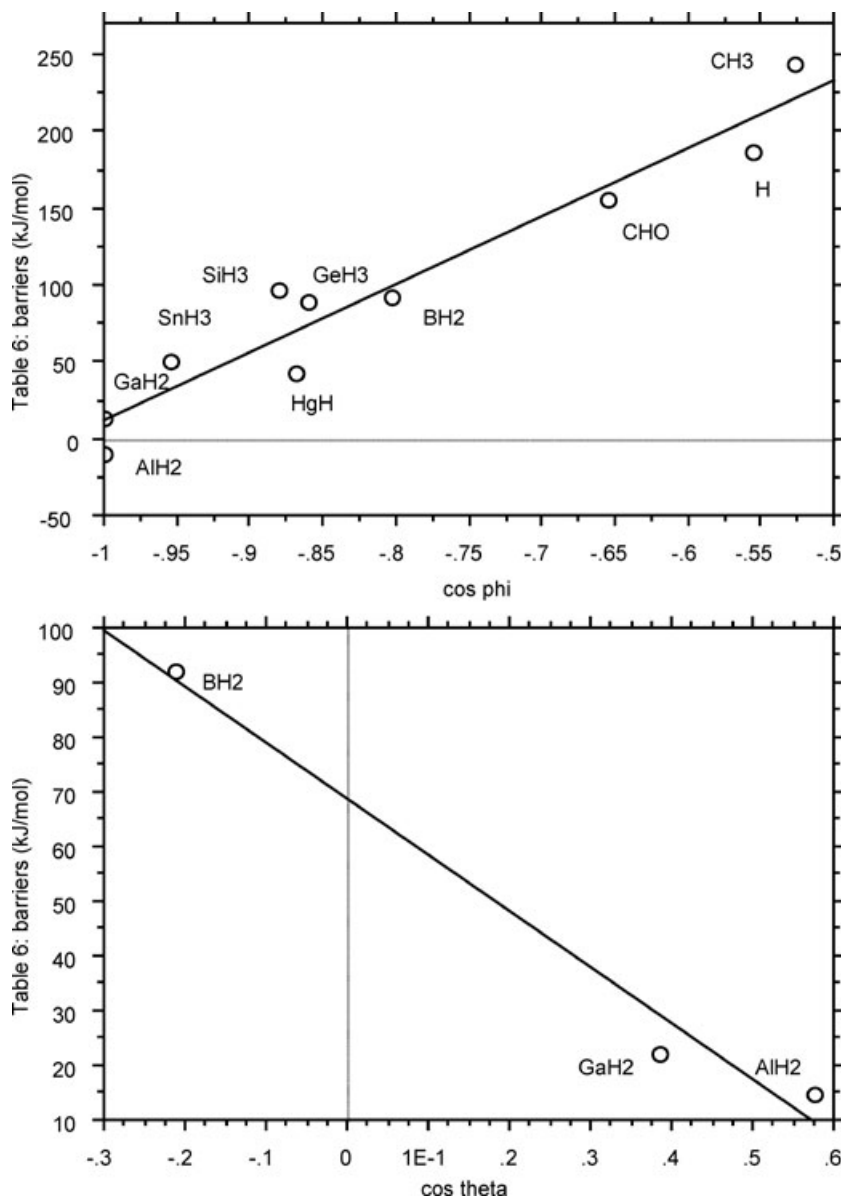


FIGURE 3 Plots of the energies of structures **1c** and **1d** (with regard to **1a**) against cosines of the angles ϕ and θ .

rearrangements of cyclopentadiene derivatives CpM [42,43]. With the following values in kJ mol^{-1} of 98.7 (H), 56.9 (Si), 51.9 (Ge), 31.4 (Sn), and 58.2 (B) [41], Eq. (3) is obtained:

$$\Delta G^\ddagger(\text{CpM}) = (9.4 \pm 3.3) + (0.49 \pm 0.03)\Delta G^\ddagger$$

(Table 6), $n = 5$, $r^2 = 0.989$ (3)

CONCLUSIONS

The energy barriers to the intramolecular migration of ten different groups (H, BH₂, CH₃, CHO, AlH₂, SiH₃, GaH₂, GeH₃, SnH₃, and HgH) have been calculated at the B3LYP/6-31G*, MP2/6-311G*,

B3LYP/CEP-121, and MP2/CEP-121 theoretical levels. When experimental barriers were available, the calculations reproduce acceptably well these data. Besides, when the processes are known to be intermolecular, the calculated barriers are very high. Two kinds of energy profiles have been discovered, one going directly through a symmetrical “triangular” TS (groups 12 and 14) and the other where this situation is a second minimum and the TS is situated between both minima (group 13). These differences are related to their differences in the number of electrons and therefore in regard to their orbital interactions and the ability to interact with the π system.

Two empirical observations have been made: first that there is a relationship between the barrier and the geometry as defined by the cosines of the angles ϕ and θ ; second that the intramolecular barriers we have estimated for pyrazoles seem to describe a general phenomena, at least, they are proportional to those measured for cyclopentadienes.

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