

# Borotropy: The Mechanism of Boron Transfer Between Adjacent N-Atoms of Pyrazol-1-yl Rings

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This manuscript is dedicated to Professor *Hans H. Limbach*

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This work examines theoretically the problem of the migration of borane groups between the nitrogen atoms of pyrazolyl rings. We have studied as a model the BH<sub>2</sub> pyrazol-1-yl derivatives to determine the effects of substituents on the pyrazole ring; also 1-(9-borabicyclo[3.3.1]nonan-9-yl)-1*H*-pyrazoles to compare the calculated barriers with the experimental ones as well as to determine steric effects, *i.e.*, how the buttressing effect increases the rate. The interacting quantum atoms methodology has been used for partitioning the energy of the systems in their stationary points into the contribution of pyrazole and BH<sub>2</sub> group and their mutual interaction.

**Keywords:** boranes, borotropy, interacting quantum atoms, pyrazolylboranes, steric effects, substituent effects, taft E<sub>s</sub> values.

## Introduction

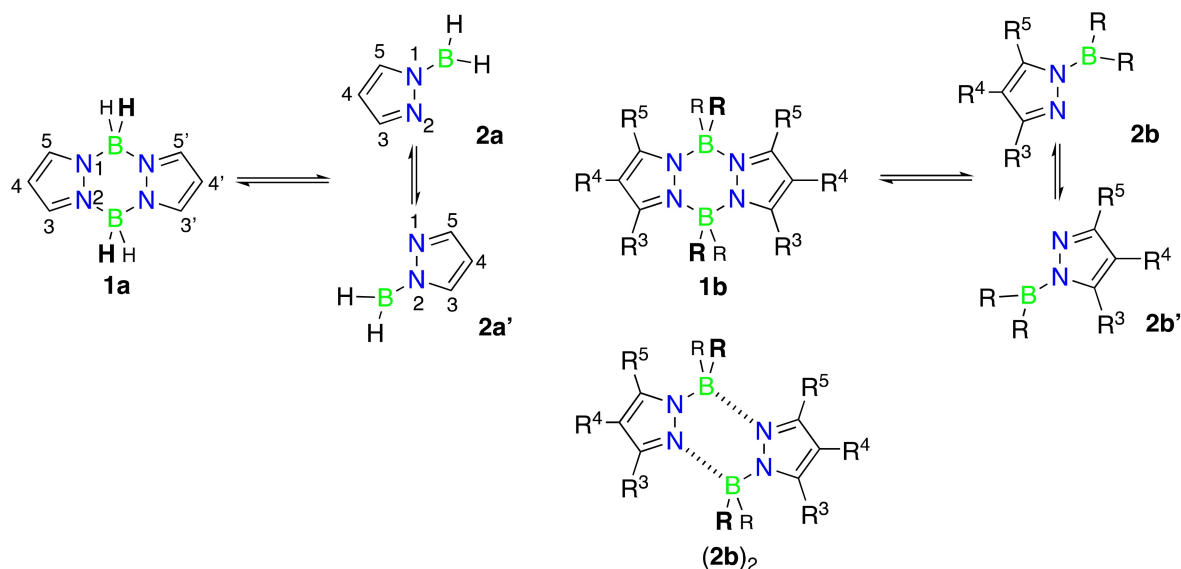
There is a classical problem in boron-nitrogen chemistry that has only been partly solved. Pyrazaboles, parent compound **1a**, general formula **1b**, exist in equilibrium with two pyrazolylboranes **2a/2a'** and **2b/2b'**, respectively, *Figure 1*.<sup>[1–3]</sup> Structures **1** and **2** are identified in solid state by X-ray crystallography and in solution by NMR. The use of NMR is based on the fact that pyrazaboles **1b** have a plane of symmetry through C4 and C4' (they also have a C<sub>2</sub> axis), the R<sup>3</sup>/R<sup>5</sup> pairs of nuclei (<sup>1</sup>H and <sup>13</sup>C), C3 and C5 (<sup>13</sup>C) and N1/N2 (<sup>15</sup>N) are isochronous. On the other hand, the **2b/2b'** pyrazolylboranes are intrinsically asymmetric and therefore the corresponding signals are anisochronous. But if borotropy, which converts **2b** to **2b'**, is fast on the NMR time scale, then these signals, depending on differences between chemical shifts and on temperature, become apparently isochronous. For distin-

guish between essential and an accidental isochrony,<sup>[4]</sup> we decided to study the process of borotropy.

The previous information corresponding to the processes represented in *Figure 1* can be divided in three groups: i) equilibrium **1–2**; ii) NMR experimental data relating to **2**; iii) previous theoretical calculations concerning the borotropy of **2**.

i) All available information on the equilibrium between **1** and **2** shows that there is never a mixture of dimers **1** and monomers **2**, and that they are always either pyrazaboles or pyrazolylboranes.<sup>[3]</sup> Classical pyrazolylboranes, that is, those in which the boron atom is attached to two carbon atoms, are only isolated when steric effects prevent dimer formation. This is not a kinetic effect because pyrazolylboranes that have both a strong Lewis acid, the boron atom, and a strong Lewis base, the lone pair at N2, always associate to form a dimer. In the absence of steric hindrance, the pyrazabole is formed with identical N–B distances and C<sub>2v</sub> symmetry when R<sup>3</sup> = R<sup>5</sup>. If steric hindrance prevents the monomers from joining to form a pyrazabole, they will form a loosely linked asymmetric dimer (**2b**)<sub>2</sub>. This is the reason why **1** and

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**Figure 1.** Monomers (pyrazolylboranes) and dimers (pyrazaboles). The numbering used for the pyrazaboles is not the standard but the same as in the pyrazolylboranes.

**2** never appear as a mixture in solution, having both a dimeric structure (Figure 1).<sup>[3]</sup>

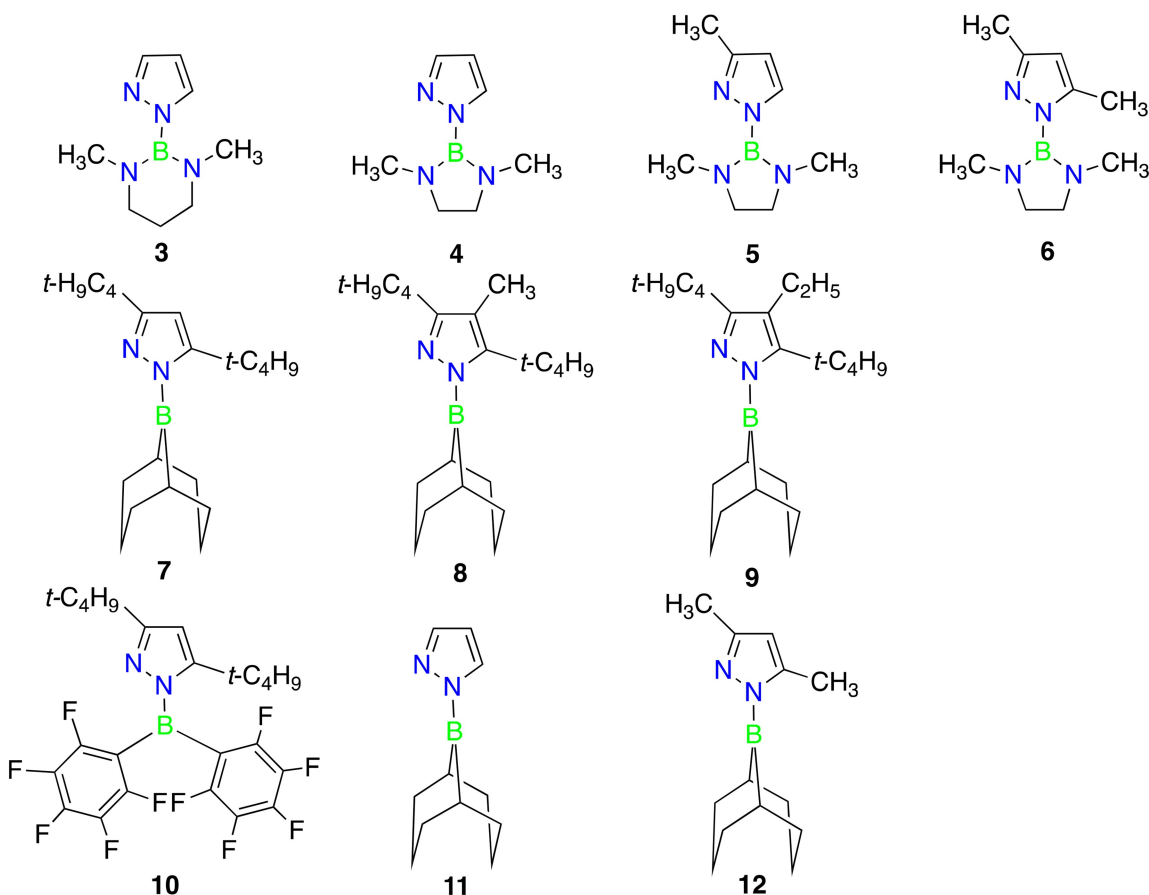
ii) Three authors have reported all the NMR information about pyrazolylboranes: Niedenzu,<sup>[5–8]</sup> Yalpani,<sup>[9–11]</sup> and Tamm.<sup>[12,13]</sup> Four papers by Niedenzu *et al.*<sup>[5–8]</sup> concern 1,3-dimethyl-2-(1*H*-pyrazol-1-yl)-1,3,2-diazaborinane **3** and 1,3-dimethyl-2-(1*H*-pyrazol-1-yl)-1,3,2-diazaborolidines **4**, **5** and **6** (Figure 2). These compounds, due to the competition of the three N-atoms surrounding the B-atoms that largely eliminates the Lewis acidity of the boron<sup>[10]</sup> do not behave like classical pyrazolylboranes and none of them present borotropy: <sup>1</sup>H, <sup>13</sup>C and <sup>14</sup>N spectra in CD<sub>2</sub>Cl<sub>2</sub>, CDCl<sub>3</sub> and neat, corresponds to monomers; the <sup>11</sup>B signal, between 24 and 29 ppm is typical of a tricoordinated boron.

The papers by Yalpani *et al.*<sup>[9–11]</sup> report the dynamic aspects (DNMR) of only three compounds of a large series of 1-(9-borabicyclo[3.3.1]nonan-9-yl)-1*H*-pyrazoles, the 3,5-di-*tert*-butyl substituted ones **7–9** (Figure 2). These compounds at room temperature in <sup>1</sup>H- and <sup>13</sup>C-NMR in CDCl<sub>3</sub> at 200.1 and 50.3 MHz, respectively, show only one set of signals for the *tert*-butyl groups; however in <sup>13</sup>C-NMR at 75.5 MHz the *tert*-butyl groups signal split and are well resolved. The boron signals of Figure 2 compounds **7–9** appear in the 63–65 ppm range. Qualitatively, the borotropy rate increases in the order **7** > **8** > **9**, *i.e.*, the buttressing effect increases the rate.

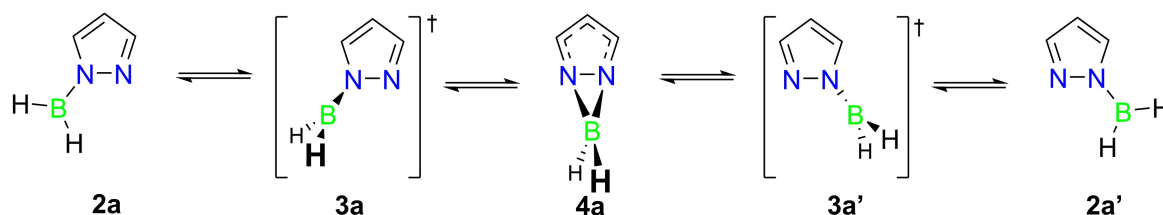
Yalpani *et al.*<sup>[9–11]</sup> described the following experiments concerning **7**: at 50.3 MHz at room temperature in <sup>13</sup>C-NMR there was only a set of signals for the *tert*-butyl both the methyl groups and the pyrazole C3 and C5 atoms; cooling to –80 °C resulted in a partial broadening and at –100 °C all these carbon atoms are well resolved. In these conditions the signals appear at 146.1 and 144.7 ppm (C3/C5) and 13.8 and 12.9 ppm (methyl groups of <sup>4</sup>Bu3/<sup>4</sup>Bu5).

The last papers are those of Tamm *et al.*,<sup>[12,13]</sup> which concern exclusively compound **10** (Figure 2). In the range +25 and –100 °C both <sup>1</sup>H and <sup>13</sup>C show only one set of signals for the two *tert*-butyl groups using 200, 300 and 400 MHz instruments. Therefore the borotropy of **10** is faster than that of **7**. In this case, the <sup>11</sup>B signal appears at +43.1 ppm.

iii) Regarding the previous theoretical calculations of the borotropy of **2**, already in 1990, Schleyer and Bühl<sup>[14]</sup> calculated the complete borotropy profile of the parent compound, as well as the chemical shifts of the different nuclei (Figure 3). That way they showed that **4a** is a C<sub>s</sub> symmetry minimum much less stable than the absolute minimum **2a**; this was an important result because Yalpani had considered that **4a** could be the absolute minimum. The relative values calculated at the MP2(FU)/6-31G\*+ZPE level are for **2a** (0.0 kJ·mol<sup>–1</sup>), **4a** (51.9 kJ·mol<sup>–1</sup>) and for TS **3a** (75.7 kJ·mol<sup>–1</sup>). The calculated <sup>11</sup>B chemical shifts were **2a** (47.6 ppm), **3a** (62.0 ppm), **4a** (19.3 ppm), this last



**Figure 2.** Diazaborinane **3**, diazaborolidines **4–6**, 1-(9-borabicyclo[3.3.1]nonan-9-yl)-3,5-di-*tert*-butyl-1*H*-pyrazoles **7–9** and **11** and **12** and 1-[bis(perfluorophenyl)boraneyl]-3,5-di-*tert*-butyl-1*H*-pyrazole **10**.



**Figure 3.** The borotropic transformation of **2a** into its degenerate isomer **2a'**.

value rules out that **4a** is the absolute minimum when compared with the experimental values.

In 2005 we carried out a theoretical study of the barriers to the 1 *N*- to 2 *N*- transfer of different groups in pyrazole itself at different levels (B3LYP and MP2 with 6-31G\* and 6-311G\* basis sets).<sup>[15]</sup> Eight groups were studied H, BH<sub>2</sub>, CH<sub>3</sub>, CHO, AlH<sub>2</sub>, SiH<sub>3</sub>, GaH<sub>2</sub> and GeH<sub>3</sub>. The BH<sub>2</sub> corresponds to **2a**, where we obtained at the MP2/6-311G\*+ZPE for the two minima **2a**

(0.0 kJ·mol<sup>-1</sup>) and **4a** (55.7 kJ·mol<sup>-1</sup>) and for the TS **3a** (97.0 kJ·mol<sup>-1</sup>); these values are similar to those of Schleyer.<sup>[14]</sup> We decided to study the effects of the substituents on the pyrazole ring keeping the boron unsubstituted and the real case of the Yalpani compounds **7** and **8** of *Figure 2* as well as other compounds, **11** and **12** bearing different substituents on the pyrazole ring, *Figure 2*.

## Results and Discussion

### Estimation of the Experimental Barrier

Since Yalpani, Köster and Boese did not use their NMR data<sup>[9–11]</sup> to calculate any kinetic property, we used the Eyring equation to do this. This equation<sup>[16–18]</sup> is  $\Delta G_T^\ddagger = 19.12 \times T_C (10.32 + \log T_C/k_C)$  in  $\text{J}\cdot\text{mol}^{-1}$  where  $T_C$  is the coalescence temperature in K,  $k_C$  is the rate at the  $T_C$  ( $k_C = \pi/\sqrt{2} \times \Delta\nu = 2.222 \times \Delta\nu$  for uncoupled sites) and  $\Delta\nu$  is the difference in Hz between the two signals.

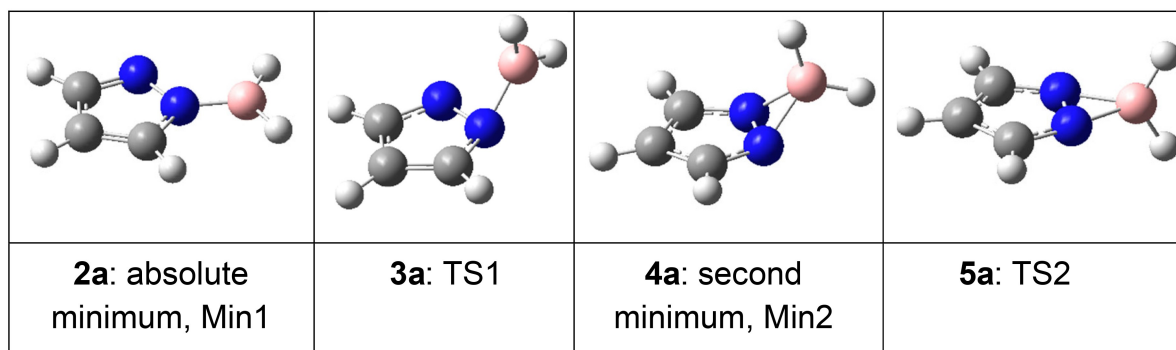
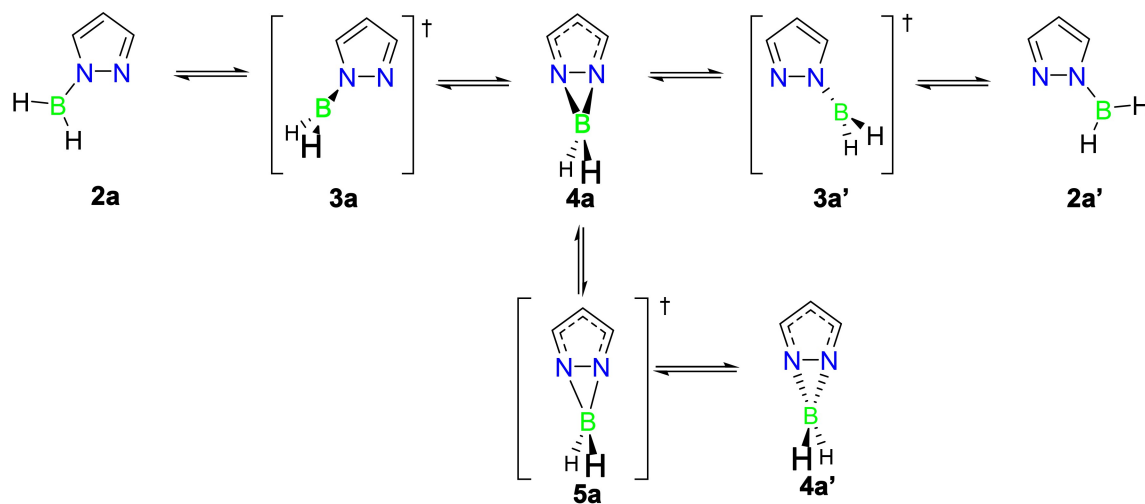
Thus, the following results were obtained:  $\Delta\nu = 1.4 \text{ ppm} = 105.7 \text{ Hz}$  (C3/C5) and  $0.9 \text{ ppm} = 68 \text{ Hz}$  (<sup>t</sup>Bu3/<sup>t</sup>Bu5);  $T_C \approx -90^\circ\text{C} = 183.15 \text{ K}$ ;  $\Delta G_{183.15}^\ddagger = 38.9 \text{ kJ}\cdot\text{mol}^{-1}$  (C3/C5) and  $40.4 \text{ kJ}\cdot\text{mol}^{-1}$  (<sup>t</sup>Bu3/<sup>t</sup>Bu5), in average for compound **7**,  $\Delta G_{183.15}^\ddagger = 39.7 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$ .

### The Case of the Parent Compound

The energetic results in  $\text{kJ}\cdot\text{mol}^{-1}$  of all previous calculations are collected in *Table 1* and the geometry of the stationary points represented in *Figure 4*.

**Table 1.** Energetic results from the literature ( $\text{kJ}\cdot\text{mol}^{-1}$ ).

| Level of theory                                  | <b>2a</b> (Min1) | <b>3a</b> (TS1) | <b>4a</b> (Min2) | <b>3a–4a</b> |
|--|------------------|-----------------|------------------|--------------|
| MP2(FC)/6-31 + G**/6-31G** <sup>[14]</sup>       | 0.0              | 82.8            | 58.2             | + 24.6       |
| MP2(FU)/6-31G**/6-31G** <sup>[14]</sup>          | 0.0              | 85.4            | 54.4             | + 31.0       |
| MP2(FU)/6-31G**//MP2(FU)/6-31G** <sup>[14]</sup> | 0.0              | 83.3            | 54.8             | + 28.5       |
| MP2(FU)/6-31G* + ZPE <sup>[14]</sup>             | 0.0              | 75.7            | 51.9             | + 23.8       |
| B3LYP/6-31G* + ZPE <sup>[15]</sup>               | 0.0              | 76.2            | 70.2             | + 6.0        |
| MP2/6-311G* + ZPE <sup>[15]</sup>                | 0.0              | 66.4            | 55.7             | + 10.7       |



**Figure 4.** The stationary points of the parent compound, 1-boranyl-1H-pyrazole.

Note that in *Table 1* for the **3a–4a** difference, there are two kinds of values, one around 27 kJ·mol<sup>-1</sup> and the other around 8 kJ·mol<sup>-1</sup>, only partly associated with the ZPE correction.

With regard to *Table 1* (no TS2 calculations), the results of *Table 2* (**a** series,  $\Delta E$  values) are similar to those reported by Schleyer *et al.*<sup>[14]</sup> not including ZPE, the closest being MP2(FC)/6-31+G\*\*//6-31G\*; the largest difference concerns the Min2 value (71.6 kJ·mol<sup>-1</sup> vs. 58.2 kJ·mol<sup>-1</sup>).

The three columns of values in *Table 2*,  $\Delta E$ ,  $\Delta H$  and  $\Delta G$ , are related,  $\Delta G = -(0.2 \pm 5.4) + (0.974 \pm 0.065) \Delta E$ ,  $n = 18$ ,  $R^2 = 0.934$ ,  $\Delta G = -(4.5 \pm 6.8) + (1.073 \pm 0.088) \Delta H$ ,  $n = 18$ ,  $R^2 = 0.903$  and  $\Delta E = -(5.1 \pm 3.0) + (1.110 \pm 0.039) \Delta H$ ,  $n = 18$ ,  $R^2 = 0.981$ . From now on, we will discuss only the  $\Delta G$  values.

We have asked ourselves if these values follow a Hammett relationship. The answer is no, the only equation being  $\text{Min2} = -(1.3 \pm 1.3) + (8.9 \pm 2.6) \sigma_{\text{m}}$ ,  $n = 6$ ,  $R^2 = 0.750$ , using the values relative to **4a**; the intercept is  $1.3 \pm 1.3$  that is close to 0 the value of  $\sigma_{\text{m}}$  for R = H. With  $\sigma_{\text{p}}$  there is no correlation,  $R^2 = 0.08$ ; both transition states are uncorrelated with either  $\sigma_{\text{m}}$  or  $\sigma_{\text{p}}$  ( $0.28 < R^2 < 0.60$ ). Using Swain and Lupton biparametric equation (field  $F$  and resonance  $R$  effects)<sup>[19,20]</sup> only Min2 shows a correlation but with a poor  $R^2$  coefficient, also 0.750. Why is there a relationship, although not good, with  $\sigma_{\text{m}}$  and not with  $\sigma_{\text{p}}$ ? If, as we will discuss below, Min1 is a neutral pyrazole and Min2 is more like a pyrazolium salt, they are related to the acid-base equilibria in pyrazoles where the substituents on the pyrazole ring behave as aromatic *meta* substituents.<sup>[21]</sup>

A qualitative analysis of O<sup>-</sup>, H and NH<sub>3</sub><sup>+</sup> substituent effects shows: i) concerning TS1,  $\Delta G$  is 82.0, 78.5 and 79.4 kJ·mol<sup>-1</sup>, respectively, indicates that the

rotation of the BH<sub>2</sub> group about the B–N bond, with its concomitant out-of-plane motion, is relatively insensitive to the nature of R, the 4-substituent on the pyrazolyl ring; ii) concerning Min2,  $\Delta G$  is 61.0, 69.6 and 77.3 kJ·mol<sup>-1</sup>, respectively, corresponds to the fact than in Min1 the pyrazolyl ring is neutral while in Min2 it is a pyrazolium cation that is stabilized by electron-donor substituents (O<sup>-</sup>, 8.6 kJ·mol<sup>-1</sup>) and destabilized by electron-withdrawing substituents (NH<sub>3</sub><sup>+</sup>, -7.7 kJ·mol<sup>-1</sup>), finally iii) in what concerns TS2, the inversion of the BH<sub>2</sub> group between Min2 invertomers, shows an effect of NH<sub>3</sub><sup>+</sup> of -1.2 kJ·mol<sup>-1</sup> of unexpected sign but very small and O<sup>-</sup> of -15.5 kJ·mol<sup>-1</sup>, this value indicates that the electron-donor O<sup>-</sup> destabilized the TS2 when compared with that of R = H, **5a**.

If we consider together the neutral and charged species, the extreme values for TS1 are F (78.0) and O<sup>-</sup> (92.0), difference  $\Delta = 14.0$  kJ·mol<sup>-1</sup>; for Min2 are O<sup>-</sup> (61.0) and NH<sub>3</sub><sup>+</sup> (77.3), difference  $\Delta = 16.3$  kJ·mol<sup>-1</sup>; for TS2 are NO<sub>2</sub> (79.6) and NH<sub>2</sub> (88.5), difference  $\Delta = 8.9$  kJ·mol<sup>-1</sup>, and for TS2–Min2 (**5–4**) are NH<sub>3</sub><sup>+</sup> (5.6) and O<sup>-</sup> (36.2), difference  $\Delta = 30.6$  kJ·mol<sup>-1</sup>. The  $\Delta$  value for TS1 is too small to be analyzed, except to indicate that the rotation of BH<sub>2</sub> about the N–B bond does not depend too much on the substituent in position 4. The Min2 for R = H has a value of 69.6 kJ·mol<sup>-1</sup>, O<sup>-</sup> stabilizes it by 8.6 kJ·mol<sup>-1</sup> and NH<sub>3</sub><sup>+</sup> destabilizes it by 7.7 kJ·mol<sup>-1</sup>; the *N,N*-disubstituted Min2 has a certain pyrazolium character compared to the pyrazole character of Min1, thus an anion should stabilize and a cation destabilize it. The TS2–Min2 (**5–4**) difference is important,  $\Delta = 30.6$  kJ·mol<sup>-1</sup>, being larger for O<sup>-</sup> than for NH<sub>3</sub><sup>+</sup>; TS2, the flip-flop of the BH<sub>2</sub> group between **4a** and **4a'**, show geometrical modifications of the angles depending on the nature

**Table 2.** Relative energies (kJ·mol<sup>-1</sup>) with respect to **2** (Min1). The substituent R is at the 4 position of the pyrazole ring.

|                 | <b>a</b> (R = H)            |            |            | <b>c</b> (F)               |            |            | <b>d</b> (NO <sub>2</sub> )              |            |            |
|-----------------|-----------------------------|------------|------------|----------------------------|------------|------------|--|------------|------------|
|                 | $\Delta E$                  | $\Delta H$ | $\Delta G$ | $\Delta E$                 | $\Delta H$ | $\Delta G$ | $\Delta E$                               | $\Delta H$ | $\Delta G$ |
| <b>3</b> (TS1)  | 81.6                        | 77.1       | 78.5       | 80.9                       | 76.3       | 78.0       | 81.9                                     | 77.3       | 78.6       |
| <b>4</b> (Min2) | 71.6                        | 70.1       | 69.6       | 72.0                       | 70.3       | 70.0       | 75.0                                     | 73.5       | 72.3       |
| <b>5</b> (TS2)  | 80.8                        | 77.2       | 81.7       | 86.4                       | 82.6       | 87.0       | 78.6                                     | 74.9       | 79.6       |
| <b>5–4</b>      | 9.2                         | 7.1        | 12.1       | 14.4                       | 12.3       | 17.0       | 3.6                                      | 1.4        | 7.3        |
|                 | <b>e</b> (NH <sub>2</sub> ) |            |            | <b>f</b> (O <sup>-</sup> ) |            |            | <b>g</b> (NH <sub>3</sub> <sup>+</sup> ) |            |            |
|                 | $\Delta E$                  | $\Delta H$ | $\Delta G$ | $\Delta E$                 | $\Delta H$ | $\Delta G$ | $\Delta E$                               | $\Delta H$ | $\Delta G$ |
| <b>3</b> (TS1)  | 82.6                        | 77.7       | 78.9       | 84.9                       | 80.1       | 82.0       | 85.1                                     | 80.9       | 79.4       |
| <b>4</b> (Min2) | 72.6                        | 70.9       | 70.7       | 61.9                       | 60.2       | 61.0       | 84.2                                     | 82.8       | 77.3       |
| <b>5</b> (TS2)  | 90.8                        | 87.0       | 88.5       | 97.2                       | 92.3       | 97.2       | 86.3                                     | 82.7       | 82.9       |
| <b>5–4</b>      | 18.2                        | 16.1       | 17.8       | 35.3                       | 32.1       | 36.2       | 2.1                                      | -0.1       | 5.6        |

of R (Table 3). The NBN, CNN and BNN angles show small variations ( $\leq 0.8^\circ$ ) and although the proton, R=H, occupies a central position between  $O^-$  and  $NH_3^+$ , they are useless to discuss the barriers.

On the other hand, the folding angle, C4-(N-N)dummy'-B, (N-N)dummy is situated in the middle of the N-N bond, changes from  $180^\circ$  in **5** to  $49.3^\circ$  ( $O^-$ ),  $39.7^\circ$  (H) and  $26.2^\circ$  ( $NH_3^+$ ). There is a linear relationship between  $\Delta G$  and the cosine of the folding angle:  $\Delta G = (99.526.9) - (107.2 \pm 34.5) \cos$ . (diff. **5-4**),  $n=3$ ,  $R^2=0.906$ , indicating, as expected, that the flatter **4** is, the lower is the barrier.

The relative electronic energy contributions of the pyrazole and the  $BH_2$  groups calculated with the IQA (interacting quantum atoms) methodology have been gathered in Table 4. A more detailed table with the contribution of the intra and inter-atomic energies of each fragment, Coulomb potential and exchange-correlation energy contributions of the Pz- $BH_2$  interaction energy, charge and volume variation of each fragment are gathered in the supplementary material.

The numerical integration used in these calculations produce a small error when the total electronic energy is compared to the sum of the IQA terms. In these sets, the absolute value of the error is always smaller than  $2.5 \text{ kJ}\cdot\text{mol}^{-1}$ .

The most important component of Table 4, in absolute value, is in all cases the energy variation of the interaction between the Pz and  $BH_2$  fragments. It presents destabilizing values between  $+57$  and  $+163 \text{ kJ}\cdot\text{mol}^{-1}$ . The variation of the coulombic contribution of the interaction Pz- $BH_2$  with respect to the corresponding value of the Min 1 is always positive (between 209 and  $78 \text{ kJ}\cdot\text{mol}^{-1}$ ) while the exchange contribution is positive for TS1, with the exception of the **3g** structure, and negative for Min2 and TS2.

In contrast, the Pz and  $BH_2$  fragments are stabilized in the neutral molecules in Min2, TS1 and TS2 with respect to Min1, with the exception of the Pz component of **d**.

An analysis of the charge variation in the different stationary points, shows that the Pz subunit loss

**Table 3.** Energy comparison between charged substituents and the parent compound, R=H.

| R        | Angles [ $^\circ$ ] | TS2 <b>5</b> | Min2 <b>4</b> | Diff. <b>5-4</b> | Diff. with R=H |
|----------|---------------------|--------------|---------------|------------------|----------------|
| $O^-$    | NBN                 | 52.0         | 51.1          | 0.9              | +0.2           |
| $O^-$    | CNN                 | 108.0        | 109.8         | -1.8             | -0.8           |
| $O^-$    | BNN                 | 64.0         | 64.5          | -0.5             | -0.2           |
| $O^-$    | C4-(N-N)dummy'-B    | 180          | 130.7         | 49.3             | 9.6            |
| H        | NBN                 | 50.6         | 49.9          | 0.7              | 0              |
| H        | CNN                 | 108.6        | 109.6         | -1.0             | 0              |
| H        | BNN                 | 64.7         | 65.0          | -0.3             | 0              |
| H        | C4-(N-N)dummy'-B    | 180          | 140.3         | 39.7             | 0              |
| $NH_3^+$ | NBN                 | 48.9         | 48.6          | 0.3              | -0.4           |
| $NH_3^+$ | CNN                 | 110.2        | 110.7         | -0.5             | +0.5           |
| $NH_3^+$ | BNN                 | 65.4         | 65.6          | -0.2             | +0.1           |
| $NH_3^+$ | C4-(N-N)dummy'-B    | 180          | 153.8         | 26.2             | -13.5          |

**Table 4.** IQA relative energies ( $\text{kJ}\cdot\text{mol}^{-1}$ ) with respect to **2** (Min1). The substituent R is at the 4 position of the pyrazole ring.

|                 | <b>a</b> (R = H)    |        |                           | <b>c</b> (F)       |        |                           | <b>d</b> ( $NO_2$ )   |        |                           |
|-----------------|---------------------|--------|---------------------------|--------------------|--------|---------------------------|-----------------------|--------|---------------------------|
|                 | Pz <sup>[a]</sup>   | $BH_2$ | Pz- $BH_2$ <sup>[b]</sup> | Pz <sup>[a]</sup>  | $BH_2$ | Pz- $BH_2$ <sup>[b]</sup> | Pz <sup>[a]</sup>     | $BH_2$ | Pz- $BH_2$ <sup>[b]</sup> |
| <b>3</b> (TS1)  | -39.6               | -29.5  | 151.7                     | -39.7              | -33.5  | 155.1                     | -35.2                 | -36.9  | 152.9                     |
| <b>4</b> (Min2) | -3.2                | -67.0  | 141.4                     | -4.5               | -69.2  | 146.5                     | 5.0                   | -67.2  | 137.2                     |
| <b>5</b> (TS2)  | -11.0               | -52.8  | 145.2                     | -14.2              | -56.8  | 158.0                     | -2.7                  | -56.3  | 137.4                     |
|                 | <b>e</b> ( $NH_2$ ) |        |                           | <b>f</b> ( $O^-$ ) |        |                           | <b>g</b> ( $NH_3^+$ ) |        |                           |
|                 | Pz <sup>[a]</sup>   | $BH_2$ | Pz- $BH_2$ <sup>[b]</sup> | Pz <sup>[a]</sup>  | $BH_2$ | Pz- $BH_2$ <sup>[b]</sup> | Pz <sup>[a]</sup>     | $BH_2$ | Pz- $BH_2$ <sup>[b]</sup> |
| <b>3</b> (TS1)  | -45.7               | -26.8  | 155.4                     | -37.3              | 10.6   | 112.2                     | -5.7                  | -70.0  | 158.5                     |
| <b>4</b> (Min2) | -11.2               | -63.1  | 147.7                     | -4.2               | -5.9   | 72.6                      | 14.6                  | -82.3  | 152.3                     |
| <b>5</b> (TS2)  | -22.6               | -48.0  | 163.1                     | 9.8                | 31.2   | 56.7                      | 5.9                   | -78.8  | 158.5                     |

<sup>[a]</sup> Energetic contribution of the pyrazole group with its substituent. <sup>[b]</sup> Energetic contribution of the interaction between the pyrazole group and  $BH_2$ .

charge in Min2, TS1 and TS2 with respect to Min 1 while the BH<sub>2</sub> group gain it in the neutral molecules and in the NH<sub>3</sub><sup>+</sup> derivative, **g**. In the case of the anionic systems, **f**, the opposite is observed, a gain of charge of the Pz and a lost of the BH<sub>2</sub> group.

The comparison of all the components listed in Table 4 and in the supplementary material with the relative energies of the Min2, TS1 and TS2 shows poor correlations indicating that these energies are due to an accumulative effect of all the components.

### The Case of Yalpani's Compounds

The three columns of Table 5 are related,  $\Delta G = -(3.3 \pm 2.0) + (1.016 \pm 0.035) \Delta E$ ,  $n = 13$ ,  $R^2 = 0.987$ ,  $\Delta G = (2.0 \pm 1.9) + (1.029 \pm 0.036) \Delta H$ ,  $n = 13$ ,  $R^2 = 0.987$  and  $\Delta E = (5.3 \pm 0.8) + (1.110 \pm 0.016) \Delta H$ ,  $n = 13$ ,  $R^2 = 0.997$ . If the values of Tables 2 and 4 were treated together the regression equation became  $\Delta G = -(2.9 \pm 1.5) + (1.008 \pm 0.021) \Delta E$ ,  $n = 31$ ,  $R^2 = 0.988$ ,  $\Delta G = (3.2 \pm 1.6) + (0.982 \pm 0.024) \Delta H$ ,  $n = 31$ ,  $R^2 = 0.983$  and  $\Delta E = (6.1 \pm 1.0) + (0.974 \pm 0.014) \Delta H$ ,  $n = 31$ ,  $R^2 = 0.994$ .

For compound **7**, as we have noted before,  $\Delta G_{183.15}^\ddagger = 39.7 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$ ; our calculations corresponding to TS2 (that that lead to a coalescence of the *tert*-butyl groups) is  $39.7 \text{ kJ}\cdot\text{mol}^{-1}$ . In the case of compound **8** the barrier decreases till  $32.1 \text{ kJ}\cdot\text{mol}^{-1}$  in agreement with the fact that the buttressing effect decreases the barrier.

There is no experimental information on compounds **11** and **12**. In the case of **7** (two *tert*-butyl groups) the barrier is  $39.7 \text{ kJ}\cdot\text{mol}^{-1}$ , replacing the *tert*-butyl groups by methyl groups, **12**, and by H-atoms, **11**, the barrier increases considerably,  $58.8$  and  $88.6 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively. These barriers are linearly correlated with steric effects; using Taft E<sub>s</sub> values,  $-1.54$  (*tert*-butyl),  $0$  (methyl),  $1.24$  (H),<sup>[22,23]</sup> the equation is barrier =  $(64.1 \pm 3.8) + (17.4 \pm 3.3) E_s$ ,  $n = 3$ ,  $R^2 = 0.965$ .

The IQA analysis of the stationary points (see Supporting Information) of these compounds shows that the interaction azole-boron is positive and the

dominant effect with a positive coulombic contribution is, in most cases, the negative one of the exchange in agreement with the results obtained for the model compounds (Table 4).

## Conclusions

Borotropy occurs through a second minimum with the B atom linked to both N atoms; the TSs are close in energy to the second minimum, except in the case of O<sup>-</sup>. Using literature NMR data, we have calculated for the first time a barrier of  $\Delta G_{183.15}^\ddagger = 39.7 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$  for compound **7**; since this is also our calculated value, this agreement supports our other calculated barriers. These values have been analyzed using different approaches such as LFER (Hammett and Swain & Lupton), buttressing effects, IQA, to provide a quantitative image of borotropy.

## Computational Methods

The geometry of the systems has been optimized with the M06-2X<sup>[24]</sup> functional and the aug-cc-pVDZ<sup>[25]</sup> basis set. Frequency calculations have been carried out to confirm that the systems obtained correspond to energetic minima. These calculations have been carried out with the Gaussian-16 program.<sup>[26]</sup>

The interacting quantum atoms (IQA) methodology,<sup>[27,28]</sup> rooted in the quantum theory of atoms in molecules,<sup>[29-31]</sup> has been used to partition the electronic energy of the systems in their stationary points into the contribution of pyrazole, BR<sub>2</sub> group and the interaction of both using the AIMAll program.<sup>[32]</sup> This methodology allows an exact partition, within the integration error, of the total electronic energy in mono-atomic and di-atomic terms. Adding the terms corresponding to a fragment, its energetic contribution can be calculated. Likewise using the di-

**Table 5.** Relative energies (kJ·mol<sup>-1</sup>) with respect to Min1.

|      | <b>11</b> (unsubstituted) |            |            | <b>12</b> (3,5-diMe) |            |            | <b>7</b> <sup>[a]</sup> (3,5-di- <sup>t</sup> Bu) |            |            | <b>8</b> (3,5-di- <sup>t</sup> Bu, 4Me) |            |            |
|------|---------------------------|------------|------------|----------------------|------------|------------|---|------------|------------|---|------------|------------|
|      | $\Delta E$                | $\Delta H$ | $\Delta G$ | $\Delta E$           | $\Delta H$ | $\Delta G$ | $\Delta E$  | $\Delta H$ | $\Delta G$ | $\Delta E$                              | $\Delta H$ | $\Delta G$ |
| Min2 | 72.9                      | 69.2       | 72.7       | 58.2                 | 53.2       | 51.8       | 27.0  | 21.5       | 24.7       | 14.4                                    | 10.8       | 10.6       |
| TS1  | 75.7                      | 69.7       | 75.6       | 78.9                 | 72.0       | 72.6       | 33.5  | 26.3       | 33.3       | 21.9                                    | 16.9       | 21.1       |
| TS2  | 85.4                      | 79.5       | 88.6       | 64.2                 | 57.2       | 58.8       | 44.8  | 37.1       | 39.7       | 34.6                                    | 29.1       | 32.1       |

<sup>[a]</sup> The calculation with PCM(CHCl<sub>3</sub>) at 183.15 K provide almost identical results.

atomic terms between two fragments, their interaction energy is obtained.

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## Data Availability Statement

The data that support the findings of this study are available in the *Supporting Information* of this article.

## Author Contribution Statement

I. A. and J. E. conceived the idea, I. A. performed the calculations. I. A. and J. E. wrote the manuscript.

## References

- [1] K. Niedenzu, J. W. Dawson, 'Boron-Nitrogen Compounds' in Book Series 'Anorganische und allgemeine Chemie in Einzeldarstellungen', 1st Edition, Springer-Verlag, Berlin, 1965.
- [2] S. Trofimenko, 'Boron-Pyrazole Chemistry. I. Pyrazaboles', *J. Am. Chem. Soc.* **1967**, *89*, 3165–3170.
- [3] C. I. Nieto, D. Sanz, R. M. Claramunt, I. Alkorta, J. Elguero, 'Pyrazaboles and Pyrazolylboranes', *Coord. Chem. Rev.* **2022**, *473*, 214812.
- [4] I. Alkorta, J. Elguero, 'Essential versus accidental isochrony of diastereotopic nuclei in NMR spectroscopy', *Struct. Chem.* **2016**, *27*, 671–679.
- [5] K. Niedenzu, W. Weber, 'Boron-Nitrogen Compounds. LXXXVII. 1,3-Dimethyl-2-(Pyrazol-1'-yl)-1,3,2-Diazaboracyclohexane, A Monomeric Pyrazol-1-ylborane Containing Trigonal Boron', *J. Organomet. Chem.* **1980**, *195*, 25–28.
- [6] W. Weber, K. Niedenzu, 'Boron-Nitrogen Compounds. LXXXIX. New Boron Derivatives of Pyrazole and Imidazole', *J. Organomet. Chem.* **1981**, *205*, 147–156.
- [7] F. Alam, K. Niedenzu, 'Boron-Nitrogen Compounds. XCVI. Studies of the Chemical Behavior of Monomeric Pyrazol-1-ylboranes', *J. Organomet. Chem.* **1982**, *240*, 107–119.
- [8] F. Alam, K. Niedenzu, 'Boron-Nitrogen Compounds. XCVIII. Preparation and Reactions of 2-(Azol-1'-yl)-1,3,2-Diazaboracycloalkanes', *J. Organomet. Chem.* **1983**, *243*, 19–30.
- [9] M. Yalpani, R. Köster, R. Boese, W. A. Brett, 'The First Monomeric Diorgano(pyrazolyl)borane: A Nonclassical Boronium Ion in Solution?', *Angew. Chem. Int. Ed.* **1990**, *29*, 302–304.
- [10] M. Yalpani, R. Boese, R. Köster, 'Monomeric and Dimeric 9-Pyrazolyl-9-borabicyclo[3.3.1]nonanes', *Chem. Ber.* **1990**, *123*, 1275–1283.
- [11] M. Yalpani, R. Boese, R. Köster, 'Addition Complexes of Pyrazolylboranes', *Chem. Ber.* **1990**, *123*, 1285–1291.
- [12] E. Theuergarten, D. Schlüns, J. Grunenber, C. G. Daniliuc, P. G. Jones, M. Tamm, 'Intramolecular Heterolytic Dihydrogen Cleavage by a Bifunctional Frustrated Pyrazolylborane Lewis Pair', *Chem. Commun.* **2010**, *46*, 8561–8563.
- [13] E. Theuergarten, J. Schlösser, D. Schlüns, M. Freytag, C. G. Daniliuc, P. G. Jones, M. Tamm, 'Fixation of Carbon Dioxide and Related Small Molecules by a Bifunctional Frustrated Pyrazolylborane Lewis Pair', *Dalton Trans.* **2012**, *41*, 9101–9110.
- [14] P. von Ragué Schleyer, M. Bühl, 'On the Nature of Pyrazolylborane. An Ab Initio/IGLO/NMR Study', *Angew. Chem. Int. Ed.* **1990**, *29*, 304–306.
- [15] I. Alkorta, J. Elguero, 'Barriers to the Intramolecular N- to N-Transfer of Different Groups in Pyrazoles: Prototropy vs. Elementotropy', *Heteroat. Chem.* **2005**, *16*, 628–636.
- [16] H. Eyring, 'The Activated Complex in Chemical Reactions', *J. Chem. Phys.* **1935**, *3*, 107–115.
- [17] J. W. Emsley, J. Feeny, L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', Pergamon, Oxford, 1965, Chapt. 9.
- [18] J. Sandström, 'Dynamic NMR Spectroscopy', Academic Press, London, 1982.
- [19] C. G. Swain, E. C. Lupton, 'Field and Resonance Components of Substituent Effects', *J. Am. Chem. Soc.* **1968**, *90*, 4328–4337.
- [20] C. Hansch, A. Leo, R. W. Taft, 'A Survey of Hammett Substituent Constants and Resonance and Field Parameters', *Chem. Rev.* **1991**, *91*, 165–195.
- [21] J. Elguero, E. Gonzalez, R. Jacquier, 'Recherches dans la série des azoles. XXXV. Relations basicité-structure dans la série du pyrazole', *Bull. Soc. Chim. Fr.* **1968**, 5009–5017.
- [22] R. W. Taft, 'Linear Free Energy Relationships from Rates of Esterification and Hydrolysis of Aliphatic and Ortho-Substituted Benzoate Esters', *J. Am. Chem. Soc.* **1952**, *74*, 2729–2732.
- [23] M. Charton, 'The Nature of the ortho Effect. II. Composition of the Taft Steric Parameters', *J. Am. Chem. Soc.* **1969**, *91*, 615–618.
- [24] Y. Zhao, D. G. Truhlar, 'The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals', *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- [25] R. A. Kendall, T. H. Dunning, R. J. Harrison, 'Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions', *J. Chem. Phys.* **1992**, *96*, 6796–6806.
- [26] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N.



- Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- [27] M. A. Blanco, Á. Martín Pendás, E. Francisco, 'Interacting Quantum Atoms: A Correlated Energy Decomposition Scheme Based on the Quantum Theory of Atoms in Molecules', *J. Chem. Theory Comput.* **2005**, 1, 1096–1109.
- [28] J. M. Guevara-Vela, E. Francisco, T. Rocha-Rinza, Á. Martín Pendás, 'Interacting Quantum Atoms – A Review', *Molecules* **2020**, 25, 4028.
- [29] R. F. W. Bader, 'Atoms in Molecules: A Quantum Theory, The International Series of Monographs of Chemistry', Eds. J. Halpen, M. L. H. Green, Clarendon Press, Oxford, 1990.
- [30] P. L. A. Popelier, 'Atoms in Molecules: An Introduction', Prentice Hall, London, 2000.
- [31] Á. Martín Pendás, E. Francisco, D. Suarez, A. Costales, N. Diaz, J. Munarriz, T. Rocha-Rinza, J. M. Guevara-Vela, 'Atoms in Molecules in Real Space: a Fertile Field for Chemical Bonding', *Phys. Chem. Chem. Phys.* **2023**, 25, 10231–10262.
- [32] T. A. Keith, AIMAll (Version 19.10.12), TK Gristmill Software, Overland Park KS, USA, 2019.

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