On structure and stability of pyrimidine ylidenes and their homologues

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Structure of six-membered cyclic aminoiminocarbenes (pyrimidine ylidenes) and their group 13–15 homologues was studied by quantum chemical calculations. Isodesmic and dimerization reaction energies, NICS values, frontier molecular orbitals, as well as NBO, Bader’s “atoms in molecules” and Laplacian bond order (LBO) analyses were employed for estimating relative stability of the studied carbenes (carbene homologues). They show a low degree of aromatic delocalization and considerable variation of electronic structure depending on the nature of divalent element. The predicted stability for the series of interest is lower than that for the corresponding five-membered Arduengo carbene structures, but comparable with Alder’s bis(dimethylamino)carbene.

1. Introduction

Since the discovery of stable carbenes by Bertrand [11] and Arduengo [2] these inquisitive species have gained a wide scope of applications as organocatalysts [3,4], ligands complexing with transition metals [3,5], and molecules stabilizing low-valent main-group elements [6,7]. A close examination of the field of N-heterocyclic carbenes allows discovering that main efforts of researchers have been focused on the five-membered cyclic carbenes. Although diverse “unconventional” types of N-heterocyclic carbenes are investigated [8], only few species with other cycle sizes have been studied [9,10]. In particular, few six-membered carbenes and their homologues synthesized to date are either saturated species [11,12] or unsaturated ones, namely pyridyldienes [8,13–15] and those, where the carbene ring is annealed with benzenic moiety [16]. As the rule, six-membered cyclic carbenes (SMCC) are less stable than the five-membered congeners, but a variety of transition metal complexes based on such carbenes are known [17–19].

A number of publications have been devoted to theoretical investigations of SMCC and their homologues. A systematic study of SMCC stabilized by phosphorus has been carried out by Nyulászi et al. [20]. One can also find several computational studies of SMCC in comparison with the group 13 and 14 homologues [21–25] and substituted (annealed) carbenes of this type [26–29]. However, to the best of our knowledge, almost all published works concerning nitrogen-containing carbenes and their homologues deal with dianimocarbenes of type I, whereas other interesting species, amino-imino carbenes II have somehow been overlooked by researchers. We have found only two examples of imino-substituted carbenes: for 1,3-azaphosphinin-2-ylidene (III) the ground state structures were determined by theoretical investigations [20]. While a number of diverse N-heterocyclic carbenes with reduced heteroatom stabilization, i.e. abnormal and remote carbenes, were synthesized to date [8,9], the amino-imino carbenes of type II are still absent in the large carbene family. It prompted us to fill this gap studying a new class of carbenes IV by means of quantum chemical calculations.

\[
\begin{align*}
\text{I} & : R=Me, R^* = H; R, R^*= -CH=CH-CH=CH- \\
\text{II} & : R^* = H, NR^*_2 \\
\text{III} & : R=Me, R^* = H; R, R^*= -CH=CH-CH=CH- \\
\text{IV} & : R=H, NR^*_2
\end{align*}
\]
The high stability of heterocyclic carbenes in the singlet ground state is traditionally referred to three main factors: (a) a presence of π-donor and σ-acceptor atoms directly attached to the carbene carbon atom (C\textsuperscript{arb}); (b) an aromaticity inherent to the carbene heterocycle and (c) a steric protection of the methylene center by bulky groups [30,31]. Structures IV generally meet criteria a and b. In particular, it has previously been shown [32,33] that in some cases the X = N— imino-function (X = C, P(V)) is even more efficient π-donor than the amino-group. The C=N double bond in IV should be strongly polarized towards nitrogen and the corresponding electron pair possesses a pure π-character. Additionally, (a) the amino group in IV should additionally reinforce π-electron density on C\textsuperscript{arb} by the push-pull mechanism donating into the formally empty p-orbital on the divalent X atom; (b) the resulting π-system, similarly to the five-membered Arduengo congeners, still meets Hückel’s rule (6π-electron system). However, II and IV are slightly at a disadvantage from the standpoint of steric shielding, which should be ensured here by only one substituent R. It has been noted previously that by geometry optimization of structures of the parent carbenes, N-H proton often migrates to the carbene center [34]. Therefore, for the current study methyl-substituted species were chosen as model compounds.

Herein, carbene 1c and its homologues 1a,b,d-f, as well as 4-amino-substituted model species 2a-f are studied computationally (DFT, MP2 and CCSD) with the aim to predict their thermodynamic stability within the series of the existing carbenes and outlooks of their possible synthetic preparation.

2. Details of calculations

All the structures were fully optimized without symmetry constraints (unless otherwise stated) using the TURBOMOLE program package [35,36] (version 6.4). The RI-SCS-MP2/cc-pVTZ approximation level [37,38] was used for geometry optimization of singlet state structures of compounds 1a-f, 2a-f. Vibration frequencies calculated numerically or analytically confirmed that the optimized structures were true minima on the potential energy surfaces. Corresponding energy values were used for calculations of the Gibbs energy magnitudes for isodesmic and dimerization reactions. To make sure that the selected approximation level was the appropriate choice for the systems of interest, the single point energy for isodesmic reactions for carbene 2c (Schemes 2 and 3) was calculated at the coupled-cluster RI-CCSD and RI-CCSD(T) [39] approximation levels employing cc-pVDZ and cc-pVTZ basis sets [38] and using the structures optimized at the RI-SCS-MP2/cc-pVTZ level of theory (see the Supplementary material (SM), Table S3 for more detail). For determination of singlet-triplet energy gaps the structures of singlet and triplet ground states of 1a-f, 2a-f were optimized at the RI-BP86/TZVP approximation level [40,41]. Cartesian coordinates for all optimized structures are collected in the SM.

Charge density matrices based on single-point energy calculations, NICS(0) and NICS(1) values [42] were derived using the GAUSSIAN-03 program set [43] within the DFT approximation. The BP86 functional [40,41] was employed in combination with the TZVP basis sets [44]. The NBO charges [45–47] were determined for the structures optimized as local minima in energy as well as for those restricted within C\textsubscript{2} symmetry using the Gaussian NBO module (ver. 3.1) implemented into the GAUSSIAN-03 [48]. Bader’s “atoms in molecules” [49] and Laplacian bond order (LBO) analyses were performed by means of the Multiwfnn program [50]. Molecular orbitals were derived using the gOpenMol program [51]. Gadget program [52] was used for structure rendering.

3. Results and discussion

3.1. Structure

Similarly to Arduengo-type carbenes, the singlet ground state seems to be preferable for 1a-f and 2a-f as compared to the triplet state; the corresponding structures involve planar cyclic cores. Valence angles at X (where X represents a divalent atom) vary in a range 94 to 120\degree. N–X bond lengths depend on the X nature and vary from 1.29 to 1.97 Å. The NNX' bond angle decreases and N–X bond distance elongates while going from right to left and from up to down in the periodic table. Noteworthy, the structural parameters of unsubstituted (1) and amino-substituted species (2) differ only slightly.

It is of interest to compare the structure of carbene 1c with those calculated for the known six- and five-membered diamincarbenes. The calculated N–C=N bond angle in 1c (113.6\degree) is wider compared to the corresponding values in five-membered carbenes (101 ... 102\degree) and similar to those found for 1 (114 ... 116\degree) [9,28,29,53,54]. The =N=C\textsuperscript{arb} bond (1.381 Å) is shorter than the >N–C=\carb one (1.389 Å). It supports the suggestion that, similarly to the amino-nitrogens in 1, the imino-function is also an effective π-donor into the formally vacant p-orbital of C\textsuperscript{arb}.

3.2. Singlet-triplet gaps and frontier orbitals

Energy differences between singlet and triplet ground states (\Delta E\textsubscript{ST}) to some extent correlate with stability of carbenes and their homologues [55], albeit this relation is not straightforward [56]. \Delta E\textsubscript{ST} values calculated for compounds 1a-f, 2a-f at the RI-BP86/TZVP level are given in Table 1. With the only exception of 1a and 2a, the \Delta E\textsubscript{ST} values are large; hence no sizeable spin contamination should be expected as a result of applying the single-determinant DFT approach to calculations of the corresponding singlet and triplet ground states.

Energies of the frontier molecular orbitals (FMOs) for structures 1a-f are listed in Fig. 1 (see also Table S4 for more detail), and the shapes of frontier orbitals for 1a-f, 2a-f are shown in Figs. 2,3. Derivatives of group 15 carry the total positive charge and this leads to lower orbital energy values, whereas for the anionic B and Al derivatives the opposite is observed. A close examination of FMOs for the studied model structures shows that the character of the frontier orbitals differs within the series. The highest
occupied molecular orbitals (HOMO) in the series 1a-f are of \( \sigma \) type and represent X’s lone pairs (LPs) with a varying portion of N’s LP. Further, the considered series of compounds can be classified into two groups: the carbenes with anti-bonding orbitals mainly located on the N\(^{2-}\) moiety (1a-d) and the other ones, in which LUMO is mainly the empty p-orbital on X. The lone pair of the silicon atom significantly contributes to the HOMO-1 providing for silylene 1d the “nitrenium cation” bonding type of structure. Another important difference is that for phosphonium cation 2f the HOMO is the \( \pi \)-type MO.

It has been shown previously that singlet-triplet splitting for saturated six-membered carbene-like structures generally increases in going downwards in the periodic table [22,57]. While \( \Delta E_{ST} \) values for compounds 1a-d and 2a-d meet this trend, this is not the case for the amino-substituted group 15 homologues: the \( \Delta E_{ST} \) values for 1e and 1f are very close, and the singlet-triplet gap for 2e (X = N\(^{2-}\)) is even larger than that for 2f (X = P\(^{2-}\)). This can be referred to the high-lying \( \pi \)-type HOMO of 2f involving p-orbitals at nitrogen and carbon atoms in the N\(^{-}\)=C\(^{2-}\) moiety (Fig. 3). The high HOMO energy decreases the \( \Delta E_{ST} \) magnitude for 2f. The lowest unoccupied molecular orbital (LUMO) of 2f is mainly the empty p-orbital on the phosphorus atom. Therefore, for all model structures, except 2f, the highest \( \pi \)-type occupied MO lies deeper and the triplet state arises from the singlet structure via a promotion of one electron from the \( \sigma \)-type HOMO to the \( \pi \)-type LUMO.

### Table 1
Calculated (RI-BP86/TZVP) singlet-triplet energy gaps (\( \Delta E_{ST} \)) for structures 1a-f and 2a-f.

<table>
<thead>
<tr>
<th>Structure</th>
<th>X</th>
<th>( \Delta E_{ST} )</th>
<th>Structure</th>
<th>X</th>
<th>( \Delta E_{ST} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>B(^{2-})</td>
<td>1.6</td>
<td>1c</td>
<td>C</td>
<td>20.1</td>
</tr>
<tr>
<td>1b</td>
<td>Al(^{3-})</td>
<td>37.5</td>
<td>1d</td>
<td>Si</td>
<td>55.6</td>
</tr>
<tr>
<td>2a</td>
<td>B(^{2-})</td>
<td>6.2</td>
<td>2c</td>
<td>C</td>
<td>32.7</td>
</tr>
<tr>
<td>2b</td>
<td>Al(^{3-})</td>
<td>40.7</td>
<td>2d</td>
<td>Si</td>
<td>61.4</td>
</tr>
<tr>
<td>1e</td>
<td>N(^{2-})</td>
<td>49.1</td>
<td>1f</td>
<td>P(^{2-})</td>
<td>52.8</td>
</tr>
<tr>
<td>2e</td>
<td>N(^{2-})</td>
<td>57.5</td>
<td>2f</td>
<td>P(^{2-})</td>
<td>51.5</td>
</tr>
</tbody>
</table>

Fig. 1. Energies of frontier molecular orbitals for 1a-f.

Fig. 2. Molecular orbital rendering for compounds 1a-f.
3.3. Charge distribution

The results of the Laplacian bond order (LBO) analysis [58] provided similar values for all derivatives 2a-f (see the SM details). The bond order variation in NCCCN moiety is approx. 0.5, it evidences low aromaticity for the series of interest. C5-C6 bond possesses a substantial double-bond character (LBO 1.5 ... 1.6). Calculated bond ellipticity values corroborate this conclusion (see the SM). Analysis of LBO shows that the bond order of the >N1A bond in 2a-f is generally lower than that for the @N3A one. For example, for carbene 2c (X=C) the LBO magnitudes for the >N1A-C2 and @N3A-C2 bonds are 0.79 and of 1.04. It demonstrates that imino-nitrogen provides more effective donation to the carbenic atom than the amino-nitrogen atom. LBOs of the H2N-C4 bonds within the series 2a-f are low (0.72 ... 1.23), which indicates a rather weak donor effect from the amino-group attached to the C@N double bond. The structure is better represented by the Lewis structures A-A0, than with conjugated species B or C.

This conclusion is corroborated by NICS values calculated for compounds 1a-f, 2a-f (Table 2). They are significantly less negative than the NICS(0) magnitudes (B3LYP/6-31+G*) previously reported for five-membered imidazole ylidene and its silicon and germainium derivatives (ca. –10 ppm) [59], evidencing lower aromaticity inherent to the series studied here. For X atoms from the same period of the periodic table, the calculated NICS values are slightly more negative for the higher group elements.

Contour maps of the Laplacian of electron density for 2a-f (Fig. 4) reveal pronounced LP charge concentration for all studied species. It is most distinct for the anionic group 13 carbene homologues and less inherent to cationic species 2e and 2f.

Since the equilibrium geometries for compounds 1a-f are almost perfectly planar in the single ground state, only negligible changes are observed by going to the C₈ symmetrical structures. NBO charges derived for optimized C₈ symmetrical structures of 1a-f, 2a-f are suitable for separating σ- and π-charges (see the SM for more detail). The total charge on the divalent atom increases on going from left to right within the row of the periodic table, especially for the B – N series. Among other atoms, N1 and N3 demonstrate the biggest charge alteration. Surprisingly, flattening the amino-group in compounds 2a-f does not noticeably influence the total atomic charges. The replacement of the amino-group by hydrogen has significant effect only on the adjacent C4 ring atom; charges on other atoms change only slightly. This is corroborated by the NBO analysis of π-electron population (Table 3, see also SM): by the substitution of the amino-group by hydrogen, the highest occupancy changes do not exceed 0.1 e; the imino nitrogen (N3) indicates the largest alteration. The nitrogen atom of the attached amino-group (N') loses 0.2–0.4 e of its π-population, but it is not accompanied by a visible increase of π-charge on the X atom compared to the corresponding unsubstituted congener 1. Thus, the contribution of the direct polar conjugation (structure B) in the structures 2a-f is negligible even for the positively charged species 2e,f. These facts along with the data on frontier molecular orbitals clearly show that the π-systems of studied compounds are split into the weakly interacting N-A-X: A-N and C-A-C fragments.

3.4. Relative stability

The relative stability of the studied series 1a-f and 2a-f will be analyzed using isodesmic reactions (Schemes 1–3). The corresponding calculated Gibbs free energy values (ΔG¹→³) are given in Table 4. First we compare the studied series with the corre-
Fig. 4. Contour maps of the Laplacian of the calculated (RI-BP86/TZVP) electron density for 2a-f, projected onto the plane of the six-membered ring. Positive and negative values are marked by dashed and solid lines, respectively. The bond critical points are represented as blue circles; ring critical points are marked by orange circles; calculated atomic boundaries, as determined by the zero-flux surface condition, are shown by solid blue lines.

Table 2
NICS values (RI-BP86/TZVP) for structures 1a-f and 2a-f.

<table>
<thead>
<tr>
<th>Structure</th>
<th>X</th>
<th>NICS(0)</th>
<th>NICS(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>B</td>
<td>-0.6</td>
<td>-4.5</td>
</tr>
<tr>
<td>1b</td>
<td>Al</td>
<td>0.1</td>
<td>-2.7</td>
</tr>
<tr>
<td>2a</td>
<td>B</td>
<td>-2.2</td>
<td>-4.9</td>
</tr>
<tr>
<td>2b</td>
<td>Al</td>
<td>-0.3</td>
<td>-2.1</td>
</tr>
<tr>
<td>1c</td>
<td>C</td>
<td>-4.0</td>
<td>-8.4</td>
</tr>
<tr>
<td>1d</td>
<td>Si</td>
<td>-2.3</td>
<td>-5.6</td>
</tr>
<tr>
<td>2c</td>
<td>C</td>
<td>-2.7</td>
<td>-6.2</td>
</tr>
<tr>
<td>2d</td>
<td>Si</td>
<td>-1.8</td>
<td>-3.9</td>
</tr>
<tr>
<td>1e</td>
<td>N</td>
<td>-5.2</td>
<td>-9.7</td>
</tr>
<tr>
<td>1f</td>
<td>P</td>
<td>-4.8</td>
<td>-8.0</td>
</tr>
<tr>
<td>2e</td>
<td>N</td>
<td>-2.3</td>
<td>-6.0</td>
</tr>
<tr>
<td>2f</td>
<td>P</td>
<td>-2.6</td>
<td>-4.9</td>
</tr>
</tbody>
</table>

Table 3
Selected NBO π-orbital occupancies for C₃ symmetrical structures of 1a-f and 2a-f.

<table>
<thead>
<tr>
<th>Atom</th>
<th>1a</th>
<th>1b</th>
<th>1c</th>
<th>1d</th>
<th>1e</th>
<th>1f</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>1.514</td>
<td>1.556</td>
<td>1.451</td>
<td>1.541</td>
<td>1.354</td>
<td>1.465</td>
</tr>
<tr>
<td>X2</td>
<td>0.254</td>
<td>0.131</td>
<td>0.565</td>
<td>0.336</td>
<td>1.034</td>
<td>0.704</td>
</tr>
<tr>
<td>N3</td>
<td>1.166</td>
<td>1.201</td>
<td>1.152</td>
<td>1.254</td>
<td>1.052</td>
<td>1.243</td>
</tr>
<tr>
<td>N₁</td>
<td>1.536</td>
<td>1.575</td>
<td>1.498</td>
<td>1.580</td>
<td>1.430</td>
<td>1.538</td>
</tr>
<tr>
<td>X₂</td>
<td>0.262</td>
<td>0.135</td>
<td>0.582</td>
<td>0.347</td>
<td>1.036</td>
<td>0.702</td>
</tr>
<tr>
<td>N₃</td>
<td>1.263</td>
<td>1.311</td>
<td>1.257</td>
<td>1.360</td>
<td>1.140</td>
<td>1.338</td>
</tr>
<tr>
<td>N’</td>
<td>1.831</td>
<td>1.830</td>
<td>1.725</td>
<td>1.740</td>
<td>1.614</td>
<td>1.619</td>
</tr>
</tbody>
</table>
sponding five-membered Arduengo-type counterparts (Scheme 1).

The carbene model structures 1a-f, 2a-f are clearly less stable than the corresponding five-membered species 6a-f (strongly negative magnitudes of \( \Delta G^1 \) are found). The largest differences in stability are predicted for carbenes 1c, 2c and nitrenium cations 1e, 2e; the smallest ones are expected for anions 1a,b, 2a,b, which is in line with the general trend of stability of carbene homologues of group 13 and 14 elements [60]. The lesser stability of 1 and 2 can be referred to the lower degree of aromaticity in these molecules compared to five-membered species 6a-f. However, it does not explain negative \( \Delta G^2 \) values inherent to the isodesmic reaction of 1c,d and 2c,d with six-membered saturated diamino-substituted carbenes (silylenes) 8c,d (Scheme 2), though \( \Delta G^2 \) values are significantly smaller than the corresponding \( \Delta G^1 \) magnitudes (Table 4). Thus, our calculations evidence that the donor effect of the imino-function, even reinforced by the attached

\[
\begin{align*}
1a-f & \quad + & 3a-f & \quad \rightarrow & 4a-f & \quad + & 5a-f & \quad + & \Delta G^1 \\
\text{a: } X=\text{B}^+, n=1 & \quad \text{b: } X=\text{Al}^+, n=1 & \quad \text{c: } X=\text{C}, n=2 & \quad \text{d: } X=\text{Si}, n=2 & \quad \text{e: } X=\text{N}^+, n=1 & \quad \text{f: } X=\text{P}^+, n=1 \\
1,4: R=\text{H}; 2,5: R=\text{NH}_2 
\end{align*}
\]

**Scheme 1.** Isodesmic reaction for estimating stability of 1a-f and 2a-f relative to five-membered species 6a-f.

\[
\begin{align*}
1c,d & \quad + & 7c,d & \quad \rightarrow & 4c,d & \quad + & 5c,d & \quad + & \Delta G^2 \\
1,4: R=\text{H}; 2,5: R=\text{NH}_2 & \quad \text{c: } X=\text{C} & \quad \text{d: } X=\text{Si} 
\end{align*}
\]

**Scheme 2.** Isodesmic reaction for comparing stability of 1c,d, 2c,d with corresponding six-membered saturated congeners 8c,d.

\[
\begin{align*}
1c,d & \quad + & 9 & \quad \rightarrow & 4c,d & \quad + & 10 & \quad + & \Delta G^3 \\
1,4: R=\text{H}; 2,5: R=\text{NH}_2 & \quad \text{c: } X=\text{C} & \quad \text{d: } X=\text{Si} 
\end{align*}
\]

**Scheme 3.** Isodesmic reaction for comparing stability of carbenes 1c, 2c and silylenes 1d, 2d with Alder’s bis(dimethylamino)carbene 10.

<table>
<thead>
<tr>
<th>Item</th>
<th>X</th>
<th>( \Delta G^1 )</th>
<th>Item</th>
<th>X</th>
<th>( \Delta G^1 )</th>
<th>( \Delta G^2 )</th>
<th>( \Delta G^3 )</th>
<th>Item</th>
<th>X</th>
<th>( \Delta G^1 )</th>
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<tr>
<td>1a</td>
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<td>1c</td>
<td>C</td>
<td>-30.8</td>
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<tr>
<td>1b</td>
<td>Al</td>
<td>-2.0</td>
<td>1d</td>
<td>Si</td>
<td>-15.0</td>
<td>-5.5</td>
<td>16.3</td>
<td>1f</td>
<td>P</td>
<td>-29.1</td>
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<td>2a</td>
<td>B</td>
<td>-8.1</td>
<td>2c</td>
<td>C</td>
<td>-28.7</td>
<td>-8.0 (-6.6)</td>
<td>0.5 (0.1)</td>
<td>2e</td>
<td>N</td>
<td>-26.1</td>
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<tr>
<td>2b</td>
<td>Al</td>
<td>-5.0</td>
<td>2d</td>
<td>Si</td>
<td>-15.7</td>
<td>-6.2</td>
<td>15.6</td>
<td>2f</td>
<td>P</td>
<td>-17.7</td>
</tr>
</tbody>
</table>

* \( \Delta G \) values derived at the CCSD(T)/[cc-pVTZ//RI-SCS-MP2/cc-pVTZ level of theory.

Table 4

Gibbs free energies (\( \Delta G \), kcal/mol, RI-SCS-MP2/cc-pVTZ) for isodesmic reactions (Schemes 1–3).
amino-group, is not as effective as that provided by cyclic ammino-nitrogen. And albeit amino-substituted compounds 2a-f are more stable than the corresponding unsubstituted species (1a-f), the predicted quantitative effect is rather modest. We suggest that the favorable polarization of π-system towards the formally vacant p-orbital at the carbenic carbon atom is partially compensated by a corresponding loss of ring aromaticity. This is supported by the more negative absolute NICS values predicted for series 1a-f as compared to those found for 2a-f (Table 2).

At first sight, such a result makes structures 1 and 2 unattractive for experimentalists. However, let us to compare stability of carbenes 1c, 2c and silylenes 1d, 2d with the known acyclic Alder’s carbene 10 (Scheme 3, Table 4, ΔG°). Accordingly to the calculation results, carbenes 1c and 2c are almost as stable as 10, whereas the ΔG° values calculated for silylenes 1d, 2d promise definitely higher stability for the latter compared to daminocarbene 10. These results evidence that the studied species can generally be synthesized, or at least used as ligands in metal complexes. In addition, substitution of methyl and amino-groups in the studied carbene-like structures by bulky moieties can significantly enhance their stability (some examples of such calculated structures are presented in the SM).

3.5. Dimerization reaction

One of the most known aspects of chemistry of carbenes is their disposition to dimerize forming ethenes [61]. Stable dimers of saturated six-membered daminocarbenes have been previously characterized [62,63]. We calculated free Gibbs energy values for the dimerization reaction for carbenes 1c, 2c and their homologues 1a,b,d-f, 2a,b,d-f (Scheme 4, Table 5). According to the calculations, E-dimers are more stable than their Z-stereoisomers by ca. 2–12 kcal/mol (with only exception of 2a, for which cis-dimer is 0.8 kcal/mol more stable). The reaction energies in Table 5 refer to trans-dimers. Values for Z-11 and Z-12 can be found in the SM, Table S5. Carbene dimers possess bent geometry; six-membered rings are turned relatively to each other (by ca. 10°) because of steric repulsion between methyl groups and ammino-nitrogen. On the contrary, flat structures with distortion from planarity less than 2° are inherent to charged dimers 11a,e, 12a,e. Disilenes 11d, 12d and dialanes 11b, 12b possess the typical “trans-bent” geometry [64], the cycles in disilenes are virtually parallel while in dialanes six-membered rings are turned on ca. 120° relatively to each other and their plains are inclined (Fig. 5). The Si=Si bond lengths in 11d, 12d are approximately 2.5 Å, the Al=Al distances in 1lb, 12b are ca. 2.2 Å. Authors were not able to localize the phosphorus-containing dimers 11f, 12f: they dissociate into 1f and 2f, respectively, during geometry optimization.

As expected, the disposition to the dimerization rapidly decreases by moving downwards in the periodic table. Carbenes 1c, 2c are mostly inclined to dimerize, their Al-, N- and P-containing homologues 1b,e,f, 2b,e,f have the least disposition, while silylenes 1d, 2d and anions 1a, 2a possess intermediate reactivity. These facts emphasize necessity of bulky substituents to provide kinetic stability to structures 1c, 2c. Nevertheless, the unsubstituted compounds are significantly more inclined to dimerization than the amino-substituted ones (by ca. 7–25 kcal/mol).

Table 5

<table>
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<th>Structure</th>
<th>X</th>
<th>ΔEd</th>
<th>ΔGd</th>
<th>Structure</th>
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<th>Structure</th>
<th>X</th>
<th>ΔEd</th>
<th>ΔGd</th>
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<td>C</td>
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<td>N</td>
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<td>52.7</td>
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<td>P</td>
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<td>C</td>
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<tr>
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<td>P</td>
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<td>–</td>
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</table>

Fig. 5. Optimized structures (RI-SCS-MP2/cc-pVTZ) of dimers 11b, 12d.
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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2017.01.024.

References


