Erratum to: Naphthologs of overcrowded bistricyclic aromatic enes: (*E*)-bisbenzo[*a*]fluorenylidene

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An important feature of the article noted above is the comparison between the two angularly benzo[*a*]annelated bistricyclic aromatic enes (BAEs) *E*-**6** and *Z*-**6** and the comparison between these diastereomers and their constitutional isomers, the linearly benzo[*b*]annelated BAEs *E*-**7** and *Z*-**7**. All these BAEs adopt twisted conformations in their ground states and are overcrowded at their *ffjord* regions. However, the degree of overcrowding in *E*-**6** and *Z*-**6** is enhanced, due to the angular benzoannulation at the *ffjord* region.

In the present Erratum, the following corrections of the original text are noted:

1. In the *Diastereoselectivity* paragraph, the correct comparison is made between the B3LYP/6-311G(d,p) calculated diastereomerization barrier for *E*-**6** → *Z*-**6** ($\Delta G_{298} = 11.4$ kcal/mol), and the calculated value

for the *Z*-**7** ⇌ *E*-**7** diastereomerization ($\Delta G_{298} = 17.2$ kcal/mol).

2. In the **Abstract** and in the *Diastereoselectivity* paragraph, the correct calculated value for the diastereomerization barrier for *E*-**6** → *Z*-**6** is $\Delta G_{298} = 11.4$ kcal/mol.
3. In the *Diastereoselectivity* paragraph, a comparison with the *E,Z*-diastereomerization barrier of 2,2'-dimethyl-bifluorenylidene (24.9 kcal/mol) was added.

Abstract

(*E*)-11*H*-bisbenzo[*a*]fluorenylidene (*E*-**6**) was synthesized by Barton's double extrusion diazo-thione coupling method from 11*H*-benzo[*a*]fluoren-11-thione (**11**) and 11-diazo-11*H*-benzo[*a*]fluorene (**13**). The reaction is probably thermodynamically controlled; in the event that the less stable *Z*-**6** is also formed, it would rapidly undergo *Z* → *E* diastereomerization to give *E*-**6**. The B3LYP/6-311G(d,p) calculated diastereomerization barrier for *E*-**6** → *Z*-**6** is $\Delta G_{298} = 47.8$ kJ/mol (11.4 kcal/mol), and the calculated equilibrium constant K_{eq} (*E*-**6** ⇌ *Z*-**6**) = 92:8 (at 298 K) is indicative of a marked diastereoselectivity of the reaction leading to *E*-**6**. The structure of *E*-**6** was established by ¹H-NMR and ¹³C-NMR spectroscopy and by X-ray analysis. **PAE E-6** crystallizes in the monoclinic space group *C2/c*. The unit cell of the crystal structure *E*-**6** contains eight molecules, arranged as four pairs of enantiomers. **PAE E-6** adopts a twisted conformation with the pure twist of the central C¹¹=C^{11'} bond $\omega = 39^\circ$. The dihedral angle ν in *E*-**6** is 60.6°, which is significantly higher than the respective dihedral angle in **PAEs Z-6**, **2**, *E*-**7**, *Z*-**7**, **14** and **15**. The large *syn*-pyramidalization angles at C¹¹ and C^{11'} ($\chi = 12.6^\circ$ and 14.8°) of *E*-**6**

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Fig. 2 Polycyclic aromatic enes (PAEs) **6** and **7**

indicates the enhanced strain in the *ffjord* regions of the molecule. The enhanced twist is primarily attributed to the double benzo[*a*]annulation of the bifuorenylidene moiety at the *ffjord* regions. The B3LYP/6-311G(d,p) calculated structure of **E-6** is in a very good agreement with the experimental X-ray structure. **PAE E-6** adopts a twisted conformation in solution, with the downfield chemical shift of $H^1/H^{1'}$ (8.31 ppm); $H^{10}/H^{10'}$ ($\delta = 7.20$ ppm) and $H^9/H^{9'}$ ($\delta = 6.86$ ppm) in **E-6** are positioned above the planes of the opposing naphthalene rings. **PAEs E-6** and **Z-6** are significantly lower in energy than their corresponding benzo[*b*]annulated isomers **E-7** and **Z-7**.

Diastereoselectivity

The formation of **E-6** in the synthesis without any indication of the formation of **Z-6** may be rationalized by assuming that the reaction is kinetically controlled. A more plausible explanation, however, is that the reaction is thermodynamically controlled and in the event that the less

stable **Z-6** is also formed, it rapidly undergoes $Z \rightleftharpoons E$ diastereomerization via an orthogonally twisted diradical transition state, to give the more stable **E-6**. This scenario is based on the plausible assumption that the energy barrier for the $Z \rightleftharpoons E$ diastereomerization is low. This assumption is supported by the reported fast **Z-7** $\rightleftharpoons$ **E-7** diastereomerization at room temperature ($\Delta G_{298} = 23.5$ kcal/mol) [44], as compared with *E,Z*-diastereomerization barrier of 2,2'-dimethyl-bifuorenylidene, $\Delta G_{443} = 104$ kJ/mol (24.9 kcal/mol) [23]. The energy barrier for **E-6** $\rightarrow$ **Z-6** is expected to be even lower, due to the enhanced destabilization of the ground states of the angularly benzo[*a*]annulated **E-6** and **Z-6**, relative to the linearly benzo[*b*]annulated **E-7** and **Z-7**. Bearing in mind that the 11*H*-benzo[*a*]fluorenyl radical, is 2.9 kJ/mol more stable than the 11*H*-benzo[*b*]fluorenyl radical, the relative stabilization of the diradical transition states (orthogonal benzo[*a*]fluorenyl radicals vs. orthogonal benzo[*b*]fluorenyl radicals) of the two diastereomerization processes is expected to be a minor factor. Indeed, the B3LYP/6-311G(d,p) calculated diastereomerization barrier for **E-6** $\rightarrow$ **Z-6** is $\Delta G_{298} = 47.8$ kJ/mol (11.4 kcal/mol), which is notably lower than the experimental barrier for the **Z-7** $\rightleftharpoons$ **E-7** diastereomerization, and the calculated barrier 17.2 kcal/mol. However, these calculated barriers should be taken with a grain of salt in view of the diradical nature of the corresponding transition states. The calculated equilibrium constant K_{eq} (**E-6** $\rightleftharpoons$ **Z-6**) = 92:8 is indicative of a marked diastereoselectivity of the reaction leading to **E-6**, but does not rule out the formation of **Z-6** as a minor product. However, the 1H -NMR spectrum of the crude product of the reaction indicates that the presence of **Z-6** as an impurity could be no more than (NMT) 2%, if any.

References

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