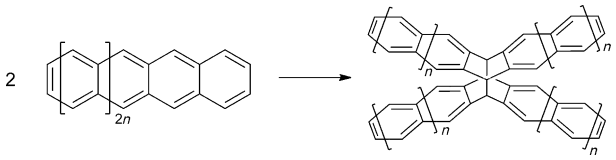
Conformational Analysis

DOI: 10.1002/anie.201304674

Dispersion-Driven Conformational Isomerism in σ-Bonded Dimers of Larger Acenes**

*Stephan Ehrlich, Holger F. Bettinger, and Stefan Grimme**

The experimental and theoretical study of acenes has seen much interest in the past years, which can in part be attributed to their possible applicability as organic semiconductors.[1] The formation of covalently bound dimers (Scheme 1) is



Scheme 1. Prototypical dimerization reaction of larger acenes with an odd number of benzene rings.

known to be a problem in those applications, and it has been investigated in some detail.[2–4] As the larger acenes have become experimentally accessible,[5] studying their properties seems worthwhile. From a theoretical point of view, the butterfly structure of the dimers with four intramolecularly π-stacked acene sub-systems makes them very interesting and challenging molecules.

It was recently reported that a *tert*-butyl substituted hexaphenylethane derivative displays a rare case of bond length isomerism, which is mainly caused by attractive London dispersion interactions between the bulky substituents.[6] Herein, we investigate possible extensions of this concept of dispersion-driven isomerism. It is shown that covalently bonded dimers of larger acenes can display an unusual conformational isomerism that is driven by strong intramolecular dispersion interactions between the π-stacked acene subunits. The two postulated structures are the common open form and a bent conformer with a π-stacked alignment of bent acene subunits (Figure 1). The stacked form was already found by Zade et al. in their theoretical investigation of the dimerization reaction of heptacene, and was described as an intermediate.[2] The acene dimers

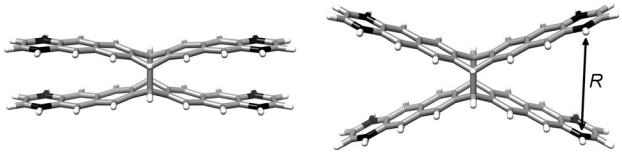


Figure 1. Stacked (left) and open (right) forms that were used for the construction of the potential energy curve of the heptacene dimer and analogously for the nonacene dimer. The atoms marked in black were kept fixed while relaxing all remaining degrees of freedom. The arrow indicates the distance variable (reaction coordinate) used throughout.

considered here are certainly not the ideal molecules for making functional systems (such as switches, parts of molecular motors) but should merely serve as model compounds for the basic process of dispersion-driven isomerism. It can be expected that similar double-minimum-shaped potential energy curves (PECs) to those reported here are inherent in other (supramolecular) π-systems.

With increasing number of annulated rings, the mostly additive dispersion interaction of the acene subunits should at some point overcome the ring bending and Pauli repulsion energy, and the stacked conformer should become more stable. This is related to the folding of long *n*-alkane chains, where the folded structure is energetically favored after a distinct turning point, as recently shown by Lüttschwager et al.[7]

Herein, we present PECs for the symmetric opening of the stacked to the open conformer for the heptacene and nonacene dimers. Opposed to the dimerization reaction itself, this conformational process does not involve any orbital crossing and can thus be investigated using single-reference quantum chemical methods. For the heptacene dimer, accurate wavefunction-based calculations were carried out, employing the efficient LPNO-CEPA implementation by Neese and co-workers.[8] The coupled electron pair approach (CEPA, version "1")[9] was already shown to yield accurate results for general thermochemistry and non-covalent interactions.[10] Combined with the localized pair natural orbitals (LPNO) approximation, significant computational speedups can be achieved without much loss of accuracy.[8] Application of somewhat simplified computational methods is mandatory as the heptacene dimer comprises 96 atoms, which is rather challenging size for a correlated wavefunction treatment. Concerning the here relevant non-covalent interactions, the LPNO-CEPA reference method was already applied to protein–ligand interaction energies with good success.[11] For comparison, two conceptually different flavors of dispersion corrected density functional theory (DFT) are employed, the well-established atom-pairwise DFT-D3[12] and a non-local

[*] Dr. S. Ehrlich, Prof. Dr. S. Grimme
Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie der Universität Bonn
Beringstrasse 4, 53115 Bonn (Germany)
E-mail: grimme@thch.uni-bonn.de
Prof. Dr. H. F. Bettinger
Institut für Organische Chemie, Universität Tübingen
Auf der Morgenstelle 18, 72076 Tübingen (Germany)

[**] This work was supported by the DFG within the framework of the SFBs 858 and 813. The authors thank Dr. A. Hansen for help with the CEPA calculations.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304674.

(NL), electron-density-based approach (DFT-NL)[13] using the adapted functional of Vydrov and van Voorhis[14] (based on earlier work by Langreth and Lundquist).[15] The M06-2X functional was also applied in order to compare the results of the two aforementioned a posteriori corrections to a functional that includes medium-range correlation (dispersion) contributions by a flexible functional form and extensive parametrization.[16] We also present (SCS-)MP2 calculations[17] that were extrapolated to the complete basis set (CBS) limit using the very extended aug-cc-pVXZ (X = T,Q) basis sets (see the Supporting Information for details).[18] As the nonacene dimer is too large for accurate (large basis set) correlated calculations, the insight gained from the heptacene dimer calculations is used to select the (dispersion-corrected) density functional for its investigation.

Geometries along the PECs of the dimers were calculated in the following way: First, stacked and open structures were freely optimized using SCS-MP2/def2-TZVP.[17,19] This method was chosen because it is known to yield reasonable structures for π-stacked systems and conveniently provides two distinct minima for the heptacene dimer. By linear interpolation between these extremes, additional structures were created for various interplane distances *R*. The resulting structures were then relaxed with SCS-MP2/def2-TZVP in D_{2h} symmetry while keeping two carbon atoms of each outmost benzene ring fixed (see Figure 1) to remove any internal strain.

The PECs of the heptacene dimer are shown in Figure 2. First, it is noted that LPNO-CEPA/CBS, which serves as a reference here, does not predict a minimum for the stacked conformation. This also intuitively reasonable result indicates that the π-stacking interaction between the anthracene subunits is not strong enough to overcome the energy penalty caused by ring bending and Pauli repulsion.

Notably, MP2 very strongly overbinds the unusual stacked conformation and finds it as the global minimum. Furthermore, there is only a very shallow minimum for the open conformer. This is clearly qualitatively wrong behavior.

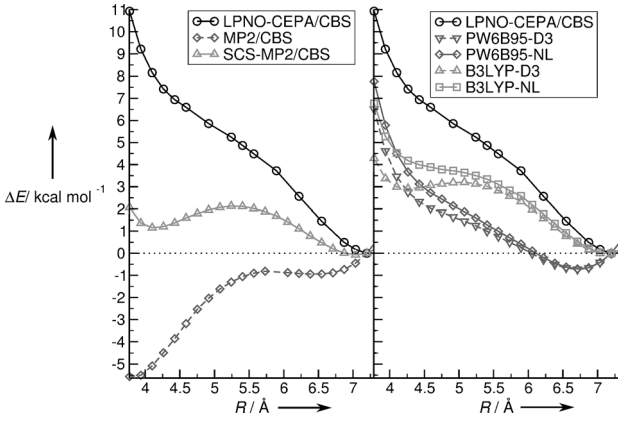


Figure 2. Potential-energy curves for the conformational isomerization (stacked (left) to open (right) in each graph) of the heptacene dimer with *R* indicating the distance between the anthracene subunits. DFT calculations employ the def2-QZVP basis set (for other technical details, see the Supporting Information). Energies were taken relative to *R* = 7.2, which is close to the SCS-MP2/def2-TZVP minimum.

Intramolecular basis set superposition error can be excluded as a reason for the failure at our high basis set extrapolation level, which leaves the bare MP2 error that was already observed for other stacked aromatic systems.[20,21] This dramatic failure (while not being surprising to experts in the field of non-covalent interactions) should be another warning[22] to users of MP2 based methods, in particular when large unsaturated fragments are involved. The use of spin-component scaling improves the results, but cannot completely overcome the failings of MP2. While the open form is correctly found to be more stable and has a distinct minimum with SCS-MP2, the stability of the stacked system is still overestimated.

The two tested hybrid functionals, B3LYP[23] and PW6B95,[24] perform significantly better than MP2 when corrected for the missing London dispersion energy (also called medium-range correlation energy for the intermediate interatomic distances investigated here; see Ref. [25]). It is encouraging that the two different flavors of dispersion correction, the pair-wise additive DFT-D3[12] and the density-dependent DFT-NL,[13] again yield similar results (for other comparisons, see Refs. [22,26]). The overall agreement with the reference is best for B3LYP-NL, closely followed by B3LYP-D3, although these differences are probably within the accuracy of the reference data. The PW6B95-based curves are slightly worse, with the minimum of the open structure shifted to shorter distances. However, no minimum is obtained for the stacked structure, which is qualitatively correct. The DFT-NL method seems to be more repulsive for the stacked conformer, which results in a better agreement with the reference. There is a qualitative difference between B3LYP-NL and B3LYP-D3, as the latter predicts a shallow minimum for the stacked conformer. However, this corresponds to a difference of only about 1 kcal mol^{-1}. When evaluating this, one has to keep in mind that we are dealing with about twice the π–π stacking interaction energy of the anthracene dimer (which is about 10 kcal mol^{-1}).[26,27] This means that the difference between the D3 and NL results is only a small fraction of the total intramolecular interaction energy of the anthracene subunits (about 5%, which is the typical error for DFT-D3 non-covalent interaction energies).

Overall, the results for the heptacene dimer indicate that there is a delicate balance between deformation energy and Pauli repulsion on the one hand, and attractive dispersion interactions on the other. This makes it a difficult case for most computational methods. We would also like to stress that uncorrected DFT and Hartree–Fock are excessively repulsive on the stacked side of the PEC and do not display the inflexion points visible in the reference curve. It should also be noted that all DFT-D3 and DFT-NL values are corrected for three-body dispersion interactions by an Axilrod–Teller–Muto type term. This correction which was shown to be necessary for larger, dense systems[22,26,28] shifts (improves) the stacked conformation by 0.6 kcal mol^{-1} to higher relative energies.

As B3LYP-NL and B3LYP-D3 have been identified as the best DFT methods for the heptacene dimer, they were applied to the PEC of the nonacene dimer as well. It can be seen in Figure 3 that the open conformer is still favored over

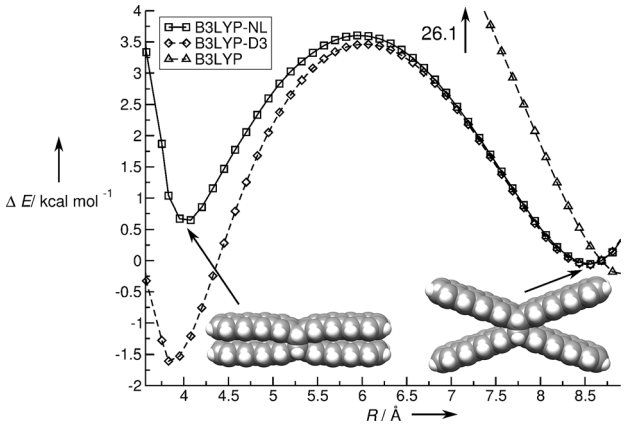


Figure 3. Potential-energy curves for the conformational isomerization (stacked to open) of the nonacene dimer with *R* indicating the distance between the tetracene subunits. The DFT calculations were carried out with the def2-QZVP basis set (see the Supporting Information for technical details and TPSS-D3 and SCS-MP2 results).

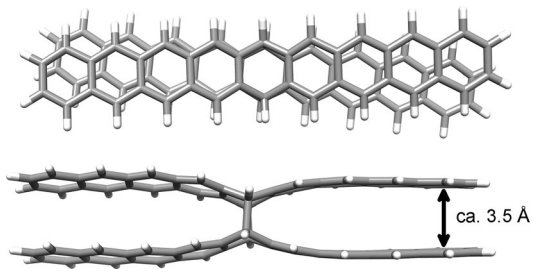


Figure 4. Two views of the parallel-displaced (pd) structure of the stacked nonacene dimer. The arrow indicates the interring distance between the two outmost rings.

Table 1: Free enthalpy of isomerization (ΔG_{tot}, at 298 K) from the open to the stacked, parallel-displaced structure of the nonacene dimer for several DFT methods.

Contribution	B3LYP-D3(-NL)[a]	M06-2X(-D3)[a]	TPSS-D3
ΔE_{gas}[b]	−4.3 (−0.6)	0.3 (−1.1)	−3.2
$\delta\Delta G_{RRHO}$[c]		1.7	
ΔG_{gas}	−2.6 (1.1)	2.0 (0.6)	−1.5
$\delta\Delta G_{solv}$[c]		6.3	
$\Sigma = \Delta G_{tot}$	3.7 (7.4)	8.3 (6.9)	4.8

[a] Values in parentheses with NL and D3 corrections for B3LYP and M06-2X, respectively. [b] The gas-phase relative energies ΔE_{gas} are calculated with the def2-QZVP basis set. [c] The rigid-rotor–harmonic-oscillator (RRHO) thermostatistical and solvation (solv, in benzene) contributions to ΔG_{tot} are added up from top to bottom.

the stacked conformation for B3LYP-NL. The B3LYP-D3 curve looks very similar, but slightly favors the stacked conformation and the difference between the two methods is again consistently about 1 kcal mol^{-1} for $R < 4$ Å. More importantly, however, both methods predict a distinct minimum for the stacked structure, which is a good evidence for the existence of dispersion-driven conformational isomerism. The barrier for interconversion is about 3.5 kcal mol^{-1}. Note that uncorrected B3LYP yields a totally unrealistic relative energy of 26.1 kcal mol^{-1} for the stacked conformer. The corresponding dispersion contributions favoring the stacked form are huge for B3LYP (−28.7 kcal mol^{-1}) and relatively large even for inherently less overrepulsive functionals, such as PW6B95 (−14.8 kcal mol^{-1}).

To make the connection to experimental conditions, thermostatistical corrections to free enthalpy in the gas phase ($\delta\Delta G_{RRHO}$) and in benzene (including additionally $\delta\Delta G_{solv}$) were calculated with TPSS-D3[29] and the COSMO-RS solvation model.[30] However, with TPSS-D3 we obtain two imaginary vibrational modes for the fully stacked, D_{2h}-symmetric structure. Distortion along these modes and re-optimization led to a D_2-symmetric structure where the tetracene subunits are slightly parallel-displaced (pd; see Figure 4). This is reasonable since already the benzene dimer avoids the fully stacked, D_{6h} symmetric structure, and this symmetry breaking is common to all acenes.[21]

As a consequence, the open, stacked, and pd structures were reoptimized at the B3LYP-D3/def2-TZVP level of theory and were used in subsequent single-point calculations of the free conformational enthalpy in solution. The fully optimized pd structure is only about 2.4 kcal mol^{-1} more stable than the symmetric stacked one at the B3LYP-D3/def2-QZVP level of theory. This suggests that our D_{2h}-symmetric PECs discussed above are reliable and likely to be only slightly biased in favor of the open form, which is a true D_{2h}-symmetric minimum.

As can be seen from the results in Table 1, all flavors of dispersion corrected DFT predict the stacked pd structure to be observable in the gas phase under ambient equilibrium conditions ($\Delta G_{gas} = -2.6$ to 0.6 kcal mol^{-1}). In benzene solution, however, it is strongly destabilized with respect to the open form owing to favorable solvation contributions in the open parts of the wings. This subtle interplay between intramolecular dispersion and solvation effects has already been discussed for the thermochemistry of the anthracene dimer.[3]

In summary, the conformational transition from the π-stacked to the open form in the heptacene and nonacene dimers has been investigated by accurate quantum-chemical methods. In the case of the heptacene dimer, the dispersion interaction of the anthracene subunits is not able to overcome the energy penalty imposed by ring deformation and Pauli repulsion. Modern dispersion-corrected density functional theory performs reasonably well for such a difficult case while the MP2 method, which is known to overestimate π-stacking interactions, fails spectacularly for this system. It is suggested as a challenging test case for approximate quantum chemical methods. For the nonacene dimer, a stable stacked conformation and the existence of two distinct dispersion-driven conformers in the gas phase is predicted. The calculated free enthalpies in benzene solution, however, show that the open conformer can profit more from interaction with the solvent, and it is expected to be the dominant species in solution. At this point, it can only be speculated about the situation in a molecular crystal where the favorable solvation terms for the open form are absent. To this end, a photochemically aided solid-state synthesis of the stacked form seems to be

most promising, although we once again would like to emphasize the conceptual character of our study regarding this unusual form of isomerism. Furthermore, the stacked forms structurally resemble common aromatic excimers, and we expect strongly red-shifted electronic absorption or fluorescence bands compared to the open forms, which might allow spectroscopic identification.

The nonacene dimer seems to be one of the rare well-documented examples for dispersion-driven conformational isomerism showing a clear double-minimum potential. From the theoretical point of view, the results underline once more the importance of the correct treatment of the intramolecular dispersion energy, not only for DFT but also for approximate wavefunction-based methods. Furthermore, this study shows that larger acenes are not completely rigid (which organic textbooks seem to suggest) and they can form new and unexpected chemical structures.

Received: May 30, 2013
Published online: August 23, 2013

Keywords: ab initio calculations · acene dimers · density functional calculations · London dispersion interactions · π stacking

[1] a) J. E. Anthony, *Angew. Chem.* **2008**, *120*, 460; *Angew. Chem. Int. Ed.* **2008**, *47*, 452; b) M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891.
[2] S. S. Zade, N. Zamoshchik, A. R. Reddy, G. Fridman-Maureli, D. Sheberla, M. Bendikov, *J. Am. Chem. Soc.* **2011**, *133*, 10803.
[3] S. Grimme, C. Diedrich, M. Korth, *Angew. Chem.* **2006**, *118*, 641; *Angew. Chem. Int. Ed.* **2006**, *45*, 625.
[4] B. Purushothaman, S. R. Parkin, J. E. Anthony, *Org. Lett.* **2010**, *12*, 2060.
[5] a) R. Mondal, B. K. Shah, D. C. Neckers, *J. Am. Chem. Soc.* **2006**, *128*, 9612; b) R. Mondal, C. Tönshoff, D. Khon, D. C. Neckers, H. F. Bettinger, *J. Am. Chem. Soc.* **2009**, *131*, 14281; c) C. Tönshoff, H. F. Bettinger, *Angew. Chem.* **2010**, *122*, 4219; *Angew. Chem. Int. Ed.* **2010**, *49*, 4125; d) B. Purushothaman, M. Bruzek, S. R. Parkin, A.-F. Miller, J. E. Anthony, *Angew. Chem.* **2011**, *123*, 7151; *Angew. Chem. Int. Ed.* **2011**, *50*, 7013; e) R. Einholz, H. F. Bettinger, *Angew. Chem.* **2013**, DOI: 10.1002/ange.201209722; *Angew. Chem. Int. Ed.* **2013**, DOI: 10.1002/anie.201209722.
[6] S. Grimme, P. R. Schreiner, *Angew. Chem.* **2011**, *123*, 12849; *Angew. Chem. Int. Ed.* **2011**, *50*, 12639.
[7] N. O. B. Lüttschwager, T. N. Wassermann, R. A. Mata, M. A. Suhm, *Angew. Chem.* **2013**, *125*, 482; *Angew. Chem. Int. Ed.* **2013**, *52*, 463.
[8] a) F. Neese, F. Wennmohs, A. Hansen, *J. Chem. Phys.* **2009**, *130*, 114108; b) F. Neese, A. Hansen, D. G. Liakos, *J. Chem. Phys.* **2009**, *131*, 064103; c) D. G. Liakos, A. Hansen, F. Neese, *J. Chem. Theory Comput.* **2011**, *7*, 76.
[9] R. Ahlrichs, *Comput. Phys. Commun.* **1979**, *17*, 31.
[10] F. Neese, A. Hansen, F. Wennmohs, S. Grimme, *Acc. Chem. Res.* **2009**, *42*, 641.
[11] J. Antony, S. Grimme, D. G. Liakos, F. Neese, *J. Phys. Chem. A* **2011**, *115*, 11210.
[12] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456.
[13] W. Hujo, S. Grimme, *J. Chem. Theory Comput.* **2011**, *7*, 3866.
[14] O. A. Vydrov, T. Van Voorhis, *J. Chem. Phys.* **2010**, *133*, 244103.
[15] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, B. I. Lundqvist, *Phys. Rev. Lett.* **2004**, *92*, 246401.
[16] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
[17] S. Grimme, *J. Chem. Phys.* **2003**, *118*, 9095.
[18] a) T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, *90*, 1007; b) R. A. Kendall, T. H. Dunning, R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796.
[19] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
[20] a) S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, K. Tanabe, *J. Am. Chem. Soc.* **2002**, *124*, 104; b) C. D. Sherrill in *Reviews in Computational Chemistry*, *Vol. 26* (Eds.: K. B. Lipkowitz, D. B. Boyd), Wiley-VCH, New York, **2009**, pp. 1–39; c) S. M. Cybulski, M. L. Lytle, *J. Chem. Phys.* **2007**, *127*, 141102.
[21] S. Grimme, *Angew. Chem.* **2008**, *120*, 3478; *Angew. Chem. Int. Ed.* **2008**, *47*, 3430.
[22] T. Risthaus, S. Grimme, *J. Chem. Theory Comput.* **2013**, *9*, 1580.
[23] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.
[24] Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2005**, *109*, 5656.
[25] a) S. Grimme, *Angew. Chem.* **2006**, *118*, 4571; *Angew. Chem. Int. Ed.* **2006**, *45*, 4460; b) S. Grimme, *WIREs Comput. Mol. Sci.* **2011**, *1*, 211.
[26] S. Ehrlich, J. Moellmann, S. Grimme, *Acc. Chem. Res.* **2013**, *46*, 916.
[27] E. G. Hohenstein, C. D. Sherrill, *J. Chem. Phys.* **2010**, *132*, 184111.
[28] S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955.
[29] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401.
[30] a) A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224; b) F. Eckert, A. Klamt, *AiChE J.* **2002**, *48*, 369; c) F. Eckert, A. Klamt, COSMOtherm, Version C2.1, Release 01.11; COSMOlogic GmbH & Co. KG, Leverkusen, Germany, **2010**.

