EurJOC
European Journal of Organic Chemistry

Full Papers
doi.org/10.1002/ejoc.202100865

Chemistry Europe
European Chemical Societies Publishing

Special Collection

Bending versus Twisting Acenes – A Computational Study

Amit Manor Armon,[a] Anjan Bedi,[a, c] Veniamin Borin,[b] Igor Schapiro,*[b] and Ori Gidron*[a]

In memory of François Diederich

Polycyclic aromatic hydrocarbons (PAHs) are widely used in organic electronic devices. The electronic, magnetic, and optical properties of PAHs can be tuned by structural modifications to the aromatic backbone to introduce an inherent distortion from planarity, such as bending or twisting. However, it remains difficult to isolate and control the effects of such distortions. Here, we sought to understand how backbone twisting and bending affect the electronic properties of acenes, as models for larger PAHs. We found that, even when highly distorted from planarity (30° per ring), acenes maintain their aromatic character and π orbital delocalization with minor mixing of the σ and π orbitals. In addition, the energy gap between the HOMO and LUMO decreases with increasing twist, while the gap is hardly affected by bending, since the energy of both orbitals increase to a similar extent. For bent acenes in the triplet state, the spin becomes more localized with increasing bend, whereas twisting produces an evenly distributed spin delocalization. These findings can guide the synthesis of PAHs with tailored properties.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are the 'brick and mortar' of organic electronic devices, such as organic field effect transistors (OFETs), organic solar cells, and organic light emitting diodes (OLEDs).[1] PAHs tend to adopt a planar conformation because of their sp^2 hybridized backbone. Upon functionalization or backbone extension, PAHs often adopted twisted and/or bent conformations possessing properties that have intrigued the scientific community and led to computational and synthetic studies of non-planar aromatics.[2] The main question relates to how distorting (bending or twisting) an aromatic molecule affects fundamental properties, such as the delocalization and aromaticity of π-electrons.[1b,3] This question is not addressed by the original definition of Hückel aromaticity, which assumes spatial separation between the π and σ frameworks.[2,4]

Following the introduction of twisted acenes (twistacenes) by Pascal,[5] Norton and Houk conducted a computational study on the effect of twisting on the electronic properties of acenes.[1d] Bodwell introduced strained pyrene cyclophanes (pyranophanes) with different degree of bending by controlling the length of the connecting alkyl chain.[6] Both systems showed that π delocalization and aromaticity are not impaired significantly by distortion from planarity. In addition, Bodwell demonstrated an increase in chemical reactivity upon bending,[7] and Houk demonstrated that the HOMO-LUMO gap slightly decreases with increasing distortion from planarity.[2,8]

Similar computational studies that were conducted on cycloparaphenylenes (CPPs) revealed that decreasing the number of benzene units, and consequently increasing the curvature, increases the strain energy dramatically from 28 kcal/mol for **[20]CPP** to 119 kcal/mol for **[5]CPP**, in addition to a similar trend of decreasing HOMO-LUMO gap and a significant decrease in fluorescence quantum efficiency, which was explained by the quinoid character of CPPs increasing with increasing deviation from planarity.[9] These changes in photophysical properties have also been noted in synthesized twistacenes, including in the tethered twistacenes that we introduced previously.[1e,10] In the twistacene case, the reduction in fluorescence quantum efficiency arose from stabilization of the triplet state with increasing twist.[11]

The synthetic challenges for obtaining curved PAHs are exemplified in the field of carbon nanobelts (CNBs). Cyclacene[9a,20] and the "Vögtle belt"[12] are examples of desired molecules that have not yet been synthesized.[9c,13] More recently, CNBs have been synthesized successfully by the Itami group, which synthesized armchair[9a] and zigzag[14] CNBs, by Chi's group, which synthesized pyrene sidewall fragment of a carbon nanotube,[15] and by the Miao group, which synthesized a chiral CNB.[16]

---

[a] *A. M. Armon, Dr. A. Bedi, Prof. O. Gidron*
Institute of Chemistry
The Hebrew University of Jerusalem
Jerusalem 9190401, Israel
E-mail: ori.gidron@mail.huji.ac.il
[b] *Dr. V. Borin, Prof. Dr. I. Schapiro*
Fritz Haber Center for Molecular Dynamics Research,
Institute of Chemistry
The Hebrew University of Jerusalem
Jerusalem 9190401, Israel
E-mail: igor.schapiro@mail.huji.ac.il
[c] *Dr. A. Bedi*
Department of Chemistry
SRM Institute of Science and Technology
Kattankulathur 603203, Tamil Nadu, India

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejoc.202100865

This article belongs to a Joint Special Collection dedicated to François Diederich.

The simplest way to induce distortion into a PAH backbone is by bending or twisting it, each of which fundamentally and uniquely changes the molecular geometry and symmetry. For parent acenes, D_2 symmetry is obtained upon twisting the four terminal carbons (Figure 1, right), whereas C_{2V} symmetry is achieved upon bending (Figure 1, left). This difference should be expressed in the electronic, (chiro)optical, and magnetic properties of acenes, from dipole moment to spectroscopic properties and optical activity. In addition, the extent of delocalization of the π system is also expected to change upon distortion.[2,4]

Acenes can be viewed as one-dimensional fragments of nanographenes and, upon bending, as the most fundamental fragment of zigzag carbon nanobelts. We therefore focussed on acenes as a model system for bent and twisted PAHs. Elucidating the isolated effects of such distortions is an important aspect in the investigation of distorted PAHs. To that end, we systematically and independently changed the twist and bend angles of parent acenes of different lengths. The twist angle was defined according to Pascal's definition using the four end carbons (ABCD) of the acene (Figure 1, right).[5a] The bend angle was defined as the angle between the two planes formed by each end carbon and the first carbon of the nearest central acene ring, similarly to the approach described by Bodwell and colleagues (Figure 1, left).[6] We performed most computations using the B3LYP/6-31G(d) level of theory, however, other methods (MP2, CAM-B3LYP, ωB97XD) were used for comparison, with all producing similar trends. To compare between acenes of different lengths, the results are normalized per ring.

Results and Discussion

Examining the geometries obtained upon twisting and bending (Figure 1), we note that the twist is evenly distributed end-to-end along the acene backbone, whereas the bend does not distribute evenly along the acene core, producing higher distortion of the central rings compared with the terminal rings.

Relaxed scan calculations (the constraints are detailed in the experimental section) revealed, as expected, that the strain energy increases with increasing distortion from planarity. For both bending and twisting, a strain energy of 15 kcal/mol is reached only after a large distortion of ca. 30° per ring (Figure 2), demonstrating that acenes can readily twist and bend out of planarity. Therefore, both twisted and bent acenes should be synthetically accessible. However, compared with bent acenes, twistacenes show a more systematic increase in strain, perhaps because of their uniform distortion from planarity.

To validate the use of the B3LYP functional, we compared the bending and twisting strain energies calculated for anthracene at different levels of theory (Figure S1). The results indicate that, for twisting of up to 10° and for bending of up to 15°, no significant change is observed between the levels of theory, whereas for higher degrees of twisting and bending, the MP2 method results in slightly higher energies (by up to 2 kcal/mol) compared with the DFT methods.

A comparison of HOMO and LUMO energies (Figure 3) shows that, for the bent acenes, both energies increase with bending in a similar extent, resulting in a minor total change in

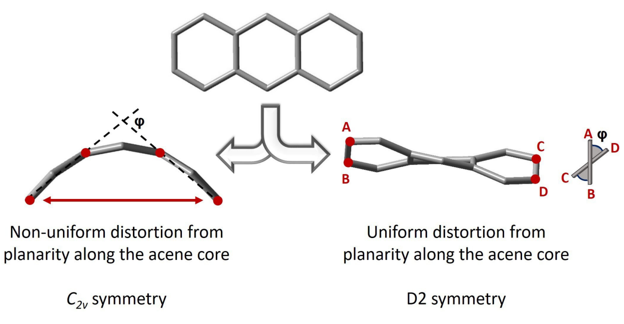

Figure 1. Schematic illustration of acene bending (left) and twisting (right).

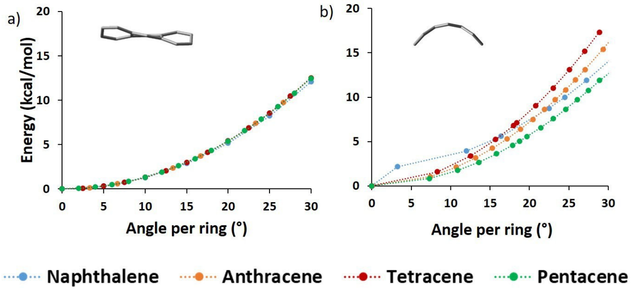

Figure 2. Strain energy per ring for a) twisting and b) bending of acenes calculated at B3LYP/6-31G(d) level of theory.

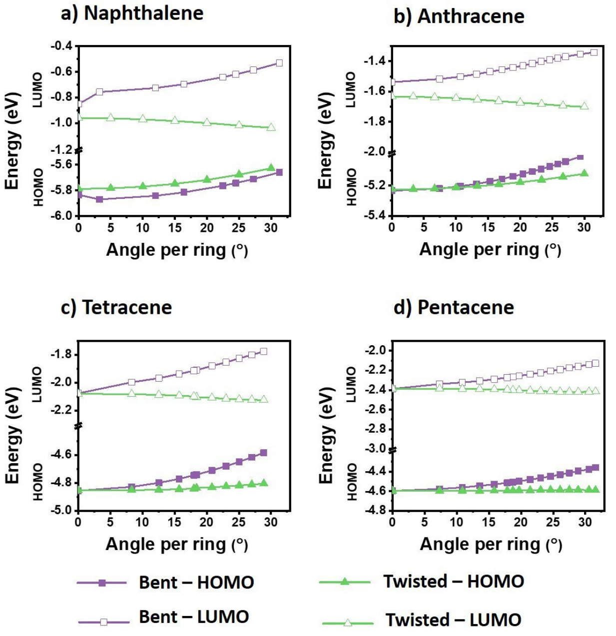

Figure 3. HOMO and LUMO energy levels of a) naphthalene, b) anthracene, c) tetracene, and d) pentacene calculated at B3LYP/6-31G(d) level of theory.[18]

the HOMO-LUMO gap even for a bend of 30° per ring. This in in contrast to the case of CPPs, where increased distortion results in smaller calculated HOMO-LUMO gaps and increased wavelengths for the absorption maxima.[9e] Twisting, on the other hand, results in a more significant decrease in the HOMO-LUMO gap values, as the HOMO energy increases with twist while the LUMO energy decreases. Moreover, it appears that longer acenes are less affected and show smaller changes in their HOMO-LUMO gaps upon distortion. For example, compared with their planar counterparts, the HOMO-LUMO gap of twisted naphthalene decreases by 0.24 eV, but for twisted pentacene the decrease is only 0.04 eV. Here, we again compared the different methods (B3LYP, ωB97XD and MP2) for the case of naphthalene (Figure S3). The three methods resulted in qualitatively similar trends.

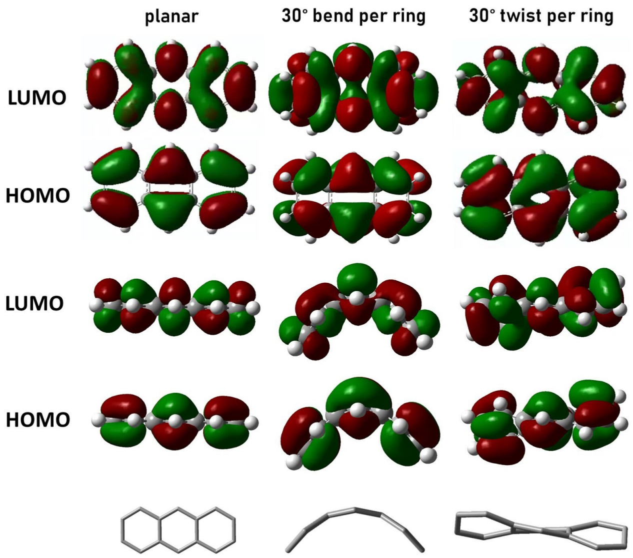

Figure 4. Anthracene HOMO and LUMO orbitals in a planar geometry and with a 30° bend or twist calculated at B3LYP/6-31G(d). Isovalue = 0.02 electrons/bohr^3.

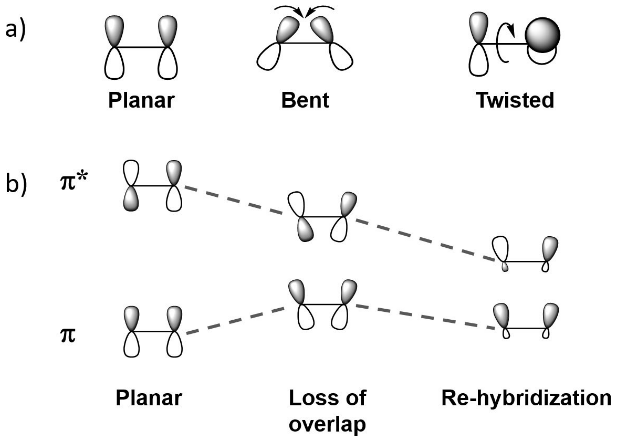

Figure 5. Orbital change upon bending and twisting a π system. Adapted from Ref. [16a].

To gain a better understanding of the above-mentioned trend, the HOMO and LUMO topologies of anthracene with 30° twisting or bending per ring were examined and compared with those of the planar molecule (Figure 4). For the twistacenes, the LUMO orbital is hardly affected by twisting, but the distribution of the HOMO surface changes, with increasing density on the central carbons (9 and 10 positions in anthracene). Bent anthracene shows the opposite trend, with a significant change in the LUMO orbital, whereas the HOMO shows no observable change. These differences are a result of a change in π-orbital overlap: bending increases the distance between adjacent nodes in one plane while decreasing the distance between adjacent nodes in the opposite plane (and therefore increasing or decreasing the overlap respectively). In contrast, twisting increases the distance between adjacent nodes in both planes evenly, since twisting is more symmetric compared with bending (twisting results in D_2 symmetry and bending in C_{2v} symmetry, Figure 5a). However, both bending and twisting result in π and σ mixing (or re-hybridization), thus affecting the HOMO and LUMO energy levels and decreasing the HOMO-LUMO gap (Figure 5b).[1b,e,17]

To estimate the degree of π and σ mixing at 30° distortion per ring, we extracted the angles between adjacent carbons on the acene backbone. For all twistacenes, a range of 116° to 120° was found, where the most distorted carbons were those connecting the rings. According to Haddon,[17b] an angle of 116° is equivalent to only 0.1 s-character in the π orbital. In the case of bent acenes, two trends emerged: the central rings show a higher degree of s-character compared with the terminal rings because of their higher distortion from planarity, and for longer acenes the deviation from sp^2 hybridization is smaller (Table 1). The maximal deviation from aromaticity occurs in naphthalene and anthracene, which also have 0.1 s-character in the π orbital, whereas tetracene and pentacene maintain a nearly completely sp^2 character, especially in their terminal rings.

For a quantitative assessment of the s orbital contribution upon distortion from planarity, we have extracted the non-zero s coefficients for the HOMO and LUMO orbitals (Figure S4, see ESI). For anthracene with 30° per ring twist, the s coefficients are 0.02 for the HOMO and 0.08 for the LUMO, while for bending (30° per ring) results in s coefficients of 0.05 for the HOMO and 0.06 for the LUMO. This indicates that upon twisting the s orbital contribution in the LUMO is more significant than for the HOMO, while no clear trend is observed upon bending.

Next, we compared the energy difference between the singlet ground state and the lowest triplet state (ΔE_{TS}). The absolute energy for the triplet ground state also increases with increasing distortion from planarity (Figure S2), however at a

Table 1. Angles of the most-distorted carbons upon bending acene to 30° per ring.

	Central ring [°]	Terminal ring [°]
Naphthalene	116	–
Anthracene	116	118
Tetracene	117	119
Pentacene	117	120

slower extent than the absolute singlet energy (Figure 6). Moreover, the decrease in ΔE_{TS} is more pronounced for bending, whereas twisting results in a very slight decrease. The decrease in ΔE_{TS} is more significant for the smaller acenes (naphthalene and anthracene). While in all cases ΔE_{TS} is too large to enable a significant contribution from the triplet state, these results imply that the diradical character of open shell acenes can be tuned by distorting them from planarity.[19] It is noteworthy that the longer acenes display a more pronounced triplet character in their planar conformation (ΔE_{TS} is smaller).[1f]

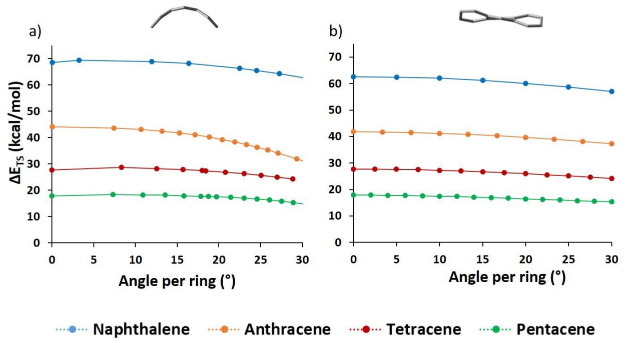

Figure 6. The energy gap between the singlet ground state and the lowest triplet state (ΔE_{TS}) of a) bent and b) twisted acenes calculated with B3LYP/6-31G(d) level of theory.

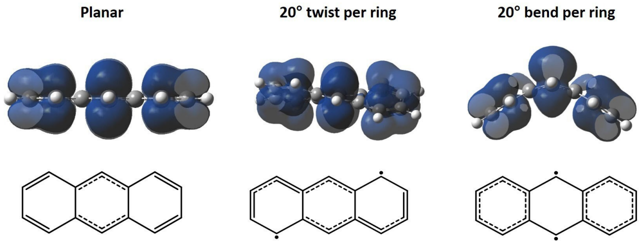

Figure 7. Spin density of the triplet state in twisted and bent anthracene calculated at B3LYP/6-31G (d) level of theory. A representative resonance structure is presented below the structures. Density |isovalue| is 0.02 electrons/bohr^3.

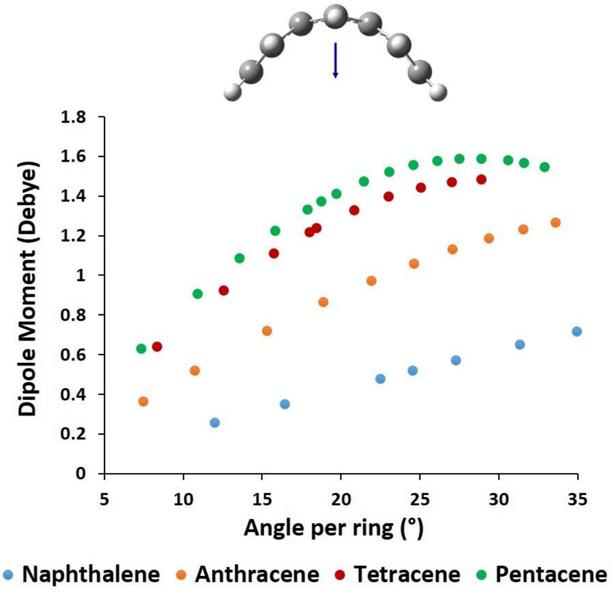

Figure 8. Dipole moment of bent acenes calculated with B3LYP/6-31G(d).

The triplet state was further characterized by visualizing the spin density. As shown in Figure 7, twisting results in increased spin density on the terminal rings. However, upon bending, a significant portion of the spin density is located on the central ring, which consequently exhibits increased diradical character. This finding arises from the non-uniform nature of the bend, which distorts the central ring to a greater extent than the other rings.

Differential effects of twisting compared with bending are also observed in the calculated dipole moment (μ). Whereas twisting acenes does not result in a net dipole moment because of their D_2 symmetric backbone, bending acenes produces a dipole moment, which increases with bend angle (Figure 8). Moreover, the larger the acene is, the greater the increase of the dipole moment, since it is proportional to both distance and charge ($\mu = q \cdot d$). For long acenes (tetracene and pentacene), μ decreases when the bend exceeds 25° per ring, probably because of a counter effect of the terminal rings in the direction perpendicular to the bend.

To evaluate the effect of twisting and bending on conjugation and aromaticity, bond length alternation (BLA) and nucleus-independent chemical shifts (NICS) calculations were performed. For the BLA calculations, bonds of both singlet and triplet states were analysed (Figures S5–S8) revealing a minor change of 0.01–0.06 Å between the planar acenes and acenes twisted or bent by 30°. Thus, the BLA data indicate bonds remain in the aromatic region (1.36–1.47 Å).[4] Nevertheless, the BLA trend is consistent with the previously discussed spin density, in that the isolated diradical triplet state increases for the bent acenes (as indicated by elongation of the central bonds and formation of an isolated benzene-like ring on the terminal rings).

Bending the backbone changes the curvature of the rings such that their outer surface becomes convex while their inner surface becomes concave.[2] The NICS calculations show a clear trend: as the degree of bending increases, NICS measured with the probe positioned 1 Å above the convex molecular plane (*i.e.*, NICS(1)) increases with increasing bend (Figure 9), and it does so to a larger extent for the longer acenes (from 30% in naphthalene to 60% in pentacene). In addition, the central rings of bent acenes appear to be significantly more affected (by 10–15%) than the terminal rings, probably because they undergo the most significant geometric change upon bending. This result indicates an overall decrease in π-delocalization with bending. However, in some part the significant increase is a result of the increasing distance between the dummy atoms and the π-orbitals, and both effects are cumulative. In the same manner, NICS(−1) slightly decreases (by up to 10%) with increasing bend due to its growing proximity to the centre of the aromatic system. In this case, the decrease in π-delocalization is slightly reduced by the opposing effect of the dummy atoms increasing proximity to the aromatic center.

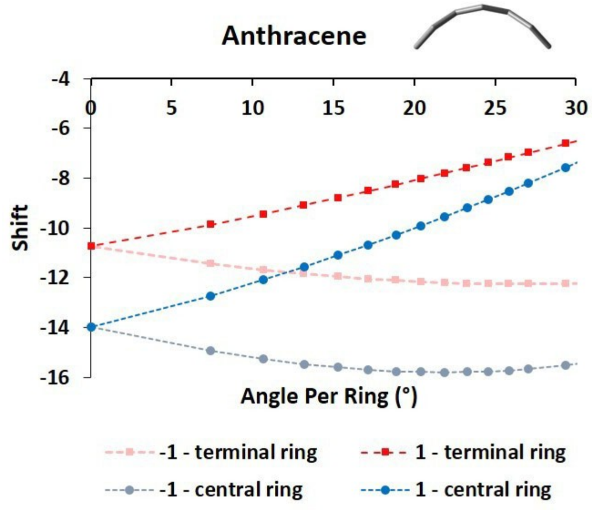

Figure 9. NICS values measured −1 Å, 0 Å, and 1 Å from the centre of each ring, for anthracene bent from 0° to 30° per ring as calculated at B3LYP/6-31G(d) level of theory. The NICS(1) dummy atom was located above the convex surface of the molecule whereas the NICS(−1) dummy atom was located below its concave surface.

Conclusion

Using quantum chemical methods, we investigated how the extent of twisting and bending acenes of various sizes affects their magnetic and electronic properties. We conclude that, even for a high degree of distortion from planarity (30° per ring), the different acenes maintain a substantial amount of the aromatic character and π orbital delocalization, as well as their singlet nature. Moreover, distortion to such a degree requires relatively little energy.

Twisting results in D_2 symmetry whereas bending results in C_{2V} symmetry, and this difference is also reflected in our results. Examination of the change in orbitals upon bending and twisting reveals that, whereas bending produces a significant change in the LUMO orbitals, twisting mostly affects the HOMO orbitals. In both cases, increasing distortion leads to a small mixing of the σ and π orbitals (less than 0.1 s-character). When twisting, the HOMO energy increases (or remains unchanged) with increasing twist, while the LUMO energy decreases, resulting in an overall total decrease in the HOMO-LUMO gap. However, bending induces a similar extent of increase in both the HOMO and LUMO energies, with only a subtle overall change in the orbital energies. Whereas twisting is evenly distributed across the acene backbone, bending in not uniform and results in a greater distortion of the central rings. This distortion affects mainly the triplet state, whose spin becomes more localized to the central ring for bent acenes. Furthermore, for both bending and twisting, the energy gap between the lowest singlet and triplet energy levels (ΔE_{TS}) decreases. Overall, by showing how bending and twisting affect the electronic and magnetic properties of nonplanar acenes, the results presented here can serve as design principles for nonplanar PAHs.

Experimental Section

All calculations were carried out using the Gaussian 16[20] program applying density functional theory (DFT).[21] All molecules were optimized using a hybrid density functional and Becke's three-parameter exchange functional combined with the LYP correlation functional (B3LYP) and with the 6-31G(d) basis set because of its reliability and widespread use for aromatic systems.[22] Some calculations were optimized using ωB97XD, CAM-B3LYP[23] and Møller–Plesset theory (MP2). All bent molecules were optimized using restricted and unrestricted calculations, to show non-energetic differences.

Twisting was induced through a scan of the end-to-end dihedral angle (angle ABCD) of the acenes (Figure 1), whereas bending required manual modification of the modelled distance between the end carbons (AB and CD) and the application of constraints on the end-to-end dihedral angle to prevent twisting (dihedral angle ABCD that was set to 0°).

NICS computations were conducted using NMR calculations and dummy atoms located in the centre of each ring of the acene (NICS (0)), as well as 1 Å above the first dummy atom (NICS(1)), and 1 Å below the first dummy atom (NICS(-1)),. It should be noted that as the molecules are bent from planarity, they develop a convex outer surface and a concave inner surface. Consequently, as bending increases, the distance of the NICS(1) dummy atom located above the convex surface increases to >1 Å, whereas the distance of the NICS(−1) dummy atom located below the concave surface decreases to <1 Å. This likely affects the accuracy of the calculations and results in higher NICS values.

Acknowledgements

This research was supported by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant Agreement No. 850836, ERC Starting Grant "PolyHelix").

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Acenes · Aromaticity · Conjugation · Curved aromatics · Organic electronic materials

[1] a) J. E. Anthony, D. L. Eaton, S. R. Parkin, *Org. Lett.* **2002**, *4*, 15–18; b) R. Kumar, H. Aggarwal, A. Srivastava, *Chem. Eur. J.* **2020**, *26*, 10653–10675; c) Q. Zhong, Y. Hu, K. Niu, H. Zhang, B. Yang, D. Ebeling, J. Tschakert, T. Cheng, A. Schirmeisen, A. Narita, K. Müllen, L. Chi, *J. Am. Chem. Soc.* **2019**, *141*, 7399–7406; d) J. E. Norton, K. N. Houk, *J. Am. Chem. Soc.* **2005**, *127*, 4162–4163; e) A. Bedi, O. Gidron, *Acc. Chem. Res.* **2019**, *52*, 2482–2490; f) M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891–4946.

[2] M. A. Dobrowolski, M. K. Cyrański, B. L. Merner, G. J. Bodwell, J. I. Wu, P. v. R. Schleyer, *J. Org. Chem.* **2008**, *73*, 8001–8009.

[3] M. Hermann, D. Wassy, D. Kratzert, B. Esser, *Chem. Eur. J.* **2018**, *24*.

[4] M. Nendel, K. N. Houk, L. M. Tolbert, E. Vogel, H. Jiao, P. v. R. Schleyer, *J. Phys. Chem. A* **1998**, *102*, 7191–7198.

[5] a) R. A. Pascal, *Chem. Rev.* **2006**, *106*, 4809–4819; b) R. A. Pascal, W. D. McMillan, D. Van Engen, *J. Am. Chem. Soc.* **1986**, *108*, 5652–5653.

[6] G. J. Bodwell, J. J. Fleming, D. O. Miller, *Tetrahedron* **2001**, *57*, 3577–3585.

[7] S. Biswas, C. S. Qiu, L. N. Dawe, Y. Zhao, G. J. Bodwell, *Angew. Chem. Int. Ed.* **2019**, *58*, 9166–9170; *Angew. Chem.* **2019**, *131*, 9264–9268.

[8] a) P. G. Ghasemabadi, T. Yao, G. J. Bodwell, *Chem. Soc. Rev.* **2015**, *44*, 6494–6518; b) G. J. Bodwell, J. N. Bridson, M. K. Cyrański, J. W. J. Kennedy, T. M. Krygowski, M. R. Mannion, D. O. Miller, *J. Org. Chem.* **2003**, *68*, 2089–2098; c) Y. Aida, J. Nogami, H. Sugiyama, H. Uekusa, K. Tanaka, *Chem. Eur. J.* **2020**, *26*, 12579–12588.

[9] a) G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi, K. Itami, *Science* **2017**, *356*, 172; b) K. Itami, *Pure Appl. Chem.* **2012**, *84*, 907–916; c) Y. Segawa, A. Yagi, H. Ito, K. Itami, *Org. Lett.* **2016**, *18*, 1430–1433; d) G. J. Bodwell, *Nat. Chem.* **2014**, *6*, 383–385; e) M. R. Golder, R. Jasti, *Acc. Chem. Res.* **2015**, *48*, 557–566; f) S. Yamago, Y. Watanabe, T. Iwamoto, *Angew. Chem. Int. Ed.* **2010**, *49*, 757–759; *Angew. Chem.* **2010**, *122*, 769–771; g) R. Jasti, J. Bhattacharjee, J. B. Neaton, C. R. Bertozzi, *J. Am. Chem. Soc.* **2008**, *130*, 17646–17647.

[10] a) A. Bedi, L. J. W. Shimon, O. Gidron, *J. Am. Chem. Soc.* **2018**, *140*, 8086–8090; b) A. Bedi, O. Gidron, *Chem. Eur. J.* **2019**, *25*, 3279–3285.

[11] C. E. Tait, A. Bedi, O. Gidron, J. Behrends, *Phys. Chem. Chem. Phys.* **2019**, *21*, 21588–21595.

[12] A. Schröder, H.-B. Mekelburger, F. Vögtle, in *Cyclophanes* (Ed.: E. Weber), Springer Berlin Heidelberg, Berlin, Heidelberg, **1994**, pp. 179–201.

[13] D. Eisenberg, R. Shenhar, M. Rabinovitz, *Chem. Soc. Rev.* **2010**, *39*, 2879–2890.

[14] a) K. Y. Cheung, K. Watanabe, Y. Segawa, K. Itami, *Nat. Chem.* **2021**, *13*, 255–259; b) Z. Xia, S. H. Pun, H. Chen, Q. Miao, *Angew. Chem. Int. Ed.* **2021**, *60*, 10311–10318.

[15] Y. Han, S. Dong, J. Shao, W. Fan, C. Chi, *Angew. Chem. Int. Ed.* **2021**, *60*, 2658–2662; *Angew. Chem.* **2021**, *133*, 2690–2694.

[16] K. Y. Cheung, S. Gui, C. Deng, H. Liang, Z. Xia, Z. Liu, L. Chi, Q. Miao, *Chem* **2019**, *5*, 838–847.

[17] a) P. J. Smith, J. F. Liebman, H. Hopf, I. Starý, I. G. Stará, B. Halton, in *Strained Hydrocarbons*, **2009**, pp. 147–204; b) R. C. Haddon, *Acc. Chem. Res.* **1988**, *21*, 243–249.

[18] Note that for bent anthracene and naphthalene, a bending of 0.01° was taken instead of planar geometry to break the symmetry constraint.

[19] Z. Sun, Z. Zeng, J. Wu, *Acc. Chem. Res.* **2014**, *47*, 2582–2591.

[20] Gaussian 09, Revision A.02, 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. 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. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. 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, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

[21] J.-L. Calais, *Int. J. Quantum Chem.* **1993**, *47*, 101–101.

[22] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[23] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

Manuscript received: July 20, 2021
Revised manuscript received: September 23, 2021
Accepted manuscript online: September 25, 2021