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Abstract

Based on experimental data of newly determined structures of *per*-substituted naphthalenes by halogen atoms (F, Cl and Br) and perchloroanthracene, as well as on molecular modeling we have shown that deviation from planarity leads to relatively small changes in cyclic π-electron delocalization of acenes. *Per*-substituted naphthalenes are twisted, whereas perchloroanthracene adopts a boat conformation in the solid state. For the most distorted case - perbromonaphthalene twisted by 34.7°, geometry-based HOMA index drops down by 0.128 of the unit only, what means *ca*. 15% reduction of the extent of π-electron delocalization as referred to naphthalene. To account the changes of the aromatic stabilization energies (ASE), exaltations of magnetic susceptibilities (Λ) and strain energies (SE) upon bending we have proposed a set of homodesmotic reactions based on *peri*-substituted systems, where the reference compounds have similar conformation as the distorted aromatics. The decrease of aromaticity is smooth, but regular in rather large range of distortion. Notably, the most extreme case - 1,4,5,8-tetra-*t*-butylnaphthalene, twisted by 51.7° with the estimated strain energy of 26 kcal/mol is still aromatic. The ASE, Λ and HOMA decrease by 19.1 kcal/mol, 7 cgs-ppm and 0.34 of the unit, respectively, as referred to naphthalene.

Introduction

The nature and the extent of cyclic π-electron delocalization in highly strained π-electron systems has been a topic of recent considerable interest, stimulated appreciably by

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† Electronic supplementary information (ESI) available. It contains labeling of atoms, a list of selected bond lengths and bond angles of the experimentally studies systems (**1**)-(**4**), point groups, absolute electronic energies, magnetic susceptibilities and Cartesian coordinates calculated at B3LYP/6-311G** for all analyzed systems.

discovery of fullerenes,[1,2] nanotubes[3] and related systems.[2] It resulted from a fact that nonplanar systems exhibit many properties related to their planar equivalents. There have been investigations concerning [*n*]metacyclophanes,[4] [*n*]paracyclophanes,[5] [*n*]pyrenophanes,[6] helicenes,[7] as well as other deformed benzenoid hydrocarbons[8] and their nonalternant analogues,[9] and Möbius systems.[10] Nowadays it is widely accepted that the term "nonplanar aromatic" is not an oxymoron.[6b]

Two important factors which are decisive about stability and physicochemical properties of non-planar cyclic π-electron compounds are strain and π-electron delocalization effects. In general both of them are large and operate simultaneously, such that a formal separation of their contributions to the overall stability is rather difficult. The effect of distortion on cyclic π-electron delocalization of deformed polycyclic benzenoid hydrocarbons can be assessed by analysis of geometric, energetic and magnetic criteria of aromaticity. Recently isodesmic or homodesmotic reactions have been the best way to obtain reliable results in aromatic systems. Resonance energies (RE)[11] and aromatic stabilization energies (ASE),[12,13] evaluate the favorable effects of cyclic electron delocalization. According to the Pauling-Wheland definition, the RE is the extent to which a real molecule is stabilized relative to the energy of its most stable (virtual) resonance contributor.[14] ASE measures the "extra" stabilization due to cyclic π-electron delocalization of an aromatic system over the stabilization of appropriate conjugated reference counterparts. However, one should be aware that the reference structure is of key importance in these cases. The perfect system should totally eliminate such effects as strain, changes of hybridization or homoaromaticity.

Along with energies, geometric and magnetic criteria also are employed to evaluate aromaticity. Geometric criteria are based on the analysis of bond lengths, which tend in aromatic systems to be intermediate between those typical for single and double bonds. Arguably, the Harmonic Oscillator Model of Aromaticity (HOMA)[15] is the most effective geometric index for gauging the extent of the cyclic π-electron delocalization. Thus, HOMA indicates that even the large distortions from planarity in [5]paracyclophane,[16] twisted naphthalene derivatives,[8a,17] bent pyrenes[6b] and pyrenophanes[6a,18] do not diminish the cyclic π-electron delocalization to large extent.

Magnetic criteria of aromaticity are based on the effects of the diatropic "ring current" induced by an external magnetic field perpendicular to the principal cyclically delocalized electronic system. They may be quantified by ^{1}H NMR chemical shifts in the "aromatic" range,[19] large magnetic susceptibility exaltations[20] and, more recently, by Nucleus-Independent Chemical Shifts (NICS).[21]

Naphthalene, the smallest acene, is a flat, rigid molecule. Nevertheless, the energy required to twist it is rather small. Distortion by 20 degrees costs only *ca.* 3.2 kcal/mol.[22] The crystal structures of most substituted acenes show some deviations from planarity as has been summarized in review by Pascal.[22] The deformation of an acene can be achieved by substitution with bulky groups in *peri* positions. Also replacing all hydrogen atoms mostly (but not always) results in deviation from planarity, because the distortion of torsion angles is much easier than changing bond angles and either stretching or compressing C-C bonds.[23] The most extreme cases among substituted naphthalenes are octakis(arylthio)-naphthalenes.[24] Their twist (measured as the angle θ described in results and discussion part) ranges between 29° and 44°.

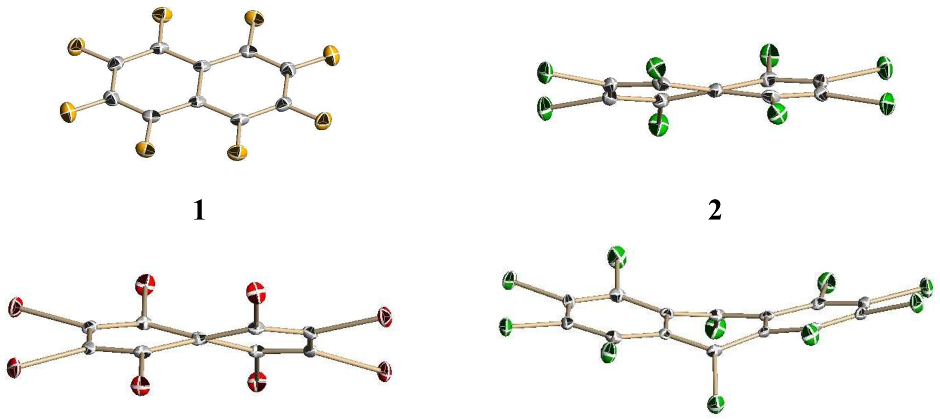
Naphthalenes *per*-substituted by halogen atoms were analyzed earlier.[25] Octachloronaphthalene and octabromonaphthalene show significant twist in hydrocarbon moiety, whereas octafluoronaphthalene is planar. It was calculated by Krygowski[17a] that HOMA value, based on data by Brady et al.,[25c] for perbromonaphthalene showed significant loss of aromaticity. Nowadays X-ray measurements are mostly carried out at low temperatures, what reduces thermal motion of atoms, giving more precise data. To make the analysis consistent we re-determined the crystal and molecular structures of naphthalenes *per*-substituted by halogens at 100 K. Based on these geometries we estimated the extent of cyclic π-electron delocalization with use of the HOMA index, which is defined on the C-C bond lengths of a system (for definition see Ref 15). We are able to show that the cyclic π-electron delocalization is reduced only very moderately, and that the lowering of aromaticity for the most twisted system (perbromonaphthalene) is much smaller than estimated before.[17a] Experimental extension of the analysis for larger acenes was successful for *per*-chloro substituted anthracene. Its crystal structure is also presented.

How much is the cyclic π-electron delocalization influenced upon the distortion from planarity? The systematic study of aromaticity for bent systems has been carried out in numerous articles,[6,18,26] but no such analysis was made for twisted moieties. In this paper we show that the cyclic π-electron delocalization is maintained in twisted acenes by comparing various indices of aromaticity (energetic, geometric and magnetic).

Results and discussion

Crystal structures

In this article we report newly-determined structures of *per*-substituted acenes: perfluoronaphthalene (**1**), perchloronaphthalene (**2**), perbromonaphthalene (**3**) and a novel structure of perchloroanthracene (**4**). They are shown in Figure 1.



1 **2**

3 **4**

Fig. 1. Molecular structures of octafluoronaphthalene (only one molecule forming an independent part of the unit cell is shown) (**1**); octachloronaphthalene (**2**); octabromonaphthalene (**3**) and decachloroanthracene (**4**). Atoms are represented by displacement ellipsoids at 50% probability level.

Octafluoronaphthalene (**1**) crystallizes in monoclinic system, space group $P2_1/c$. An asymmetric part of the unit cell is formed by one and a half of the molecule. One of them lies in general position, whereas another lies on the center of inversion and adopts C_i symmetry. Fluorine is the most electronegative element,[27] so one can expect the repulsive interactions between halogen atoms at carbons C_1 and C_8. The distance between hydrogen atoms at carbon atoms C_1-C_8 in naphthalene equals to 2.463 Å (for numbering of atoms see Figure 2). Taking into account that the sum of van der Waals radii of two fluorine atoms is 2.94 Å,[28] a distortion from planarity might be expected. In the case of octafluoronaphthalene the repulsion of fluorine atoms is stronger than for the hydrogen atoms in naphthalene (the contact is 2.586 Å),[29] but this is not significant enough to twist the molecule. Our results confirm earlier findings:[25a] both molecules of formal C_1 and C_i symmetry are planar within experimental error, while the strain in the structure is mainly reflected in the increase of the bond angles between fluorine and carbon atoms. Figure 1a presents one of the molecules of formal C_i symmetry (for the Figure showing an independent part of the unit cell see the ESI). The exohedral F-C-C angles involving ring-conjunctive carbon atoms (*e. g.* $F-C_1-C_9$) are significantly larger, ranging from 120.0 (1)° to 120.4 (1)° in perfluoronaphthalene, as compared with equivalent H-C-C angles in naphthalene, where they are 118.7°-118.8°.[29] In this situation, also the C-C bond lengths involving the carbons: α and the ring-conjunctive (C_α-C_9 or C_α-C_{10}) should be somewhat elongated in perfluoronaphthalene as compared with the parent system. However, contrary to these expectations they are shorter and range between 1.404(2)-1.417(2)Å versus 1.421-1.422Å, respectively, what is associated with substituent effect of highly electronegative fluorine atom.

Octachloronaphthalene (**2**) crystallizes in monoclinic system, space group $P2_1/n$. There are four molecules in the unit cell, of which one in the asymmetric unit. The molecule is situated in the general position and adopts C_1 symmetry. The sum of the van der Waals radii of two chlorine atoms is much bigger than before (3.50 Å[28]). This leads both to the deviation of the exohedral Cl-C-C bond angles (121.6(1)-122.4(1)°), larger than in the case of octafluoronaphthalene, elongation of the C-C bonds (C_α-C_9 or C_α-C_{10}) to 1.431(2)-1.439(2) Å, but also to significant distortion from planarity. The twist in naphthalene derivatives can be defined in several ways e.g. the θ angle,[22] the angle between the two naphthalene ring planes, ΔP planarity index, which takes into account the mean deviation from the naphthalene moiety,[17a,30] or alternatively maximal deviation of heavy atoms of substitutent.[17a] These measures are almost equivalent for the description of the extent of twist (deviation from planarity), see Figures 5,6 in the ESI. Here we chose θ, proposed by Pascal, as the simplest, but probably also most representative for the description of degree of twist. The rings are twisted by $\theta = 23.3°$ (the twist angle defined as the angle between two terminal bonds C_β-C_β, here: C_2-C_3-C_6-C_7, see Fig. 2), almost to the same extent as in the structure measured at the room temperature.[25b] Notably, the twist of the naphthalene moiety achieved by chlorine atoms is comparable with the one introduced by methyl groups (where θ equals to 26.5°).[31]

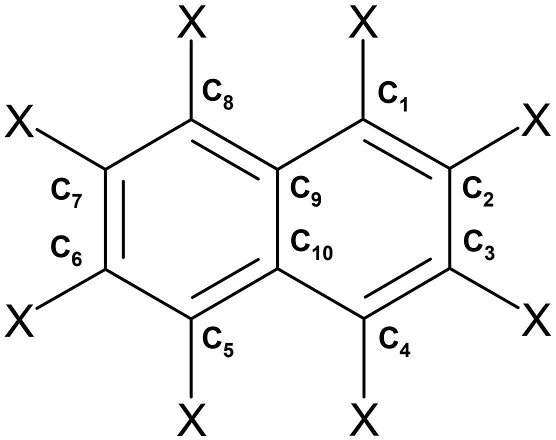


Fig. 2. Numbering of carbon atoms in *per*-substituted naphthalenes.

Octabromonaphthalene (**3**) crystallizes in orthorhombic system, space group *Pbcn*. The asymmetric part of the unit cell is formed by half of the molecule, which is situated at the special position and adopts C_2 symmetry. Consequently, as expected from sum of the van der Waals radii for bromine (3.7 Å), perbromonaphthalene should be characterized by the largest twist in this set. Indeed, the θ angle is 34.7°, significantly larger than in the room-temperature structure (θ=30.8°).[25c] This might be attributed to lower vibrations of atoms at 100 K, however it is fair to note that the quality of the room-temperature measurement is too low to make far-reaching conclusions. Also the deformations of the exohedral Br-C-C bond angles (119.8(2)-120.1(2)°) and the elongation of the C_α-C_9 or C_α-C_{10} (1.433(3)-1.436(3)Å) are observed, but notably, they are very similar as in the case of perchloronaphthalene.

Decachloroanthracene (**4**) crystallizes in triclinic *P-1* space group with one molecule in an independent part of the unit cell (see Figure 1). Contrary to the expectations[32] release of strain is not realized by twist but by bending of the molecule, what results in a “boat-like” shape. Although the difference in energy between the two conformations (twist vs boat) is not large and equals to 3 kcal/mol (estimated at B3LYP/6-311G** level of theory), indicating that the lowest energy system is the one observed in the crystal lattice, this is the only available structure of *per*-substituted acene adopting such conformation.[33] The definition of the distortion from the planarity is modified in this case. It is based on best-planes calculated for two fragments including outer six-membered ring and two carbon atoms in the central ring, as shown in Figure 3. In this case the angle Φ is very high and equals to 19.2°. Despite large deviation from planarity it retains aromatic characteristics of planar anthracene molecule.

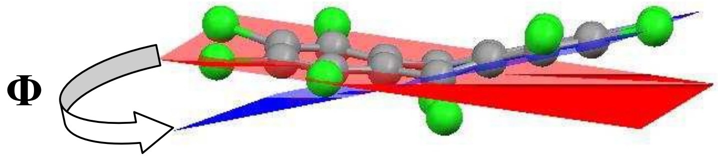


Fig. 3. The definition of Φ angle.

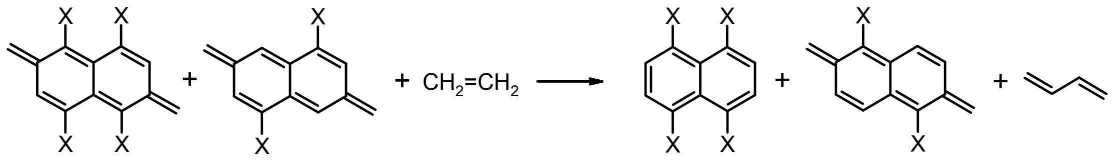
Cyclic π-electron delocalization, stabilization and strain energies

The experimental geometries of perfluoro-, perchloro- and perbromonaphthalene can be used to assess the extent of π-electron delocalization as quantified by the geometry-based index of aromaticity HOMA. The values are presented in Table 1 (for definition of the index see Ref. 15). As can be seen, they systematically decrease with an increase of the twist angle θ. However, it is worth noting, that the lowering of aromaticity is monotonic (see Figure S7 in the ESI†), but rather small. The values drop down only by 0.128 of the HOMA unit (HOMA is defined in the range 0-1), with the twist angle increased up to 34.7°. To compare how do these values refer to the systems without intermolecular interactions in the crystal lattice, we also fully optimized the molecules at B3LYP/6-311G** level of theory. The differences between experimental and theory-based aromaticity values are rather small and do not qualitatively affect final results and the discrepancies.

Tab. 1. Twist angles θ (°) and HOMA indices for *per*-substituted naphthalenes based on experimental and calculated data.

Compound	**X-RAY**		**B3LYP/6-311G****	
	θ (°)	**HOMA**	**θ (°)**	**HOMA**
Naphthalene[34]	0	0.806	0	0.806
Perfluoronaphthalene	0.0	0.783	0	0.816
Perchloronaphthalene	23.3	0.716	27.7	0.687
Perbromonaphthalene	34.7	0.678	36.3	0.662

Apart from geometry, which is most often the easiest accessible source of information about aromaticity, energetic and magnetic criteria are also very substantial.[13c] Next step was to estimate aromatic stabilization energy (ASE) for naphthalene and its derivatives. In the case of polycyclic systems defining a model homodesmotic reaction (of key importance to obtain comparable results) is rather difficult. The main reason is that the acyclic reference structure do not balance strain and hyperconjugation, besides differences in types of bonds and hybridization are often not taken into account. The problem was discussed in review by Cyrański.[12] It seems that the most rational way is to compare the energy of given aromatic system with the model π-electron system, where there is a formal localization of single $C_{sp^2} - C_{sp^2}$ and double $C_{sp^2} = C_{sp^2}$ bonds and the geometry (strain) is similar to the aromatic system. In this article we propose the reactions, where the reference structure is a dimethylene derivative of considered compound. The basis of this method are the radialene systems, properly reproducing the ASE of benzene[12] and other benzenoid hydrocarbons.[35,36] We applied dimethylene derivatives that enforce fully localized model structure of considered system and allow to balance strain without any additional contributions. In fact it is impossible to estimate ASE for *per*-substituted naphthalene derivatives using that kind of reaction, due to lack of reference systems. Instead, a model approach for *peri*-substituted derivatives can be used. These systems are significantly twisted as well. In the case of reference structure used for both *peri*-substituted compounds and naphthalene itself, there are interactions between hydrogen atoms from methylene groups and the atom in position 1 and 5. They can be balanced using additional reference systems, *i.e.* substituted in positions 4, 8 and 1, 5. Then the reaction takes the following form:

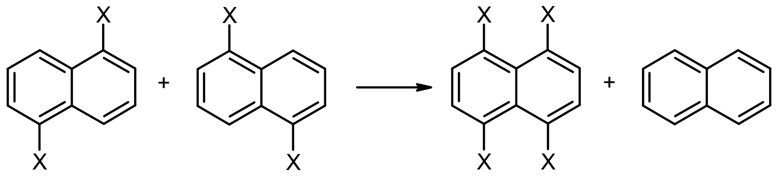


X = -H, -Cl, -Br, -CH_3, -*t*-but

(1)

Above-mentioned reactions can be also used for estimation of magnetic susceptibility exaltations, Λ, replacing the energy values by appropriate susceptibility values. In order to extend the analyses methyl and *t*-butyl substituents were included. The ASE and magnetic susceptibility values are given in Table 2.

Another structural effect which operates simultaneously with aromaticity, influencing the stability of a system, is molecular strain.[37] In order to estimate strain energy effect (SE), we proposed another homodesmotic reaction. The strain is balanced using *peri*-substituted naphthalene and derivatives 1, 5:

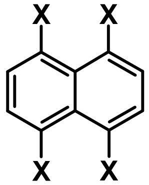


X = -H, -Cl, -Br, -CH_3, -*t*-but

(2)

Apart from aromaticity indices Table 2 presents the values of twist angles, and strain energies for all studied naphthalene derivatives. As might be expected, the largest twist is observed for 1,4,5,8-*t*-butyl-naphthalene, due to large steric effects between the substituents. It is worth mentioning that even the mostly twisted system (θ = 51.7°) preserves *ca.* $^1/_3$ of the stability due to cyclic π-electron delocalization in respect to the parent naphthalene. In this context it is striking to note that the values of HOMA decrease to smaller extent than ASE, whereas the magnetic susceptibility exaltations variation is even smaller for all substituted systems. As it is expected an increase of the deviation from planarity is accompanied with an increase of the strain. Its increase is comparable with the decrease ASE.

Tab. 2. Twist angles θ (°), HOMA indices, aromatic stabilization energies ASE (kcal/mol), strain energies SE (kcal/mol), magnetic susceptibility exaltations Λ (cgs-ppm) for *peri*-substituted naphthalene derivatives.

	**θ [°]**	**HOMA**	**ASE [kcal/mol]**	**SE [kcal/mol]**	**Λ [cgs-ppm]**
-H	0	0.806	31.6	0	27.9
-CH_3	14.5	0.577	27.0	-15.6	21.0
-Cl	17.1	0.641	29.4	-22.5	22.2
-Br	23.0	0.638	28.1	-25.8	22.1
-t-but	51.7	0.467	12.5	-26.0	20.9

The dependence between aromatic stabilization energy and twist angle θ is shown in Figure 4. Although the dependence is not perfect, most probably due to substituent effect influencing the aromatic system, it is apparent that the cyclic π-electron delocalization of strained systems decreases in a regular way with increasing the twist and is preserved to a high extent even for large angles. The dependencies between strain energy and other parameters look a little bit worse (see Figure S8 in ESI†), but the qualitative relationships are still preserved.

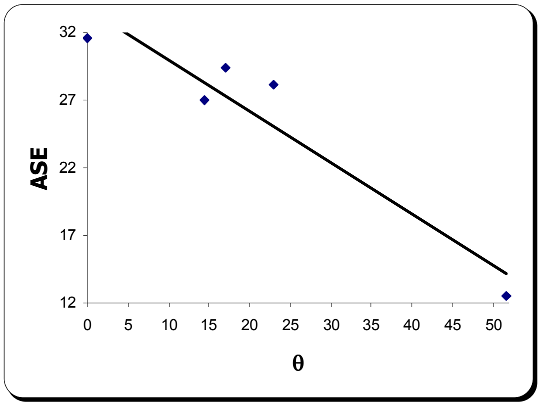
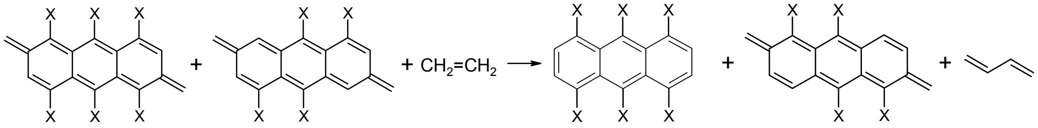


Fig. 4. The dependence of ASE and θ angle, R = 0.950.

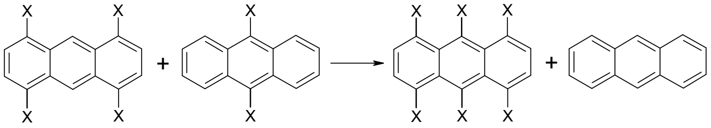
The analysis has been further extended for anthracene derivatives. As previously mentioned decachloroanthracene moiety adopts boat conformation, which is the most stable one. Despite of significant degree of bent (Φ=19.2°) its aromaticity estimated by the HOMA index is retained to high extent (HOMA= 0.656) as compared with the parent planar molecule[38] (HOMA=0.685). Starting with this geometry we have modeled *peri*-substituted analogues using *ab initio* methods.[39] In order to evaluate the aromatic stabilization energies, but also exaltations of magnetic susceptibility, we propose a similar approach as for naphthalene, with use of the components having the same type of conformation. The reaction scheme is as follows:



X = -H, -Cl, -Br, $-CH_3$

(3)

Consequently, to evaluate the strain energies we proposed the following scheme:

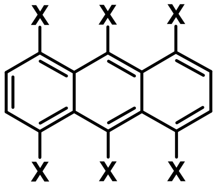


X = -H, -Cl, -Br, $-CH_3$

(4)

The bent angle values, indices of aromaticity: HOMA, ASE, Λ and strain energies are gathered in Table 3. While the Φ angle changes by 17.7°, the variability of ASE and HOMA index is only 6.1 kcal/mol and 0.184 unit, respectively. Based on these data it can be concluded that aromaticity of anthracene derivatives deviated from planarity changes slightly, but much less regularly with an increase of the Φ bent angle. Anthracene is less aromatic system than naphthalene, therefore some larger discrepancies between aromaticity indicators may be observed. Notably, the exaltation of magnetic susceptibility for methyl derivative is higher than for the *peri*-bromoanthracene, despite the Φ angle being smaller. It is also worth mentioning that the strain energy estimated for methyl derivative is much smaller than for *peri*-bromoanthracene or *peri*-chloroanthracene, what may result from the fact that, in anthracene derivatives strain is released not only by distortion from planarity, measured in a simple way by Φ bent angle, but also by twist of the molecule, which is difficult to be easily defined. These two factors may also influence the methylene derivatives used for ASE, Λ and SE estimations to much higher extent than in the case of naphthalene moiety.

Tab. 3. The values of Φ angles (°), HOMA indices, aromatic stabilization energies ASE (kcal/mol), strain energies SE (kcal/mol), magnetic susceptibility exaltations Λ (cgs-ppm) for *peri*-substituted anthracene derivatives.

	**Φ[°]**	**HOMA**	**ASE [kcal/mol]**	**SE [kcal/mol]**	**Λ [cgs-ppm]**
-H	0	0.713	35.1	0	41.3
-Cl	15.7	0.599	30.2	-44.0	32.7
$-CH_3$	16.8	0.529	31.4	-30.4	35.6
-Br	17.7	0.587	29.0	-48.6	30.1

Despite of these limitations, it is worth noting that aromaticity parameters as well as strain energies correlate with the Φ angle reasonable well. The relations are shown in Figures S10(**a**), (**b**), (**c**) in the ESI†. They show a slight decrease of cyclic π-electron delocalization with increasing deviation from planarity of the systems.

Experimental

Synthesis

Perfluoronaphthalene (**1**) was purchased from Sigma-Aldrich. Perchloronaphthalene (**2**) and perbromonaphthalene (**3**) were newly synthesized according to procedure described by Deacon and Farquharson in reference [40]. The synthesis of periodonaphthalene in a similar way not successful. Perchloroanthracene (**4**) was synthesized in the following way: 1,2,3,4,5,6,7,8,9,9,10,10-dodecachloro-4a,9,9a,10-tetrahydroanthracene was obtained from anthracene and large excess of sulphuryl chloride, in the presence of catalytic quantities of aluminum (III) chloride and dichlorosulphur. The compound was reduced with sodium dithionide in aqueous solution of dimethylformamide. Then the product was purified by recrystallization from tetrachloroethylene. The synthesis of perbromoanthracene in the analogous way was not successful.

X-ray diffraction

Crystals of (**1**), (**2**) and (**3**) suitable for X-ray measurements were obtained by slow evaporation of ethanol, whereas crystals of decachloroanthracene (**4**) were grown by slow evaporation from toluene. The X-ray measurements were performed at 100 (2) K on a KUMA CCD k-axis diffractometer with graphite-monochromated Mo Kα radiation (0.71073 Å). The crystals were positioned 62.25 mm from the KM4CCD camera; 214 frames were measured at 0.25° intervals with a counting time of 25s, 150 frames were measured at 0.25° intervals with a counting time of 10s, 300 frames were measured at 0.5° intervals with a counting time of 25s, 250 frames were measured at 0.25° intervals with a counting time of 15s, respectively for (**1**), (**2**), (**3**), (**4**). Data collection, cell refinement and data reduction for (**1**), (**2**), (**3**), (**4**) were carried out with the KUMA Diffraction programs: CrysAlis CCD and CrysAlis RED.[41] The data were corrected for Lorentz and polarization effects and absorption correction was applied for octabromonaphthalene. The structures were solved by direct methods[42] and refined using SHELXL.[43] The refinement was based on F^2 for all reflections except for those with very negative F^2. The weighted R factor, wR and all goodness-of-fit S values are based on F^2. The non-hydrogen atoms were refined anisotropically. The atomic scattering factors were taken from the International Tables.[44] Crystal structures and refinement are specified in Tables S1 and S5 in the ESI†. A list of selected bond lengths and bond angles is given in Tables S2, S3, S4 and S6 (ESI†). The figures were generated with Mercury (ver. 3.5).[45] Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1436913-1436916. These data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Computational details

All systems (except for perbromonaphthalene) were fully optimized at B3LYP/6-311G** level of theory.[46] All species corresponded to minima at the B3LYP/6-311G** level, with no imaginary frequencies. For perbromonaphthalene hybrid density functional calculations were performed, using effective core potential for the bromine atoms (recommended by Stanger, B3LYP/LanL2DZ theoretical level, reliably reproducing the crystal structure of octakis(bromomethyl)naphthalene).[47] Due to several problems connected with convergence for *peri*-*t*-butyl-substituted anthracene as well as for its methylene derivatives, this system has not been taken into account in the analyses. The magnetic susceptibilities (Λ) were computed at the CSGT/B3LYP/6-311G** level of theory[48] by using optimized geometries at the B3LYP/6-311G** DFT level. The calculations were performed using the Gaussian 03 program.[49]

Conclusions

Based on experimental data as well as on molecular modeling for series of *per*- and *peri*-substituted naphthalenes and anthracene derivatives we have shown that deviation from planarity leads to relatively small changes in cyclic π-electron delocalization. To estimate the aromatic stabilization energies and exaltations of magnetic susceptibilities, but also strain energies we have proposed a set of homodesmotic reactions based on systems having similar conformations. They revealed that the deviation from planarity (both by twist and bent) in the simplest linear acenes does not lead to dramatic changes in π-electron delocalization. The situation looks very similar to curved aromatic molecules such as pyrenophanes.[6a] In fact it is not easy to compare the extent of changes in both cases as pyrene and naphthalene (anthracene) differ by size, topology, and stability, however, in both cases a smooth, but regular decrease of aromaticity is observed in rather large range of distortion. For per-substituted naphthalenes the aromaticity, as measured by the HOMA geometry-based index, is retained in 84% going from most planar to the most twisted by 34.7°, while for series of pyrenophanes it is 91% going from (planar) pyrene to the most bent system by *ca.* 40°.[6a]

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