Interplay of π-Electron Delocalization and Strain in [*n*](2,7)Pyrenophanes

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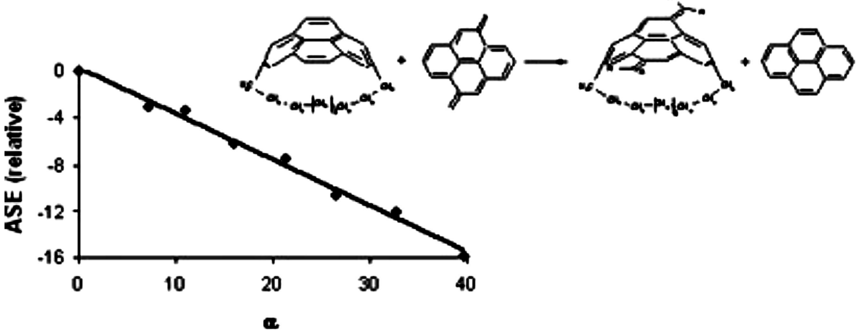

The geometries of a series of [*n*](2,7)pyrenophanes ($n = 6-12$) were optimized at the B3LYP/6-311G** DFT level. The X-ray crystal structures determined for the [9](2,7)- and [10](2,7)pyrenophanes agreed excellently with the computed structures. The degree of nonplanarity of the pyrene moiety depends on the number of CH_2 groups in the aliphatic bridge and, as analyzed theoretically, influences the strain energy and the extent of π-electron delocalization in the pyrene fragment. Various indices, e.g., the relative aromatic stabilization energies (ΔASE), magnetic susceptibility exaltations (Λ), nucleus-independent chemical shifts (NICS), and the harmonic oscillator model of aromaticity (HOMA) were used to quantify the change in aromatic character of the pyrene fragment. ΔASE and relative Λ values (with respect to planar pyrene) were evaluated by homodesmotic equations comparing the bent pyrene unit with its bent quinoid dimethylene-substituted analog. The bend angle, α, ΔASE, and Λ were linearly related. The aromaticity decreases smoothly and regularly over a wide range of bending, but the magnitude of the change is not large. The differences between planar pyrene ($\alpha = 0°$) and the most distorted pyrene unit ($\alpha = 39.7°$ in [6](2,7)pyrenophane) are only 15.8 kcal/mol (ΔASE) and 18.8 cgs-ppm (Λ). Also, the geometry-based HOMA descriptor changes by only 0.07 unit. The local NICS descriptors of aromatic character also correlate very well with the global indices of aromaticity. In line with the known reactivity of pyrenophanes, the variations of NICS(1), a measure of π-electron delocalization, were largest for the outer, biphenyl-type rings. The strain energies of the pyrene fragments were much larger and varied more than those evaluated for the bridge. Both strain energies were interrelated (correlation coefficient $R = 0.979$) and depend on the bend angle, α.

Introduction

The consequences of the competing energetic effects of aromatic stabilization and strain in highly distorted π-electron systems, long subjects of broad interest, are of recent concern in fullerenes,[1,2] nanotubes,[3] and related systems.[2] Nonplanar cyclic π-electron systems like [*n*]paracyclophanes,[4] [*n*]metacyclophanes,[5] and helicenes,[6] as well as other deformed benzenoid hydrocarbons[7] and their nonalternant analogues,[8] and Möbius systems[9] exhibit many of the physicochemical properties associated with their planar counterparts. Such observations have established that planarity is not a condition sine qua non for aromaticity.[10] This traditional perception was based on the preference for planarity of conventional mono- and polycyclic

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aromatic systems and the expectation that substantial π-electron delocalization can take place only in planar systems where p-orbital overlap is optimum. In contrast, it is now widely accepted that the term "nonplanar aromatics" is not an oxymoron.[11] The loss of p overlap between adjacent p orbitals is insignificant for small degrees of twist; even 30° twist angles reduce overlap modestly, by less than 15%.[12]

The geometrical preferences of the σ framework may be more important. Indeed, conformational flexibility increases with the size of an aromatic system.[13] The decrease in the out-of-plane "wagging" vibrational frequencies along the series of linear acenes is illustrative: their animation resembles the wings of a sea gull in flight.[14] For pyrene the calculated lowest out-of-plane vibrational frequency, b_{3u}, is 92.1 cm^{-1}.[15] Even the weak intermolecular interactions in crystals of benzene lead to significant distortion from planarity of the rings.[16] Importantly, aromaticity is only one of the determinants of the overall stability and other physicochemical properties, especially of highly distorted molecules where strain effects involving the σ framework may dominate.[17−20]

The effect of distortion on the aromatic character of deformed polycyclic benzenoid hydrocarbons can be judged by comparing their energetic, geometric, and magnetic properties with those of appropriate planar model systems. Aromatic species are stabilized by cyclic π-electron delocalization, but both their π and σ systems are destabilized by distortions from optimal geometries. Distortion also increases the strain of, e.g., the tethering side chains in cyclophanes. We address the problem of dissecting changes in both ring and side-chain strain from aromaticity variations in the present paper. As neither strain nor aromaticity are observable (directly measurable) properties, methods as free as possible from other perturbing influences must be devised.[20,21]

Resonance energies (RE)[18] and aromatic stabilization energies (ASE)[12,19−21] 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.[21] ASEs measure the "extra" stabilization relative to nonconjugated or partly conjugated references. Necessarily, ASEs are inherently much smaller than RE values, but these are often not adequately distinguished in the literature.

Many methods, theoretical as well as those based on experimental data, have been employed to evaluate REs and ASEs. Isodesmic[22] reactions conserve the number of bonds of each formal type, e.g., C−H, C−C, C=C, while allowing the relationships among the bonds to vary. Homodesmotic[23] evaluations aim to balance hybridization and demand more sophisticated, but often arbitrary, choices of reference molecules. More than one "homodesmotic" definition has been followed.[20] "Bond separation reactions", the simplest isodesmic approach, are nonarbitrary and well-defined[24] but do not correct for all hybridization differences. It has been pointed out that "stabilization energy" estimates for the same molecule in the literature vary substantially (e.g., by ca. 50 kcal/mol for benzene, if one includes both RE and ASE evaluations).[25] This unsatisfactory disagreement is due to conceptual differences, to flaws in the choices of reference compounds, and in the formulation of the reaction schemes[19d] as well as the level of theory[20,26] (the quality of experimental data).[27] When perturbing influences are removed or compensated, it has been shown recently that various equations give essentially the same estimates of REs or of ASEs.[21b]

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The problem becomes much more complex in strained polycyclic aromatic systems, where the stabilization due to cyclic π-electron delocalization and the destabilization due to strain can both be large. It is very difficult to unambiguously separate their opposing contributions to the total energy. Strain energies also are evaluated by homodesmotic (or isodesmic) treatments. Many methods used to estimate ASEs for strained systems are flawed. A classic and highly instructive example pertinent to the present work is the highly distorted [5]paracyclophane,[28,29] which was employed in Minkin et al.'s book on aromaticity and antiaromaticity[19a] to illustrate the ambiguities and difficulties of aromaticity evaluations. The Möbius system prepared by Herges and his co-workers is another very recent example.[9] It is hard to establish if the central [16]annulene moiety is stabilized or not.

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. The precise values of ring bond lengths emerge from the interplay of σ and π effects,[30] which also requires consideration. Moreover, bond lengths based on the internuclear separations of adjacent atoms do not necessarily describe bonding properly in highly strained systems; the "bent" bond path may be a more suitable description.[31] Despite these shortcomings, geometry-based criteria are widely used, often as "first indications", since the requisite data are readily available (both experimentally and theoretically). Arguably, the harmonic oscillator model of aromaticity (HOMA)[25,32] 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,[25] twisted naphthalene derivatives,[7a,32] bent pyrenes,[11] and pyrenophanes[33] do not diminish to large extent the cyclic π-electron delocalization.

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. These criteria have been quantified by ^{1}H NMR chemical shifts in the "aromatic" range,[34] large magnetic susceptibility anisotropies[35] and exaltations,[36] and more recently, by highly negative nucleus-independent chemical shifts (NICS). Magnetic-field-induced current maps[37] afford extremely instructive visualizations of π-electron delocalization effects, but highly bent systems are complicated by $\sigma-\pi$ mixing.[8c,38,39] Note that the term "π electron delocalization", employed in our paper for highly bent systems, is an approximation because of the $\sigma-\pi$ mixing.

It is well accepted that planarity is no longer a necessary prerequisite for effective π overlap.[11,40] The more important question of exactly how much the degree of distortion from planarity affects the cyclic π electron delocalization has been addressed, for example, by using Haddon's POAV method[40] but has not been answered fully. It is imperative to employ methods that separate aromaticity and strain contributions to the total energy effectively. Pyrene, a highly symmetrical benzenoid hydrocarbon, was chosen as the basic system to answer these questions. Bodwell et al.'s investigations of a series of [*n*](2,7)pyrenophanes showed that the degree of bending of the pyrene units not only spans a wide range but also can be fine-tuned by adjusting the constitution of the bridge.[11,41,42] The magnetic and geometric criteria of aromaticity, applied to a series of pyrene models constrained to mimic the distorted experimental geometries of pyrenophanes, indicated that the π-electron delocalization was well preserved, even in the most bent systems. However, the energetic evaluations were far from conclusive.[11] The present paper overcomes this problem and presents a general approach for the reliable estimation of ASE changes as well as strain contributions in deformed polycyclic molecules, ranging from planar to highly bent geometries. The relationships among the π-electron delocalization in the pyrene unit, the strain induced by its distortion from planarity, and the strain in the bridge are elucidated.

Results and Discussion

The X-ray diffraction single crystal structures of [9](2,7)pyrenophane[42] and [10](2,7)pyrenophane[41e] were determined at

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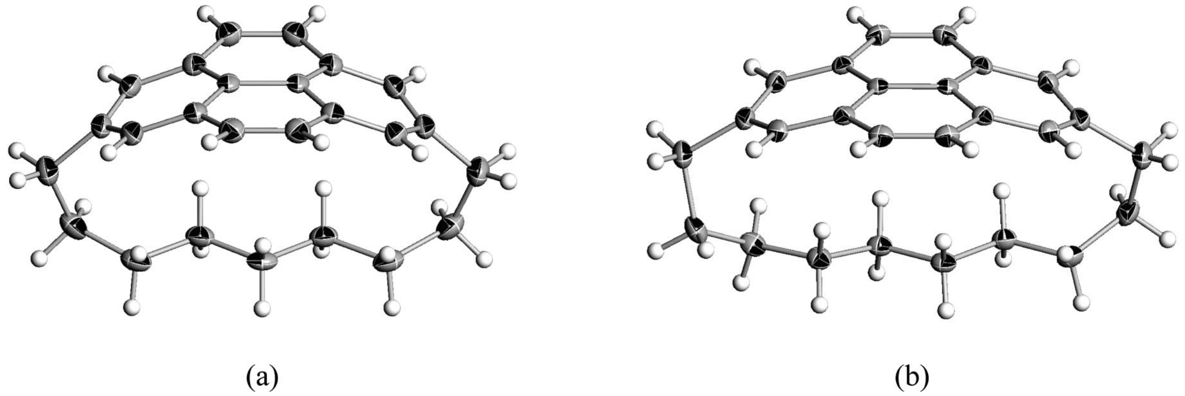
(a) (b)

FIGURE 1. Molecular structures of [9](2,7)pyrenophane (a) and [10](2,7)pyrenophane (b). The displacement parameters are drawn at the 50% probability level. The disorder of the alkyl bridge is not shown.

TABLE 1. Selected Experimental and B3LYP/6-311G-Optimized (in Bold) Bond Lengths [Å] and Bend Angle α [deg] for [9](2,7)Pyrenophane, [10](2,7)Pyrenophane, and Pyrene**[a]

	point group	α	B1, B1′	B2, B2′	B3, B3′	B4, B4′	B5, B5′	B6
[9](2,7)pyrenophane	C_{2v}	20.5	1.389(2)	1.397(2)	1.419(2)	1.430(3)	1.359(3)	1.425(5)
	C_s	**21.3**	**1.396**, **1.399**	**1.399**, **1.400**	**1.423**, **1.425**	**1.438**, **1.440**	**1.358**, **1.358**	**1.422**
[10](2,7)pyrenophane	C_{2v}	15.0	1.391(1)	1.401(2)	1.422(1)	1.437(1)	1.355(2)	1.425(3)
	C_2	**15.9**	**1.398**, **1.396**	**1.400**, **1.400**	**1.425**, **1.423**	**1.438**, **1.438**	**1.359**, **1.359**	**1.421**
pyrene	C_1	0.0[b]	1.385	1.402	1.422	1.436	1.352	1.427
	C_1	0.0[c]	1.383	1.399	1.423	1.438	1.341	1.428
	D_{2h}	**0.0**	**1.391**	**1.402**	**1.426**	**1.436**	**1.358**	**1.426**

[a] For the latter system the experimental bond lengths are given as mean values for equivalent bonds. Geometrical parameters are defined in Figure 2. [b] Data for polymorph I.[44] [c] Data for polymorph II.[45]

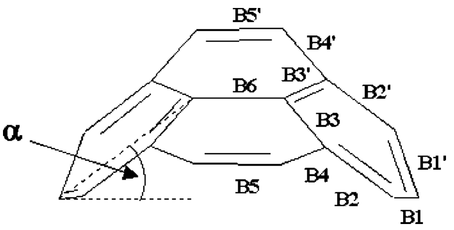

FIGURE 2. Structural parameters in bent pyrenes and definition of the bend angle, α.

100 K (see Figure 1; Table 1 gives selected bond lengths) in order to augment the known experimental geometries of [*n*](2,7)pyrenophanes[42] and their derivatives with oxygen atoms[11,41] or aromatic fragments[43,44] incorporated in the bridge. Attempts to grow crystals of [7](2,7)pyrenophane of sufficient quality for X-ray structure determination were unsuccessful.

The crystal structures of the two [*n*](2,7)pyrenophanes are similar: both crystallize in the *Pmmn* space group. The molecules are constrained to have C_{2v} symmetry since they lie on two mirror planes so that an independent part of the unit cell is formed by one-fourth of the molecule. Consequently, the bridges are forced to be disordered over two positions (not shown in Figure 1, see Supporting Information). This situation is not unusual: although the pyrene moieties lie in general positions in its crystal lattice (and therefore have C_1 symmetry),[44,45] distorted systems often have higher molecular symmetries. For example, [8](2,7)pyrenophane,[42] 1,9-dioxa[9](2,7)pyrenophane,[11] and 1,10-dioxa[10](2,7)pyrenophane[11] have the point groups C_2, C_s, and C_{2v}, respectively.[11] For [*n*](2,7)pyrenophanes, where the *n* is even, this results from the fact that they may exist in two enantiomeric forms, which are impossible to separate out. It is clear that the 15−20° distortion from planarity (the bend angle, α, as defined in Figure 2) of the pyrene systems in [9](2,7)pyrenophane and [10](2,7)pyrenophane does not lead to significant changes in the bond lengths of the pyrene units, compared to each other and to pyrene itself. The largest discrepancy is the slight elongation of the pyrene CC bonds (1.389−1.391 vs 1.383 Å) at the sites of bridge formation due to the substitution.

The optimized geometries (computed at the B3LYP/6-311G** DFT level) agree almost perfectly with experimental values for equivalent types of bonds. The mean CC bond length differences are 0.003−0.005 Å for the pyrene moieties and 0.007−0.011 Å for the bridges. Moreover, the bend angle, α, differs minimally (0.8−0.9°) from the experimental value (see Supporting Information for geometrical details). Such excellent agreement, especially in view of the experimental errors expected from the static disorder in the crystals, validates the level of theory employed, at least for the geometries. This paper is chiefly concerned with relative energies; these should be given satisfactorily as well due to error cancelation.

The relationship between the effects of π-electron delocalization and the nonplanarity of the pyrene moiety were investigated systematically by optimizing seven [*n*](2,7)pyrenophanes, with [*n*] ranging from 6 to 12, as well as the parent pyrene system, at the same DFT level. The successive removal of CH_2 units from the bridge increases the bend angle, α, from 7.2° ($n = 12$) to 39.7° ($n = 6$) (see Table 2). This distortion from planarity is not much larger than that of 1,7-dioxa(7)(2,7)pyrenophane,[41b] (the most highly bent pyrene to have been isolated and characterized to date), where α is 36.8°.

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(43) Bodwell, G. J.; Miller, D. O.; Vermeij, R. J. *Org. Lett.* **2001**, *3*, 2093–2096.

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TABLE 2. Descriptors of π-Electron Delocalization of [*n*](2,7)Pyrenophanes[a]

system	k	point group	α [deg]	ΔASE [kcal/mol]	rel Λ [cgs-ppm]	HOMA
[6](2,7)pyrenophane	0	C_2	39.7	−15.8	18.8	0.672
[7](2,7)pyrenophane	1	C_S	32.7	−12.1	17.5	0.703
[8](2,7)pyrenophane	2	C_2	26.5	−10.6	14.3	0.725
[9](2,7)pyrenophane	3	C_S	21.3	−7.5	11.3	0.736
[10](2,7)pyrenophane	4	C_2	15.9	−6.2	9.5	0.744
[11](2,7)pyrenophane	5	C_S	11.0	−3.4	7.0	0.742
[12](2,7)pyrenophane	6	C_2	7.2	−3.1	6.3	0.742
pyrene		D_{2h}	0	0.0	0.0	0.742

[a] k is defined in eq 1 and the bend angle, α, in Figure 2. The ΔASE and relative Λ values are based on pyrene.

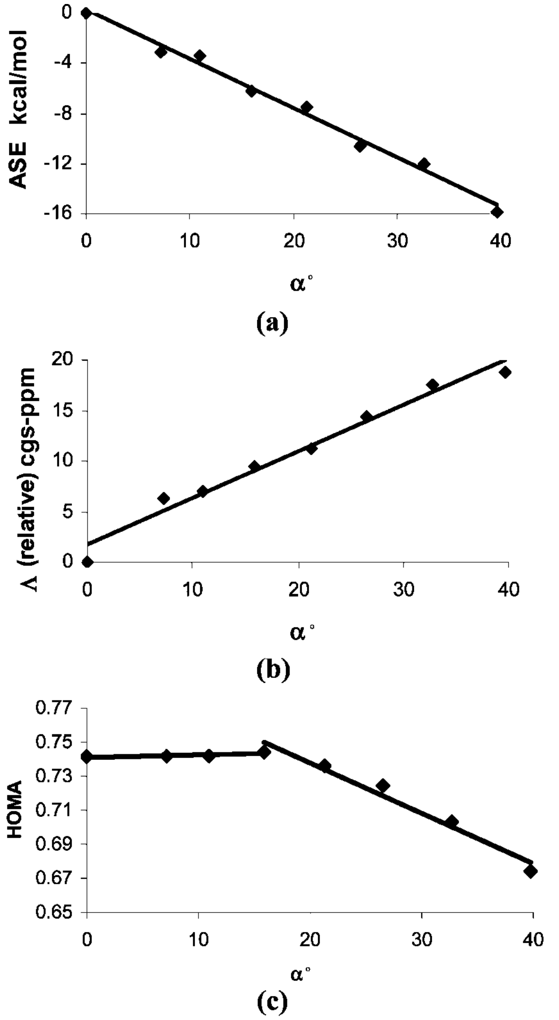

FIGURE 3. Dependence between α° and the relative stabilization energy, relative Λ and HOMA: (a) relative aromatic stabilization energy versus α° (R = 0.996, eight points); (b) exaltation of magnetic susceptibility (cgs-ppm), relative Λ, versus α° (R = 0.988, eight points); (c) HOMA versus α° (R = 0.983 for the right part, five points).

The opposing effects of π-electron delocalization (aromaticity) and strain need to be dissected in some reasonable way. The aromaticity component might be evaluated indirectly[11] based on correlations of stabilization energies with other descriptors of aromaticity, but this is not always reliable.[19c] Alternatively, ASEs can be estimated by comparing the energies of the bent aromatic system of interest with a similarly bent nonaromatic analog. Strain estimates based on distortion from planarity of such cyclic references are far more appropriate than those based on linear (or branched) polyene models. This strategy, which effectively cancels or significantly reduces the effects of strain, is applied in the isomerization stabilization energy (ISE) method.[12] This compares the total energies of two species: a methyl derivative of the aromatic system (e.g., toluene) and its nonaromatic, conjugated isomer with an exocyclic methylene group (e.g., methylenecyclohexa-2,5-diene (isotoluene)). Application of this ISE method to strained systems revealed, contrary to previous expectations,[29] that the stabilization due to π-electron delocalization may only be reduced modestly by out-of-plane deformation. This reduction was about 12 kcal/mol in [5]paracyclophane[12,29] (relative to undeformed benzene). Despite the enforced nonplanarity, bridged 10 π-electron 1,6-methano[10]annulene[12,46] is still stabilized by ca. 25.4 kcal/mol, approximately half as much as naphthalene.[47] The ISE method can easily be extended to heterocycles, charged species (e.g., the cyclopropenium cation), radicals, or systems with open shell character (e.g., benzynes), and polycyclic compounds.

While the stabilization energies of methyl-substituted aromatics are expected to be similar to those of their parent systems,[48] nonaromatic cyclic reference isomers with a single exocyclic methylene group and one saturated carbon atom in the ring have imperfections due to the concomitant incorporation of an sp^3-hybridized carbon into the ring. Such isomers may not balance the strain of their aromatic counterparts closely, and they may be perturbed by extra stabilization due to hyperconjugation and/or homoaromaticity. Instead, ideal reference systems should have only sp^2-hybridized carbons and fully localized π-electron structures. Incorporation of a second exocyclic methylene group can solve both objectives. A pair of methylene groups at appropriate sites enforces highly conjugated but nonaromatic reference molecules with localized single and double bonds throughout the entire system. Such quinoidal reference systems model the sigma framework of the corresponding aromatic compound closely. A great advantage of this approach is the convenience of its application to both monocyclic and polycyclic systems. For example, the ASE of benzene based on 1,4-quinodimethane, ethylene, and 1,3-butadiene (corrected for *syn-anti* conformation imbalance, see below)[20] is consistent with other ASEs based on isodesmic reactions, e.g., the ISE,[12] on reactions with radialenes as references,[20,21] and with the 28.8 kcal/mol ASE value recommended recently.[20,21b] As in polyenes and radialenes,[49] the localization of bonds leads to additive energy relationships. Quinoidal structures have also been used as reference systems for estimating the ASEs of giant polycyclic aromatic hydrocarbons, recently.[50] However, more than one

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(46) Vogel, E.; Roth, H. D. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 228–229.

(47) Ciesielski, A.; Cyrański, M. K.; Krygowski, T. M.; Fowler, P. W.; Lillington, M. *J. Org. Chem.* **2006**, *71*, 6840–6845.

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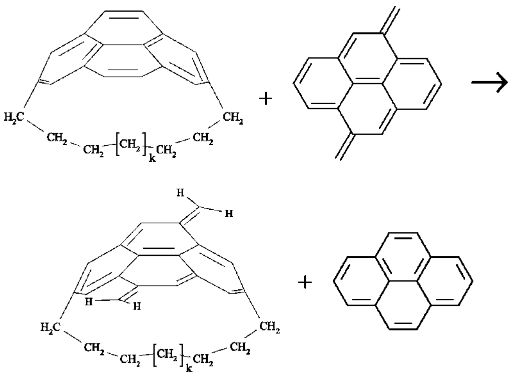
(50) Hajgato, B.; Deleuze, M. S.; Ohno, K. *Chem. Eur. J.* **2006**, *12*, 5757–5769.

reference system may be available and its selection may influence the determination of the ASE value. For pyrene, three reference systems, 2,7-didehydro-2,7-dimethylenepyrene, 4,9-didehydro-4,9-dimethylenepyrene and 2,4-didehydro-2,4-dimethylenepyrene, have enforced quinoid structures. Since their energies differ, the estimated ASE values may depend on their choice.

The need for corrections due to imbalances in the number of formal *syn-anti* butadiene structural subunits[12] is a significant complication of the dimethylene/quinoid method. The *anti* conformation of butadiene is *ca*. 3.6 kcal/mol more stable than the *syn*. The aromatic (pyrene) and the nonaromatic refereence molecules (the didehydrodimethylenepyrene isomers) differ in the number of *syn* and *anti* subunits they contain, so that ASE estimations require appropriate corrections. As this is not straightforward, details will be discussed in a subsequent paper, where we recommend a 77.8 kcal/mol ASE value for pyrene based on both BLW[21] and isomerization energy[12,20] approaches. This is not an issue in the present paper, since it is focused on the *changes* of aromaticity upon bending (ΔASE), rather than the absolute aromaticity values of each pyrenophane. Since the same evaluation method is used for the entire [*n*](2,7)pyrenophane series, no interpretive ambiguities are involved. We base the *relative* energy evaluations (ΔASE) on eq 1, a fully homodesmotic reaction relating the ASE of a pyrenophane relative to that of pyrene:



(1)

This strategy is particularly useful for evaluating the ASEs of nonplanar aromatic systems, since the reference compounds and the parent aromatics are strained to similar extents and the hybridization of all of their atoms match. As expected, the aromatic stabilization energy of the pyrenophanes decreases with increasing bending, but the range (ΔASE = 15.8 kcal/mol) is rather small (see Table 2). This indicates that π-electron delocalization is still very effective in the most distorted system ([6](2,7)pyrenophane).

As the literature values of the RE and ASE of pyrene vary considerably,[20,51] we adopt our recommended value ASE = 77.8 kcal/mol, mentioned above. This choice is not critical here. On this basis, the most highly bent pyrene system, i.e., the one in [6](2,7)pyrenophane ($\alpha = 39.7°$), preserves 80% of the stabilization energy of pyrene. This high retention of aromaticity is especially remarkable since [6](2,7)pyrenophane has not yet been prepared.[42] The main obstacle to the synthesis of this compound is that the combined strain energies of the pyrene fragment and the bridge (see Table 4 below), far outweigh the ASE stabilization. The smallest parent [*n*](2,7)pyrenophane isolated to date, [7](2,7)pyrenophane[42] (ΔASE = −12.1 kcal/mol), retains 84% of the aromaticity of planar pyrene.

Figure 3a illustrates the impressively good linear dependence ($R = 0.996$, eight points) between the relative stabilization energy and the bend angle α (defined in Figure 2). Astonishingly, extrapolating this relationship to ASE = 0 would result in a physically completely unrealistic bend angle of 199.8°! Considering that pyrene starts to "roll up on itself" at a bend angle of about 90°, it would seem that aromaticity is a highly robust phenomenon.[52]

The magnetic susceptibility exaltations (relative Λ), evaluated by using the same eq 1, are in complete agreement with these findings. Distortion from planarity reduces relative Λ regularly down to 18.8 cgs-ppm for [6](2,7)pyrenophane (Table 2). Using the literature value for the exaltation of pyrene based on local group increments[53] ($\Lambda = -57.3$ cgs-ppm), Λ is lowered by only 33%. Figure 3b documents the well-behaved linear relationship between relative Λ and α ($R = 0.988$, eight points). Like the ASE case, extrapolating Λ linearly to 0 would result in a physically unachievable bend angle (112°).

Likewise, HOMA,[25,32,54] the geometry-based measure of π-electron delocalization, also indicates that the loss of delocalization upon distortion from planarity is rather small (range = 0.07 unit). However, unlike ASE and Λ, the change is not very regular (Table 2). In contrast to bent pyrenes,[11] HOMA in the [*n*](2,7)pyrenophanes is practically constant up to $\alpha = 16°$ (HOMA = 0.744). A regular lowering down to HOMA = 0.672 (90% retention of aromaticity) is observed for larger α values (Figure 3c). The lengths of $C(sp^2){-}C(sp^2)$ bonds tend to be insensitive to small or even moderate deviations from planarity. This seems to be general because, in the case of benzene, weak intermolecular interactions can disrupt its planarity rather easily but do not change the CC distances appreciably.[16]

Analyses of changes in the local descriptors of cyclic π-electron delocalization also are important. Table 3 summarizes NICS[55,56] and HOMA values for the outer (biphenyl-like) and inner pyrene rings in the pyrenophanes. NICS(0) is computed at the geometric centers of the six carbons comprising individual rings and NICS(1) 1 Å above these points (on the convex face of the pyrene surfaces), where local σ-electron contributions diminish with respect to the ring current effects.[57] Additionally, the zz tensor component corresponding to the principal axis

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[51] (a) George, P. *Chem. Rev.* **1975**, *75*, 85–111. (b) Bird, C. W. *Tetrahedron* **1996**, *52*, 9945–9952. (c) Havenith, R. W. A.; van Lenthe, J. H.; Dijkstra, F.; Jenneskens, L. W. *J. Phys. Chem. A* **2001**, *105*, 3838–3845.

[52] Feixas, F.; Matito, E.; Poater, J.; Solà, M. *J. Phys. Chem. A* **2007**, *111*, 4513–4521, and references therein.

[53] Dauben, H. J.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 811–813.

[54] HOMA (harmonic oscillator model of aromaticity) is defined as follows: $\mathrm{HOMA} = 1-\alpha/N\,\Sigma(R_{\mathrm{opt}} - R_{\mathrm{i}})^2$, where N is the number of bonds taken into the summation; α is an empirical constant fixed to give HOMA = 0 for a model non-aromatic system and HOMA = 1 for a system with all bonds equal to an optimal value R_{opt}, assumed to be realised for fully aromatic systems. R_{i} stands for a running bond length.

[55] NICS originally was defined as the negative value of the absolute isotropic shielding computed at the geometric centre of a ring (see ref 56a). Significantly negative (diatropic) NICS(0) values indicate aromaticity, in proportion to the magnitude of the value. NICS can also be computed at other points, inside or around molecules. Subsequent refinements have greatly increased the sophististication of NICS analyses (see ref 56b,c). In particular, the sum of the perpendicular out-of-plane zz tensor components of the π MO contributions, $\mathrm{NICS}(0)_{\pi zz}$, is now recommended as the definitive method (see ref 56c).

[56] (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318. (b) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842–3888. (c) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863–866.

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TABLE 3. Descriptors of Local Aromaticity: NICS, NICS(1), NICS(1)$_{zz}$, and HOMA[a]

system	NICS^{o} [ppm]	NICS(1)^{o} [ppm]	NICS(1)$_{zz}{}^{o}$ [ppm]	HOMA^{o}	NICS^{i} [ppm]	NICS(1)^{i} [ppm]	NICS(1)$_{zz}{}^{i}$ [ppm]	HOMA^{i}
[6](2,7)pyrenophane	−10.1	−7.8	−23.3	0.869	−4.0	−4.1	−10.3	0.577
[7](2,7)pyrenophane	−10.4	−8.7	−25.7	0.869	−3.7	−4.5	−11.5	0.619
[8](2,7)pyrenophane	−10.8	−9.6	−28.1	0.869	−4.1	−5.2	−13.7	0.641
[9](2,7)pyrenophane	−11.2	−10.6	−30.2	0.869	−3.9	−5.5	−14.4	0.650
[10](2,7)pyrenophane	−11.2	−11.3	−32.0	0.869	−4.1	−6.2	−16.0	0.662
[11](2,7)pyrenophane	−11.4	−12.0	−33.3	0.867	−3.8	−6.4	−16.2	0.659
[12](2,7)pyrenophane	−11.4	−12.6	−34.4	0.863	−4.0	−7.0	−17.3	0.658
pyrene	−11.9	−13.9	−36.1	0.858	−4.4	−7.8	−18.0	0.638

[a] Outer and inner rings are denoted by o and i superscripts.

TABLE 4. Estimated Distortion and Strain Energies (kcal/mol) of the Pyrene and Bridge Fragments in [*n*](2,7)Pyrenophanes[a]

pyrenophane	pyrene distortion energy (DE$_{pyrene}$)[b]	pyrene strain energy (SE$_{pyrene}$) DE$_{pyrene}$ − ΔASE	bridge strain energy (SE$_{bridge}$)
[6](2,7)pyrenophane	66.0	50.2	33.9
[7](2,7)pyrenophane	47.6	35.5	28.4
[8](2,7)pyrenophane	32.7	22.1	26.7
[9](2,7)pyrenophane	21.4	13.9	20.0
[10](2,7)pyrenophane	12.6	6.4	16.1
[11](2,7)pyrenophane	6.6	3.2	17.1
[12](2,7)pyrenophane	3.1	0.0	14.5

[a] The SE of the pyrene fragment is corrected for aromaticity loss (ΔASE, Table 2). [b] The distortion energy of only the pyrene fragment.

perpendicular to the ring plane, NICS(1)$_{zz}$[58] is included in the analysis. This index is also less contaminated by σ contributions.

All indices agree with the expectation[11,59] that the outer "biphenyl-type" pyrene rings are clearly more aromatic than the inner rings, which resemble the central ring of phenanthrene.[60,61] The lowering of aromaticity by bending is documented by the NICS descriptors, especially by NICS(1) and NICS(1)$_{zz}$. Since HOMA and isotropic NICS(0) are both influenced by σ-electron effects and to irregular extents, they do not correlate well with each other, or with the indices for outer and inner rings, or with global descriptors of aromaticity such as stabilization energies or Λ. Consequently, HOMA and isotropic NICS(0) are not useful indices here.

In contrast, NICS(1) of the inner and the outer ring both correlate very well with relative Λ ($R = 0.990$ and $R = 0.993$, respectively, see Figure 4a. NICS(1)$_{zz}$ also correlates nearly as well with relative Λ ($R = 0.961$ and 0.975, respectively, for the inner and outer rings). Such dependences are expected because both descriptors are largely based on the same physicochemical properties. Because relative Λ correlates impressively with the stabilization energy ($R = 0.982$), NICS(1) and NICS(1)$_{zz}$ do so as well (see the Supporting Information). Distortion from planarity results in a decrease in NICS(1) for both the outer rings (range = 6.1 ppm) and inner rings (range = 3.7 ppm), which correspond to the retention of 56% (outer rings) and 53% (inner rings) of the aromaticity of planar pyrene in the most distorted structure ([6](2,7)pyrenophane). The excellent correlations ($R = 0.996$, see Figure 4b), as well as those for NICS(1)$_{zz}$ ($R = 0.995$), suggests that the ring current around the pyrene perimeter, as revealed by the ipsocentric mapping technique[37] for planar pyrene,[62] is preserved after bending up to α = 40°.

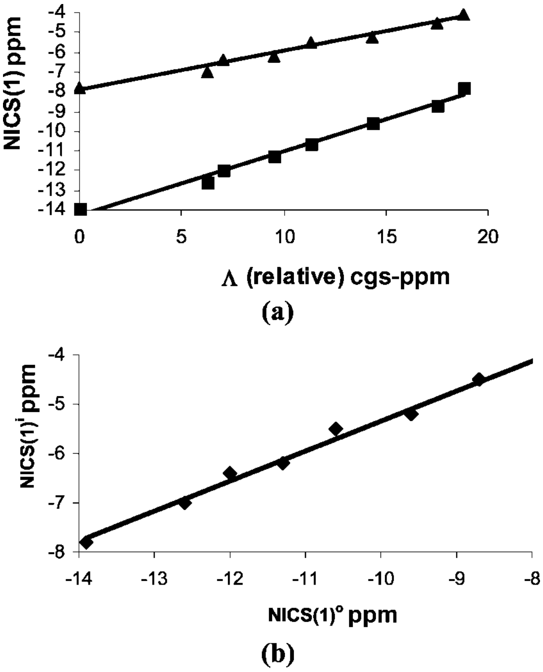

FIGURE 4. (a) Dependence between NICS(1) of the inner ring (▲) and outer ring (■) and the exaltation of magnetic susceptibility, relative Λ. The correlation coefficients are $R = 0.990$ and $R = 0.993$, respectively, eight points. (b) Dependence between NICS(1) of the outer ring (denoted as NICS(1)^{o}) and NICS(1) of the inner ring (denoted as NICS(1)^{i}). The correlation coefficient is $R = 0.996$, eight points.

Although ascertaining the changes of π-electron delocalization in the pyrene moiety upon bending was a primary goal of this study, estimation of the strain energy changes was not only of equal importance but also very challenging. The strain due to geometrical distortions is distributed over the entire molecule, i.e., the bridge as well as the σ skeleton of the pyrene unit.

The strain energies of the pyrene fragment SE$_{pyrene}$ (Table 4) were estimated by comparing the total energy of planar pyrene with those of deformed pyrene models, the structures of which were taken from the pyrenophanes (and terminated with hydrogen atoms). Since the resulting energy differences also reflect the decrease of stabilization due to π-electron delocalization, the total distortion energies (DE$_{pyrene}$, Table 4) were corrected for ΔASE (the change in ASE, relative to pyrene).

The strain energies of the bridges (SE$_{bridge}$, Table 4) were estimated by employing a similar strategy. The energy of the

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(61) Schleyer, P. v. R.; Manoharan, M.; Jiao, H.; Stahl, F. *Org. Lett.* **2001**, *3*, 3643–3646.

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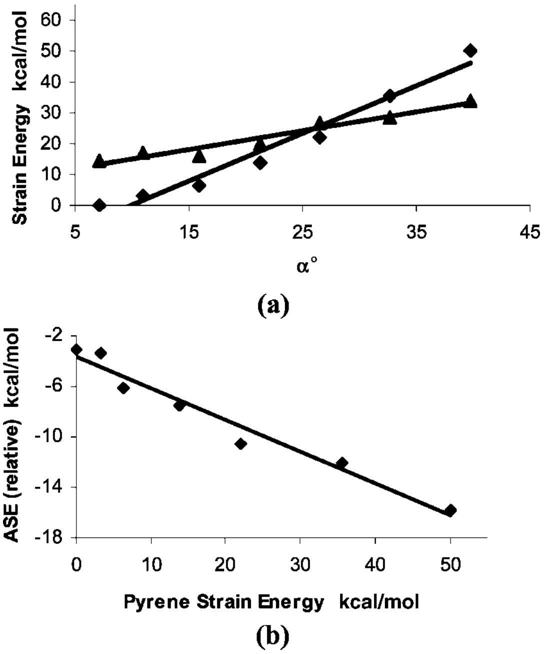

FIGURE 5. (a) Dependence between strain energies and the bend angle, α. The triangles denote data for the bridge (correlation coefficient $R = 0.974$, seven points). The squares denote strain of the pyrene unit (correlation coefficient $R = 0.982$, seven points). (b) Dependence between the relative ASE and the strain energy (SE) of the pyrene fragment (correlation coefficient $R = 0.982$, seven points).

aliphatic chain in the geometry adopted in a pyrenophane was compared with the energy of the analogous fully relaxed parent chain; both systems were terminated by vinyl groups (in order to model pyrene). The vinyl group conformations of the aliphatic chain models reflected those of the ring fragment (see Supporting Information for details).

The strain energies, evaluated in these simple ways, follow expectations well. They depend strongly on the pyrenophane curvatures shown in Figure 5a. SE_{pyrene} and SE_{bridge} are interrelated ($R = 0.979$). Individually, both SEs correlate well with the bend angle, α ($R = 0.982$ and 0.974, respectively), but the SE_{pyrene} range (50.2 kcal/mol) is much larger than that for SE_{bridge} (19.4 kcal/mol).

The change in SE_{pyrene} in going from [12](2,7)pyrenophane (with a nearly planar pyrene moiety) to the most bent unit in [6](2,7)pyrenophane (50.2 kcal/mol) is four times larger than the change in ΔASE (12.6 kcal/mol). Both changes correlate extremely well (see Figure 5b).

Conclusions

Geometrical deformations of [*n*](2,7)pyrenophanes by decreasing the length of the bridge raises the total energy as well as the energy of the pyrene moieties due to a combination of strain increase and aromaticity loss. The σ-electron structure changes most; the simultaneous strain energy increases of the pyrene moiety and of the aliphatic bridge are both large. Bending also decreases the π-electron delocalization regularly over a wide range, but the effect is smaller energetically. Even the most bent (α = ca. 40°) pyrene unit in [6](2,7)pyrenophane retains most of the aromatic character of planar pyrene. These findings are supported by both magnetic and geometric aromaticity indices, but the energetic response is the most important chemical consequence. The changes in aromatic stabilization energies even of these highly nonplanar polycyclic systems, the most difficult cases, can be estimated easily and reliably by the methods described in this paper.

Experimental Section

Crystal Data. Suitable crystals of [9](2,7)pyrenophane and [10](2,7)pyrenophane[63] for X-ray diffraction experiments were obtained by crystallization from toluene/benzene solutions. Data collection, cell refinement, and data reduction were carried out with the Kuma Diffraction programs: CrysAlis CCD and CrysAlis RED.[64] The data were corrected for Lorentz and polarization effects, but no absorption correction was applied. The structures were solved by direct methods[65] and refined by using SHELXL.[66]

[9](2,7)Pyrenophane. $C_{25}H_{26}$, $M = 326.46$, orthorhombic *Pmmn*, $a = 9.645(2)$ Å, $b = 12.712(3)$ Å, $c = 7.360(2)$ Å, $V = 902.4(3)$ Å^3, $T = 100(2)$ K, $Z = 2$, $D_x = 1.201$ mg/m^3, $F(000) = 352$, absorption coefficient μ(Mo Kα) = 0.067 mm^{-1}, the collected data range was $4.23° < \theta < 25.00°$. ($-11 \le h \le 11$, $-15 \le k \le 15$, $-8 \le l \le 8$), 6471 reflections measured, 875 unique ($R_{int} = 0.0800$), which were used in all calculations. The final R and $wR(F_2)$ were, respectively, 0.0934 and 0.0900 (all data), 0.0420 and 0.0746 (for 538 $I > 2\sigma(I)$), maximum and minimum difference electron densities were 0.186 and −0.150 e Å^{-3}.

[10](2,7)Pyrenophane. $C_{26}H_{28}$, $M = 340.48$, orthorhombic *Pmmn*, $a = 9.708(2)$ Å, $b = 13.081(3)$ Å, $c = 7.337(2)$ Å, $V = 931.7(3)$ Å^3, $T = 100(2)$ K, $Z = 2$, $D_x = 1.214$ mg/m^3, $F(000) = 368$, absorption coefficient μ(Mo Kα) = 0.068 mm^{-1}, the collected data range was $4.20° < \theta < 25.11°$. ($-11 \le h \le 11$, $-15 \le k \le 15$, $-7 \le l \le 8$), 6732 reflections measured, 912 unique ($R_{int} = 0.0302$), which were used in all calculations. The final R and $wR(F_2)$ were, respectively, 0.0409 and 0.1027 (all data), 0.0358 and 0.0986 (for 804 $I > 2\sigma(I)$), maximum and minimum difference electron densities were 0.201 and −0.141 e Å^{-3}.

Computational Details

The HOMA values were based on geometries optimized at the B3LYP/6-311G** DFT level using the Gaussian 03 program.[67] All molecules in eq 1 were minima with no imaginary vibrational frequencies. The ASE evaluations included zero point energy corrections. The CSGT/B3LYP/6-311G**//B3LYP/6-311G** level was selected for the magnetic susceptibility computations since the value for pyrene (−151.5 cgs ppm) agrees well with experimental data (−149.4[68,69] and −154.9[68,70]). NICS values were computed

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(63) Crystallographic data (excluding structure factors) for the structures in this paper have been also deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 673556 and CCDC 673557. These data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax: +44(0)-1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

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at GIAO/B3LYP/6-311G**; the NICS(1) points are 1 Å above ring centers, perpendicular to the averaged planes of the rings.

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Supporting Information Available: Cartesian coordinates, absolute electronic energies at B3LYP/6-311G**, zero point vibrational energies (ZPE) at B3LYP/6-311G**, and magnetic susceptibilities calculated at CSGT/B3LYP/6-311G** for molecules used in eq 1, single point energies, Cartesian coordinates of pyrenophane fragments and related molecules for the estimation of strain energies, and the crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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