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Molecular and Electronic Structure of 1,8-Peribridged Naphthalenes

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The crystal and molecular structure of 1,8-thianaphthalene has been determined and compared with other single-atom peribridged naphthalenes (SAPN). The measured CSC angle is 73.06°, which is the smallest bridging angle yet recorded for a SAPN derivative. The ab initio calculations using G3(MP2)//B3LYP method were performed for peribridged naphthalenes in order to determine how the strain of the four-membered ring is influenced by the type of bridge linking 1,8 positions. The electronic structure of 1,8-thia- and 1,8-sulfonenaphthalenes has been studied by UV photoelectron spectroscopy. We have tried to identify and distinguish the strain effect on the electronic structure of the naphthalene moiety.

Introduction

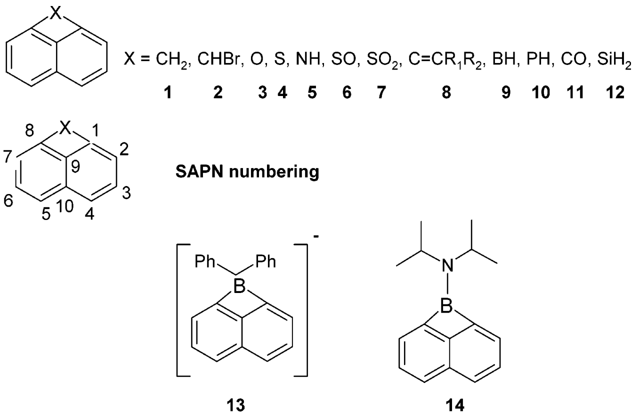
The strain in molecules containing three- or four-membered rings has been studied extensively.[1] Such molecules are often unstable and difficult to synthesize. The single-atom peribridged naphthalene (SAPN) contains a four-member ring and is a highly strained molecule (Scheme 1).[2] The effects of ring strain, e.g., possible distortion of the aromatic system and the propensity of the four-membered ring to undergo ring-opening reactions are interesting subjects for experimental and computational study.

Only the molecular structures of SAPN derivatives **2**, **7**, and **8** have so far been accurately determined by X-ray diffraction.[3,4] As already mentioned, SAPN compounds are often unstable, which makes it difficult to obtain single crystals necessary for X-ray diffraction measurements. We report the molecular structure of **4** together with accurate calculations of ring strain for the SAPN series (Scheme 1). Ab initio calculations for peribridged naphthalenes have been reported previously by Roohi et al.[5] These authors used medium accuracy semiempirical and DFT methods and calculated geometries and enthalpies of formation for SAPN. They also calculated pyramidal inversion barriers for **5**, **6**, and **10** derivatives. However, they did not calculate ring strain energies (RSE), which require the use of higher level, more accurate quantum chemical methods. Our aim in this work was to obtain accurate ring strain energies, to obtain additional information on the geometry of SAPN, and to study how the ring strain affects the electronic structure of the aromatic system.

Experimental and Theoretical Methods

The compound **4** was prepared according to the synthetic procedures described previously,[3,6] and its molecular and crystal structure was determined by X-ray diffraction. The details of the crystal structure are given in the Supporting Information. Selected molecular parameters for SAPNs are listed in Table 1.

SCHEME 1



The quantum chemical calculations were performed with the Gaussian 03 program.[7] The total electronic energy for each molecule was computed using the G3(MP2)//B3LYP method,[8] which has rms deviation of 8 kJ/mol. The method includes full geometry optimization at the B3LYP/6-31G* level followed by single-point QCISD type calculations. To estimate RSE of SAPN and their isomers, we used the enthalpies of isodesmic reactions, which are given in Scheme 2.

The ring strain energies (RSE) thus obtained are listed in Table 2.

The HeI/HeII photoelectron spectra were recorded on a Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe or Ar gas that were added to the sample flow. The spectral resolution in HeI and HeII spectra was 25 and 70 meV, respectively, when measured as fwhm of the $3p^{-1}$ $^2P_{3/2}$ $Ar^+ \leftarrow Ar$ $(^1S_0)$ line. The resolution in the HeII spectra

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TABLE 1: Key Geometry Parameters of SAPN and Naphthalene Obtained by X-ray Diffraction[a,b]

molecule	C1−X−C8 (deg)	C1−C9−C8 (deg)	C4−C10−C5 (deg)	C9−C10 Å	C1−X Å	C1−C9 Å
2	83	99	138	1.382	1.567	1.368
4	73	103.5	134.4	1.372	1.829	1.387
7	75.4	106	132.5	1.374	1.819	1.391
8	86	98	137	1.371	1.536	1.392
13 (anion)	80.5	103.2	132.5	1.400	1.695	1.408
14	86.2	102.6		1.404	1.599	1.404
$C_{10}H_8$		121.5	121.5	1.410		1.435

[a] In 8, $R_1{=}R_2{=}$phenyl. [b] X-ray structure data are from refs 21 and 22.

SCHEME 2

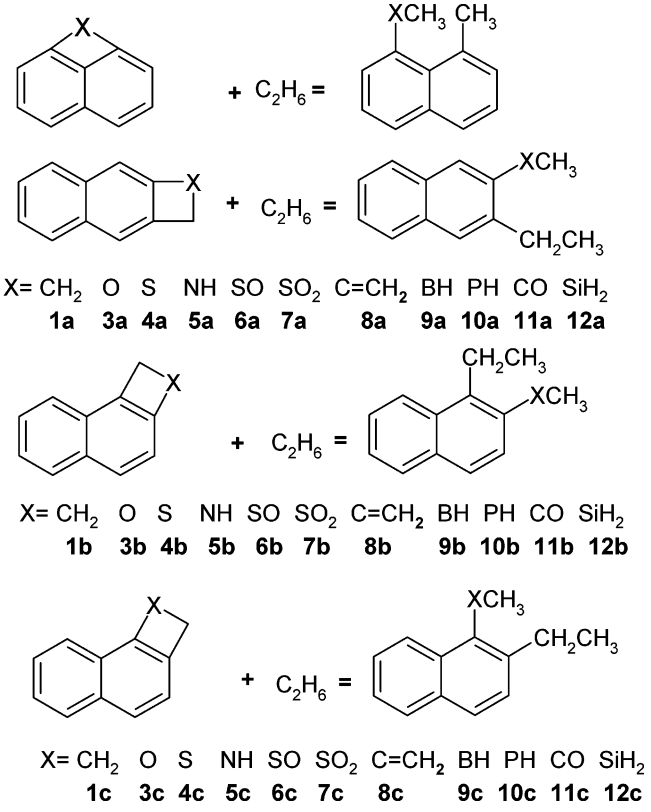


TABLE 2: Ring Strain Energies RSE (kJ/mol) of Peribridged Naphthalenes and Their Monocyclic Analogues Calculated at G3(MP2)//B3LYP Level (Schemes 1−3)[a,b,c]

1	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
201.9	289.7	148.1	256.5	160.5	141.5	214.3	178.9	125.2	197.2	123.4
1a	**3a**	**4a**	**5a**	**6a**	**7a**	**8a**	**9a**	**10a**	**11a**	**12a**
134.6	140.6	95.8	147.3	99.5	107.3	134.2	140.0	92.5	117.8	112.7
1b	**3b**	**4b**	**5b**	**6b**	**7b**	**8b**	**9b**	**10b**	**11b**	**12b**
127.1	137.3	90.9	142.4	91.4	101.1	130.7	119.5	86.6	109.2	101.2
1c	**3c**	**4c**	**5c**	**6c**	**7c**	**8c**	**9c**	**10c**	**11c**	**12c**
127.1	135.1	91.7	129.8	82.7	85.4	134.3	120.7	90.0	110.6	98.9
1d	**3d**	**4d**	**5d**	**6d**	**7d**	**8d**	**9d**	**10d**	**11d**	**12d**
112.7	109.9	84.3	111.2	89.8	90.0	114.8	115.5	88.5	108.0	97.6
1e	**3e**	**4e**	**5e**	**6e**	**7e**	**8e**	**9e**	**10e**	**11e**	**12e**
111.6	84.2	79.7	95.7	80.7	80.4	118.6	134.8	96.0	106.0	120.3
−112	*−82.8*	*−77.8*	*−96.4*						*−106*	
−112	*−84.2*	*−79.7*	*−95.8*						*−106*	

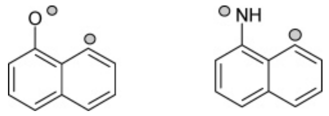
[a] **1b** = **1c**. [b] Calculations for **8** correspond to R1═R2═H. [c] In the bottom row, the numbers in italics or underlined correspond to enthalpies of isodesmic reactions 1 and 2 from Scheme 4. The values in italics were calculated from G3(MP2)//B3LYP total energies of reactants and products. The underlined values were calculated from experimental standard enthapies of formation (ref 11).

was always inferior to HeI, which implies that certain bands that are well resolved in HeI may become unresolved in the corresponding HeII spectrum. The sample inlet temperatures were in the range 70−100 °C. These temperatures were necessary in order to obtain sufficient vapor pressure in the ionization region. For the assignment of photoelectron spectra, full geometry optimization was performed using the DFT method at B3LYP/6-31G* level. Subsequently, a single-point Green's function (GF) type calculation[9] using the 6-311G* basis set was performed in order to obtain vertical ionization energies. The use of this method obviates the need to rely on Koopmans' approximation.

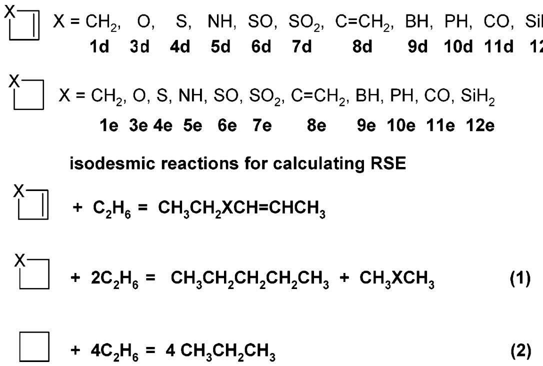
Results and Discussion

Molecular Structures and Ring Strain. The key experimental molecular parameters of **2**, **4**, **7**, **8**, **13**, and **14** are compared in Table 1. The aromatic rings, inclusive of the bridging atom (X) have planar configuration. Comparison of **2**, **4**, **7**, **8**, **13**, and **14** geometries with the parent naphthalene[2] reveals structural traits related to the ring strain. The naphthalene moiety near the bridge is contracted. This can be seen from C1−C9 and C9−C10 bonds lengths, which are 3−5% shorter, and from C1−C9−C8 angles, which are up to 20% smaller than in the parent naphthalene. The part of the naphthalene moiety away from the bridge expands, e.g., C4−C10−C5 angles are increased by up to 12% vs naphthalene. This is a good illustration of relative magnitudes of stretching and bending force constants, with the former being several orders of magnitude bigger than the latter. The C1−X−C8 and C4−C10−C5 angles increase when the bridging sulfur atom is replaced by carbon. The opposite is true for the C1−C9−C8 angle. The larger sulfur atom can accommodate smaller bridging angles than the carbon; for example, **4** has the smallest C1−X−C8 bridging angle observed to date among SAPN. The dependence of bridging angle on the nature of X can be explained by the simple geometrical argument. Assume that C1, X, and C8 form an isosceles triangle with the fixed length of the base (C1−C8 distance). The longer the sides of the triangle are (i.e., the longer the C−X bond length), the more acute the C1−X−C8 bridging angle will become. Shechter and co-workers[4b] have demonstrated that, for **8**, the naphthalene can accommodate a large strain and that the portion of the molecule near the bridge becomes compressed while the opposite portion expands. We confirm this to be true for other SAPN, but the extent of compression/expansion depends on the type of the bridging atom present. Therefore, both geometrical parameters, i.e., bond lengths and angles, are adjusted to achieve maximum strain relief. The deformation of the naphthalene skeleton leads to CC bond length alternation and to a reduction of aromatic delocalization, i.e., π-bonds are more localized in the strained SAPN than in the naphthalene, as was pointed out by Shechter et al.[4b]

SCHEME 3



SCHEME 4



The changes in aromatic delocalization can be expected to influence the electronic structure (energy levels), which shall be discussed in the next section.

The ring strain energies of SAPN are shown in Table 2. In the following discussion, we recall that the accuracy of the theoretical method employed is not better than 8 kJ/mol. We note that molecules **1**, **3**, **5**, **8**, **9**, and **11**, whose bridging atom belongs to the first row of the periodic table, have higher RSE than the molecules, which have the bridging atom from the second row, i.e., **2**, **4**, **6**, **7**, **10**, and **12**. Atoms from the second row are larger than those from the first row, which helps to reduce the strain. The O-bridged SAPN has the highest and Si-bridged the lowest RSE in the "principal series" **1**−**12**. Our results suggest that the silicon-bridged derivative should be amenable to synthesis. The change in hybridization of the bridging atom has only a small influence on the RSE, as can be seen by comparing RSE of **4**, **6**, and **7**. The fact that oxidation state/hybridization of the bridging atom does not have a strong influence on RSE is an indication of the dominance of strain over possible resonance interactions between X and the aromatic system. The RSE is generally smaller than the aromatic stabilization of the naphthalene (255 kJ/mol), at least in the SAPNs, which have been synthesized so far. When RSE is comparable to the aromatic stabilization of the parent naphthalene (e.g., **3** and **5**), we predict that such molecules would be highly unstable under the standard laboratory conditions and difficult to synthesize. In view of the similarity of RSE and aromatic stabilization energies for **3** and **5**, we have also checked the relative stabilities of 1,X-biradical species (Scheme 3) in their singlet and triplet states. Biradicals of **3** and **5** in their most stable (triplet) states are 28 and 85 kJ/mol less stable than the bridged, closed-shell forms.

The ring strain energies of SAPN span a range of values; in some members of the class, they are larger than that of cyclobutane (110 kJ/mol).[1c] In other SAPN where the bridging atoms are large, e.g., in **12**, the RSE values are comparable in magnitude to C_3H_6X analogues (**d** or **e** series in Scheme 4). Such, relatively low RSE values may partly account for the remarkable fact that a four-member ring is retained in many chemical reactions involving SAPN.[2]

To set our present discussion within context, we recall that the steric strain and compression in 1,8-disubstituted naphthalenes has been well recognized.[10] Thus, for example, in 1,8-diiodonaphthalene,[10a] iodine atoms are twisted out of the naphthalene plane by 5−17° due to the steric compression of vicinal iodines. In the naphthalenes containing diatomic bridges (C−X−X−C) that span 1 and 8 positions,[10b] the strain relief occurs via splaying (increase of CCX angles from 120°) or by distortion of the planar naphthalene skeleton.

It is interesting to analyze how the RSE values of the "principal series" compare with their counterpart molecules that have a four-membered ring fused at a different position of the naphthalene core (**a**, **b**, and **c** series). The members of the **a**, **b**, and **c** series (Scheme 2) have considerably lower RSE than their counterparts in the "principal series" (Table 2). This can be expected because the four-membered ring is more flexible if one rather than two of its sides are part of the rigid aromatic system. The exception is **12**, which contains a large Si atom and has relatively small RSE. In the **a**−**c** series, the largest RSE appears in the N-bridged and the lowest in the P-bridged derivative. When the bridging heteroatom is an element from the second row, the variation in RSE values among isomers of **a**−**c** series is small, being at most twice the uncertainty limit of the G3(MP2)//B3LYP method. When the four-membered ring is not attached to the naphthalene core as in the **d** or **e** series (Scheme 4), the RSE values are smaller than in the "principal" or **a**−**c** series. The RSE values among the members of the **d** series are slightly bigger than in the case of the **e** series, presumably due to the geometrical constraints imposed by the double bond. When the reverse is true (as in **8**−**12**), the inversion can be attributed to stabilizing resonance interaction between X and the π-bond.

We have calibrated and checked our RSE values by obtaining theoretical and experimental enthalpies of isodesmic reactions 1 and 2 in Scheme 4. First, we used G3(MP2)//B3LYP total energies for reactants and products to obtain theoretical reaction enthalpies. Subsequently, we used experimental enthalpies of reactants and products[11] (where available) to obtain experimental reaction enthalpies. The comparison of two sets of values (Table 2, bottom row) suggests that our RSE values are within the uncertainty range of the theoretical method used.

Electronic Structure. The electronic structures of **4** and **7** have been investigated by UV photoelectron spectroscopy (UPS) and quantum chemical calculations. The photoelectron spectra are shown in Figures 1−2, and the spectral assignments are given in Table 3. We shall use the interaction between energy levels of the composite molecular fragments as the qualitative framework for understanding the observed ionization energy shifts.

The assignment of the spectra can be facilitated by measuring relative band intensities at various photon energies and GF calculations, which help us to determine the number of ionization events associated with each band. The HeII/HeI photoionization cross-sections for C2p, O2p, and S3p orbitals are 0.31, 0.64, and 0.14, respectively.[12] This suggests that bands pertinent to ionization from the orbitals with mainly sulfur character (sulfur lone pairs) would show a pronounced decrease and bands related to orbitals with oxygen lone pair character a pronounced increase in relative intensities on going from HeI to HeII photon energy.

Naphtho[1,8-bc]thiete (4). We compared our HeI/HeII spectra of **4** with the HeI spectra of naphthalene[13a] and **4**,[13b] measured relative band intensities, and HeI/HeII intensity changes. Our HeI spectrum is fully consistent with the one reported by Bock et al.,[13b] whose assignment was based on HMO calculations. On the basis of all the experimental evidence, we assign the first two partially resolved bands at 8.30 and 8.50 eV (Figure 1) to two ionizations: the former associated with

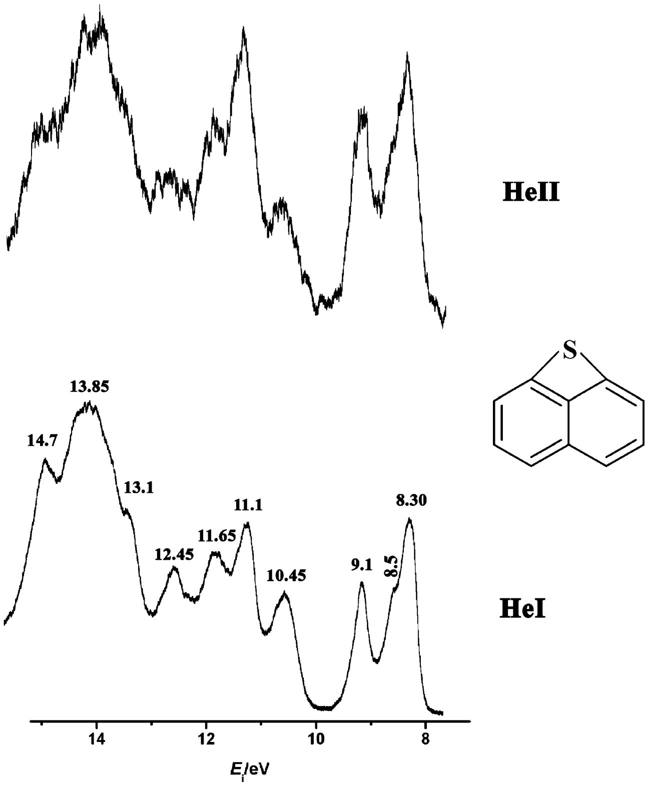


Figure 1. HeI and HeII photoelectron spectra of **4**.

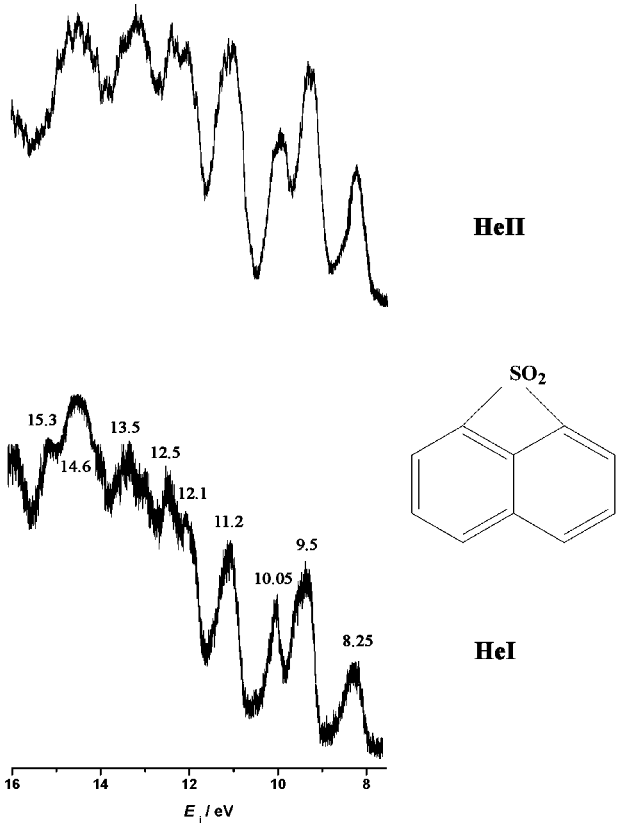


Figure 2. HeI and HeII photoelectron spectra of **7**.

the π_5 type orbital of the naphthalene moiety (Scheme 5) and the latter with the out-of-plane sulfur lone pair (π_S). The π_S assignment is consistent with the decrease in relative intensity of the 8.30 eV band as a whole compared to the increase in relative intensity of the neighboring 9.1 eV band. The latter band can be unambiguously attributed to π_4 type ionization.

TABLE 3: Experimental Vertical Ionization Energies (E_i/eV), Calculated Ionization Energies (GF/eV), Band Assignments, and Relative HeII/HeI Band Intensities for Peribridged Naphthalenes and Naphthalene ($C_{10}H_8$)[a]

molecule	band	E_i	GF	assignment	HeII/HeI
4	X	8.30	8.05	π_5 (a_2)	1.0
	A	8.50	8.08	π_S (b_1)	
	B	9.1	8.58	π_4 (b_1)	1.4
	C	10.45	10.61	σ_S (a_1)	0.65
	D−E	11.1	11.10, 11.35	π_3 (b_1), π_2 (a_2)	1.17
	F	11.65	12.11	σ	0.77
	G	12.45	12.63	σ	
	H	13.1	13.58	π_1(b_1) ??	
7	X	8.25	8.41	π_5 (a_2)	1.0
	A−B	9.5	9.30, 10.12	π_4 (b_1), n_O (b_1)	1.08
	C	10.05	10.24	π_3 (b_1)	1.14
	D−E	11.2	10.94, 11.31	n_O (b_2), π_2 (a_2)	1.29
	F	12.1	11.47	n_O (a_1)	
	G	12.5	11.88	n_O (a_2)	
$C_{10}H_8$	X	8.09		π_5	
	A	8.81		π_4	
	B	9.95		π_3	
	C	10.85		π_2	
	F	12.56		π_1	

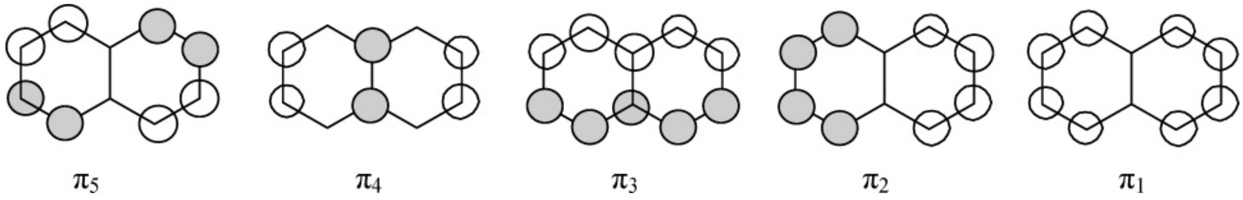
[a] Both **4** and **7** have C_{2v} symmetry; the molecular plane is *yz* plane.

The 10.45 eV band intensity shows a very pronounced HeI/HeII decrease, which is expected of the in-plane sulfur lone pair (σ_S). The 11.1 eV band can on the basis of its relative intensity and HeI/HeII intensity variation be attributed to π_3 and π_2 orbital type ionizations. The 11.65 and 12.45 eV bands can then be assigned to σ ionizations. The most stable π orbital (π_1) appears as a shoulder at 13.1 eV. However, because of the high density of ionic states in this region, the assignment of 13.1 eV band to π_1 orbital ionization is tentative. The MO description and labeling of occupied π-orbitals in naphthalene is given in Scheme 5 based on the established assignment of its UPS spectrum.[13a]

Comparison of the sulfur lone pair ionization energies in dimethylsulfide (8.72, 11.30 eV),[14] thietane **4e** (8.65, 11.89 eV)[15] and **4** (8.5, 10.45 eV) reveals that, while the out-of-plane sulfur lone pair (π_S) in **4** is destabilized by only 0.2 eV, the in-plane lone pair (σ_S) is destabilized by 0.85 eV. The CSC angles in the three molecules are 99°, 77°, and 73°, respectively,[16,17] and indicate the increasing rehybridization of sulfur atomic orbitals that lose S3s and gain S3p character. Because the S3p orbital has higher energy than S3s, this can account for the observed destabilization. The influence of the sulfur bridge on the π-electronic structure of the aromatic system can be assessed by comparing the UPS of **4** with the spectra of naphthalene[13a] (Table 3), thietane[15] (**4e**), and diphenylsulfide.[18] Our final assignment for **4** is consistent with the previous partial one,[13b] deduced from the less complete set of observations.

Three types of influences on aromatic π-orbitals can be envisaged as the result of bridging. Inductive stabilization would affect all π-orbitals to a similar extent. Resonance interaction between orbital localized on X and on the aromatic system may destabilize or stabilize a particular π-orbital depending on energies of the interacting orbitals and on their symmetries. Finally, the distortion of the aromatic skeleton (strain effect) with concomitant bond localization[4b] may also affect the π-orbitals, and we shall try to estimate its magnitude from spectral data. The inductive effect in **4** due to the presence of the sulfur bridge is negligible because sulfur has almost the same electronegativity as carbon. This leaves only resonance stabilization and strain effect to be considered. The electron density distribution in the π_4 orbital is such that it precludes resonant

SCHEME 5



interaction with the out-of-plane orbital on the bridging sulfur (Scheme 5). This is due to the presence of the nodal plane at the bridging carbons in 1,8 positions. Noting that the π_4 orbital is stabilized by 0.29 eV (vs naphthalene), we estimate the strain effect to be of this magnitude. The π_3 orbital can be expected to be influenced by both stabilizing resonance and the strain effect, and thus its energy shift vs naphthalene should be large. The observed shift of 1.15 eV is consistent with this expectation. The deformation leading to strain effect is evident in the molecular structure of **4**, where the CC bond lengths alternate in the range of 1.34−1.43 Å.

Naphtho[1,8-bc]thiete-1,1′-dioxide (7). The molecule **7** does not have sulfur lone pairs, but its sulfone group introduces four additional valence ionizations (strongly localized on oxygens) that can be detected in the low-energy UPS region.[19] The oxygen lone pairs of appropriate symmetry are capable of resonant interactions with the π-orbitals of the aromatic system, provided they are well matched in energy.[19] In addition, the electronegative oxygens are expected to exercise inductive stabilization on all π-ionizations. We recall that the bands associated with the ionizations from oxygen lone pairs are expected to show an increase in relative intensity on going from HeI to HeII radiation. Taking into consideration relative band intensities, HeI/HeII intensity changes, and comparison with the spectra of naphthalene, thiete 1,1′dioxide[19] (**7e**), and diphenyl sulfone (Ph−SO_2−Ph),[18] we conclude that bands at 8.25 and 10.05 eV correspond to ionizations from π_5 and π_3 type orbitals, respectively. The band at 9.5 eV contains two ionizations (it has twice the intensity of 8.25 eV band): one from the π_4 type orbital and one from the oxygen lone pair (n_O). The relative intensity and HeI/HeII intensity change of the 11.2 eV band indicates that it also comprises two ionizations: one associated with π_2 type orbital and the other with the oxygen lone pair (n_O). We then assign the 12.1 and 12.5 eV bands to ionizations from the remaining two oxygen lone pairs (n_O) of a_1 and a_2 symmetry. The energy shifts of π_5, π_4, π_3, and π_2 type orbitals in **7** (vs naphthalene) are 0.16, 0.69, 0.10, and 0.35 eV, respectively. The energy shifts appear smaller than in **4** due to the reduction of π-orbital destabilizations by the stabilizing inductive effect of the SO_2 group. The unravelling of the strain effect is now much more difficult than in **4** because of the simultaneous influence of three effects: inductive, resonance, and strain. Nonetheless, we can compare shifts in oxygen lone pairs to give us a general indication of the total extent of interactions. Four oxygen lone pairs in Ph−SO_2−Ph appear at 10.2, 10.97, and 11.74 eV[18] and in $(CH_3)_2SO_2$ at 10.8, 11.15, 11.75, and 12.07 eV.[20] The oxygen lone pairs in **7** are shifted away considerably from these values, signifying that the total effect (which includes the three components mentioned above) of the SO_2 bridge on the aromatic system is large. We note that the RSE of **4** and **7** are similar, and hence we can expect similar magnitude for strain effect. The π_4 orbital is least subject to resonant interactions (see above), and its stabilization by 0.69 eV contains mostly inductive and strain effect contributions. The inductive effect of the SO_2 group can be estimated from the shift of π_5 orbital, which is 0.16 eV. A “back-of-the-envelope” calculation then suggests that strain effect has the magnitude of 0.5 eV. This is the best estimate of strain effect that can be given on the basis of the available data. It is worth pointing out that the ionization energies themselves contain uncertainties due to band overlap and this would naturally affect the calculated energy shifts. Thus, for instance, the 9.5 eV band contains two overlapping ionizations, which makes it impossible to determine the π_4 ionization energy with great precision.

Summary

We discussed molecular structure and strain energy of peribridged naphthalenes on the basis of available experimental results and high-level ab initio calculations. We have observed the smallest bridging angle reported to date in **4** and established that heavier elements make better bridges, i.e., impose less strain on the aromatic moiety. This is due to longer C−X bonds. Our observed bridging CSC angle in **4** is smaller even than the bridging CBC angles in 1,8-naphthalenediylbis(2,4,6-trimethylphenyl)-borate (**13**) or *N*,*N*-bis(1-methylethyl)-1*H*-naphtho-[1,8-bc]boret-1-amine (**14**), which are 80.5° and 86.2°, respectively.[21,22]

We predict on the basis of RSE that phosphorus- and silicon-bridged SAPN would be stable and amenable to synthesis. The significant distortion of naphthalene geometry is reflected in changes in the electronic structure of the naphthalene's π-system. We estimate that the strain effect is of the order of 0.3−0.5 eV.

Supporting Information Available: Crystal structure data for **4**, G3(MP2)//B3LYP energies and calculated geometries for SAPN. This material is available free of charge via the Internet at http://pubs.acs.org

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