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Out-of-plane deformation of the azulene ring in crystal structures of simply substituted azulene derivatives

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Abstract—The crystal structures of 1,3-bis(4-bromophenyl)- and 1,3-di(2-thienyl)azulenes (**5** and **6**) were elucidated by X-ray analysis. Two aryl groups connect to the azulenyl core with dihedral angles of 34.9–41.6° and the two aryl planes of the groups slant against the azulene ring toward different ways in their crystal structures. It was also found that the azulene rings of **5** and **6** showed a slight out-of-plane deformation in the way that the hydrogen atoms at the 4- and 8-positions are apart from the neighboring aryl *ortho*-hydrogen atoms to fill in the vacant space made by the slanting aryl planes.

Planarity of an aromatic ring can be interfered with circumstances around the ring, such as by bulky substituents attached at the ring as scrutinized in structural analysis of substituted acenes,[1] by bridging the ring with another carbocycle as observed frequently in cyclophanes,[2] and also by molecular distortion as found in helicenes.[3] An extraordinary example was presented by the crystal structure of 9,10,11,12,13,14,15,16-ocataphenyldibenzo[*a*,*c*]naphthacene (**1**), which has a twist angle of 105° between the two benzene rings located at the ends of the benzene array.[4] Since there has long been general interest in the relationship between distortion of an aromatic ring and its aromaticity, organic chemists have tried to force aromatic compounds and to know how they could sustain their aromatic nature under such circumstances. The results of those studies informed us that aromatic molecules try to relieve the forced strain in various fashions, such as by stretching of bonds, deflections of substituents, and distortion or buckling of the aromatic ring itself. Although numerous studies of these kinds of deformations in benzenoid aromatics have been reported, there have been only a few such studies in non-benzenoid compounds, particularly in azulene derivatives.[5] Itô and Fukazawa reported the bending of the azulene ring along its long molecular axis through the C2–C6 line in azulenophanes **2** and **3**. On the other hand, Hoppe et al. reported that the azulene derivative **4** showed out-of-plane deformation along the short molecular axis through the C4–C8 line.[6] The latter compound has many substituents around the azulene ring and the Dreiding model study of **4** indicates that steric hindrance between the substituents is severe and rotation of the phenyl rings at the five-membered ring was seriously restricted. Herein we report another example of out-of-plane deformation of an azulene ring along the short molecular axis in crystal structures of 1,3-bis(4-bromophenyl)- and 1,3-di(2-thienyl)azulenes (**5** and **6**), which are simply substituted by the rotary aryl groups at the *peri* positions of the azulene with slight forced strain (Charts 1 and 2).

Eichen et al. recently reported the crystal structure of 1,3-di(2-pyrrolyl)azulene (**7**) in which the planes of the two pyrrole rings are slightly tilted with a torsion angle of 29.1° (C2–C1–C2′–N1′) and both N–H bonds point to the same direction.[7] In its crystal structure the azulene ring is planar. On the other hand, the crystal structures of similar derivatives **5** and **6**, synthesis of which we had already reported,[8,9] were quite different from that of **7**. Their single crystals were obtained by recrystallization from dichloromethane–hexane for **5** and from toluene–hexane for **6** and their analyzed crystal

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Keywords: Azulenes; Planarity; Out-of-plane deformation; X-ray crystallographic analysis; Density functional calculations; Rotational conformers.

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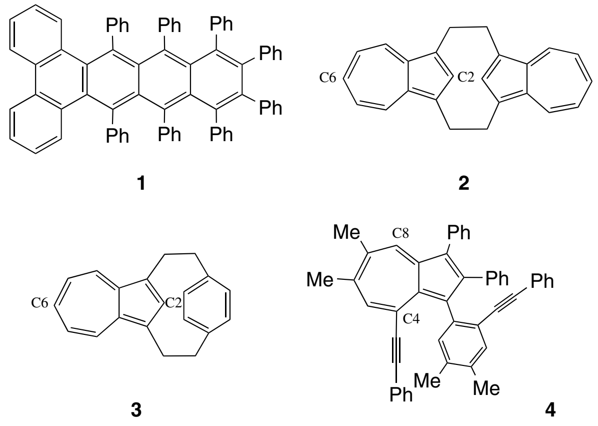

Chart 1.

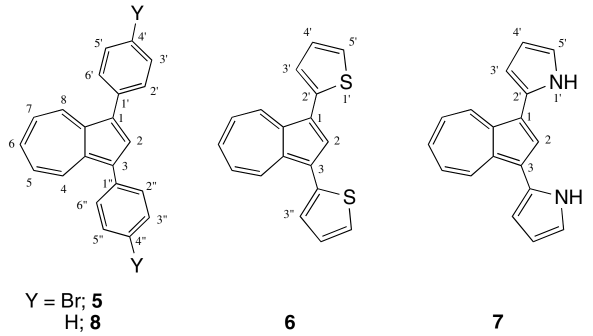

Chart 2.

structures are shown as ORTEP drawings in Figures 1 and 2.[10,11]

Both the bromophenyl and thienyl rings attached at the 1- and 3-positions connect to the azulenyl core with average dihedral angles of 35.9° and 38.3°, respectively.[12] As seen in the figures, the two phenyl rings of **5** slant to different ways and so do the two thienyl rings of **6**. The two sulfur atoms of **6** sit at the side of the 2-position of the azulene ring, causing its greater dipole moment. Surprisingly, the two seven-membered rings of the azulene moieties of **5** and **6** show out-of-plane deformation, which is best realized in side views of the ORTEP drawings. Table 1 indicates the deformations with the twist angles[13] of the C3a–C8a, C4–C8, and C5–C7 lines against the C1–C3 line. Figure 3 shows deviations of the seven-membered ring carbons from the plane of C1–C2–C3. In the figure, plus values mean that the carbons are in front of the plane and minus values at the back side of the plane when readers look toward the page. The carbon atoms at 6′ in **5** and at 3′ in **6** are in front of the plane and the carbons at 6″ in **5** and at 3″ in **6** are at the back side of the plane there. Thus, the hydrogen atoms at the 4- and 8-positions of **5** should be located apart from the neighboring H6′ and H6″ hydrogen atoms and those of **6** from the H3′ and H3″ hydrogen atoms to fill in an opened space made by the slanting aryl planes.[14]

Density functional theory (DFT) calculations[15] at the B3LYP/6-31G(d) level predict several possible conform-

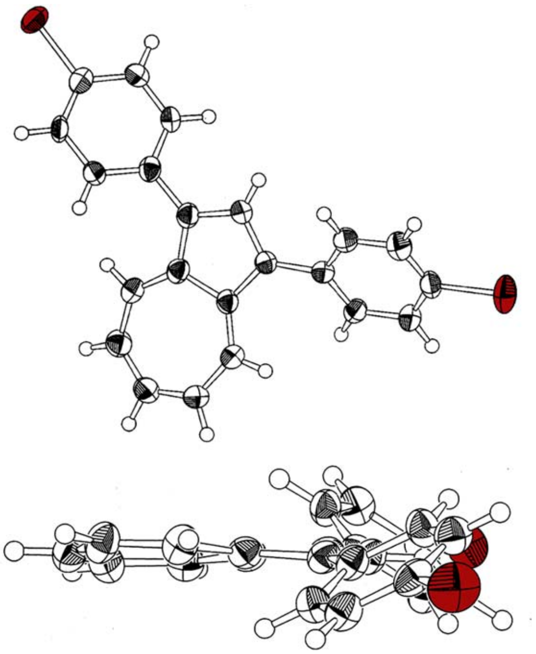

Figure 1. ORTEP drawings of **5**.

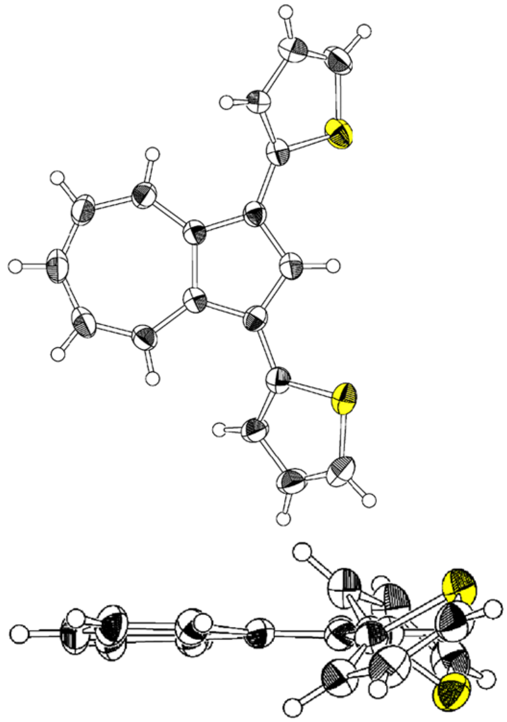

Figure 2. ORTEP drawings of **6**.

Table 1. Out-of-plane deformation of crystal structures of **5**, **6**, and **7** as shown by twist angles

Compound	Twisted angles (in degree) for C1–C3		
	C3a–C8a	C4–C8	C5–C7
5	3.16	7.27	9.69
6	1.39	4.80	6.56
7	0[a]	0[a]	0[a]

[a] Obtained from crystal data of **7** in Ref. 7.

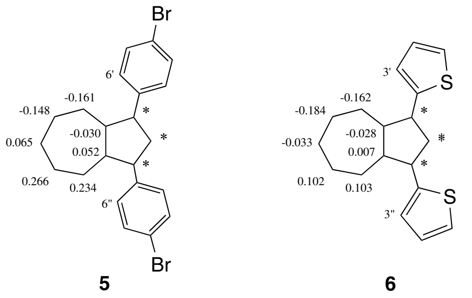

Figure 3. Deviation (Å) from the C1–C2–C3 plane in the crystal structures of **5** and **6**.

Table 2. Out-of-plane deformation of calculated conformers of **6**, **7**, and **8** as shown by twist angles

Compound	Twisted angles (in degree) for C1–C3		
	C3a–C8a	C4–C8	C5–C7
6A	1.641	5.612	7.730
6B	1.098	4.151	5.680
6C	0.077	0.163	0.227
6D	0.038	0.163	0.081
7A	1.406	4.853	6.719
7B	1.886	6.042	8.201
7C	0.001	0.001	0.002
7D	0.026	0.011	0.020
8A	1.034	4.684	6.440
8C	0.801	0.781	0.786

ers for **6**, **7** and 1,3-dipehylazuelene (**8**), instead of **5**; there are four (**6A**, **6B**, **6C**, and **6D**) for **6**, four (**7A**, **7B**, **7C**, and **7D**) for **7**, and two (**8A** and **8C**) for **8** (Fig. 4).[16] The conformers **A** and **B** have the aryl substituents slanting in different ways and the conformers **C** and **D** have the aryl substituents slanting in the same way. Among them, the conformers observed in the crystal state for **5** and **6** are the most stable, but not for **7**. Table 2 lists the twist angles[13] showing the out-of-plane deformation for the conformers. The optimized conformers **A** and **B** show clear out-of-plane deformation of their azulene rings, while the conformers **C** and **D** show negligible twist angles and can be thought to have almost planar azulene rings; results of the calculations support the experimental data not only on the deformation of **5** and **6** but also on the planarity in the crystal structure of **7**.[17] Therefore, it is best assumed that the conformers **A** and **B** make the vacant space, to where the H4 and H8 hydrogen atoms are able to spread their bond, up and down against their mean azulene plane. The phenyl- and thienyl groups can rotate around their affixing C–C single bonds in either solution or gas phase at ambient temperature, because the rotational barriers

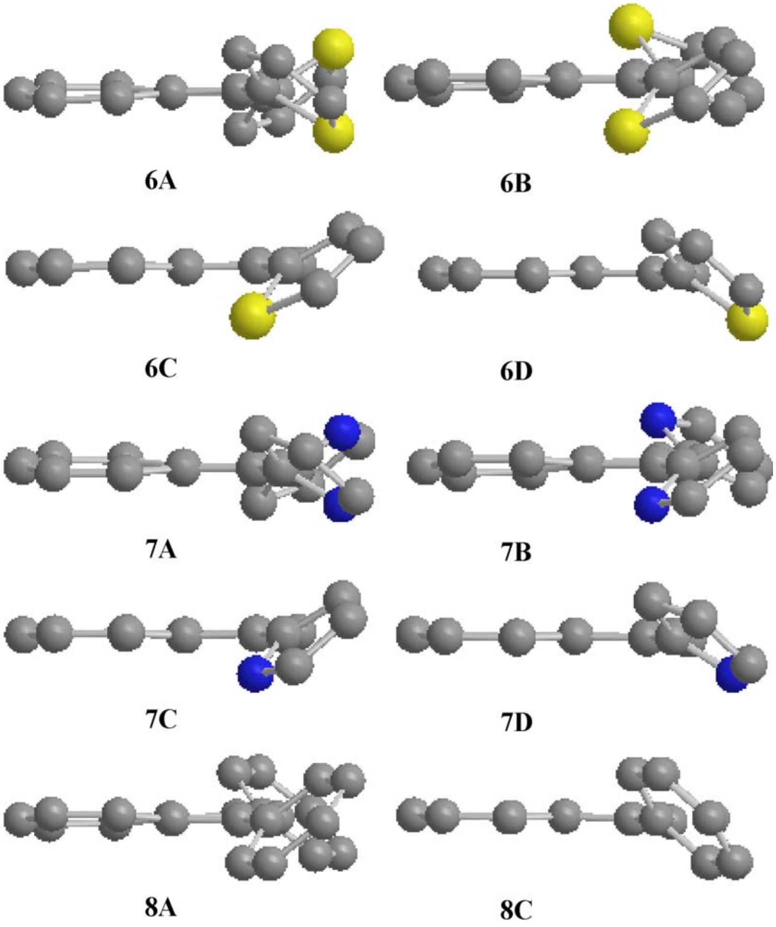

Figure 4. Optimized conformers (Chem3D output) of **6**, **7**, and **8**. Hydrogens are omitted. Carbon atoms are shown in gray, sulfur in yellow, and nitrogen in blue.

of 1-phenyl- and 1-(2-thienyl)azulenes are estimated to be less than 6 kcal/mol by DFT calculations.[18,19] Thus, one may imagine that the molecules can evade the deformation by rotating the aryl rings. However, the calculations predict that the molecules can relieve the strain by slight out-of-plane deformation for themselves. In other words, we have now become aware that an azulene ring can basically tolerate such a slight out-of-plane deformation and thus deform even under such circumstances.

In summary, we have elucidated the crystal structures of simply substituted azulene derivatives **5** and **6** and disclosed another example of the out-of-plane deformation along its short molecular axis. In spite of the inconsiderable forced strain, these molecules relieve the strain by out-of-plane deformation for themselves. We have also demonstrated that DFT calculations predict the deformation of 1,3-diarylazulenes approximately depending on their conformations, supporting the experimentals.[20]

Acknowledgments

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10. The X-ray data for **5**: $C_{22}H_{14}Br_2$, MW = 438.16, 0.40 × 0.30 × 0.50 mm^3, monoclinic, space group $P2_1$ (#4), $a = 4.021(3)$, $b = 10.936(4)$, $c = 19.451(2)$ Å, $\beta = 91.71(2)°$, $V = 854.9(7)$ Å^3, $Z = 2$, $D_{\text{calc}} = 1.702$ g cm^{-3}, μ(Mo-Kα) = 47.54 cm^{-1}, 2623 independent reflections, 218 parameters, $R = 0.052$ ($I > 2\sigma(I)$, 724 reflections), $wR = 0.095$, $S = 1.073$, $T = 296$ K. Those for **6**: $C_{18}H_{12}S_2$, MW = 292.40, 0.40 × 0.20 × 0.10 mm^3, orthorhombic, space group $Pbca$ (#61), $a = 17.402(4)$, $b = 7.3384(9)$, $c = 22.111(3)$ Å, $V = 2823.7(8)$ Å^3, $Z = 8$, $D_{\text{calc}} = 1.376$ g cm^{-3}, μ(Mo-Kα) = 3.62 cm^{-1}, 2007 independent reflections, 182 parameters, $R = 0.061$ ($I > 2\sigma(I)$, 1405 reflections), $wR = 0.137$, $S = 0.807$, $T = 298$ K. Estimated standard deviations for the bond lengths and angles are 0.004–0.007 Å and 0.2–0.4 °, respectively, for the non-hydrogen atoms. Crystallographic data excluding structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 288903 for **5** and CCDC 289169 for **6**, respectively. A copy of the data can be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ. UK [Direct line: +44 1223 762910, fax: +44 (0) 1223-336033 or e-mail: linstead@ccdc.cam.ac.uk; deposit@ccdc.cam.ac.uk].
11. Although Lai et al. have recently reported X-ray crystallographic analysis of **5**, we had analyzed its crystal structure independently. Both results are almost the same. However, they did not claim any deformation of the azulene ring, which we have reported herein. Wang, F.; Han, M.-Y.; Mya, K. Y.; Wang, Y.; Lai, Y.-H. *J. Am. Chem. Soc.* **2005**, *127*, 10350–10355.
12. These values were obtained as a dihedral angle between the mean planes of the azulene five-membered ring and the mean substituted aryl plane; 34.94° and 36.95° for **5** and 35.01° and 41.61° for **6**. Average torsion angles are 36.6° for **5** (C2–C1–C1′–C2′ and C2–C3–C1″–C2″) and 37.0° (C2–C1–C2′–S1′ and C2–C3–C2″–S1″) for **6**.
13. The twist angles were obtained by the way reported in the following reference: Symth, N.; Van Eugen, D.; Pascal, R. A., Jr. *J. Org. Chem.* **1990**, *55*, 1937–1940.
14. Unusual bond length and angle were not observed in crystal structures of **5** and **6**. No short contact between the intermolecular atoms was found for **5** but there is one between one of the sulfur atoms and the hydrogen at 3′ on the thienyl ring of another molecule with a distance of 2.997 Å in **6**, assumed to be CH–S interaction. There is no disorder derived from crystal packing. Therefore, these deformations can only be ascribed to the intramolecular steric hindrance.
15. DFT calculations were conducted by using the Mulliken (ver. 2.0.0, IBM Inc.) program.
16. Relative total energies (kcal/mol) of the calculated conformers are as follows: For **6**, **A**: 0, **B**: 1.005, **C**: 1.188, **D**: 0.104, for **7**, **A**: 0, **B**: 1.417, **C**: 1.757, **D**: 0.546, and for **8**, **A**: 0, **C**: 0.197.
17. The crystal structure of **5** shows slightly shorter atomic distance by 0.026 Å between the C8- and 8a-positions at the azulene ring than that in the calculated structure of **8A**. This may cause to a little greater difference of the twisted

angles between the crystal structure of **5** and the calculated structure of **8A**. Other slightly shorter atomic distances are observed between the C1- and 2-positions at the azulene ring by 0.032 Å and between the C1″ and C2″ carbons at the phenyl group by 0.024 Å than that in the calculated structure of **8A**. The other differences are less than 0.015 Å.

18. The rotational barriers of 1-phenyl- and 1-(2-thienyl)azulenes are estimated as 5.33 and 2.67 kcal/mol, respectively, from total energies of the optimized structures with the locked dihedral angles. Calculations were carried out at the B3LYP/6-31G(d) level of theory.
19. The free rotation is also supported by NMR experiments; the ^{1}H NMR spectra of **5** and **6** in CD_2Cl_2 at low temperature of −90 °C did not show any intrinsic signal broadening based on the rotational process.
20. Quite recently Yamamura et al. reported a non-planar azulene structure in helical molecules: Yamamura, K.; Kawabata, S.; Kimura, T.; Eda, K.; Hashimoto, M. *J. Org. Chem.* **2005**, *70*, 8902–8906; For other example of a non-planar azulene structure in helicene, see: Ito, S.; Nomura, A.; Morita, N.; Kabuto, C.; Kobayashi, H.; Maejima, S.; Fujmori, K.; Yasunami, M. *J. Org. Chem.* **2002**, *67*, 7295–7302.