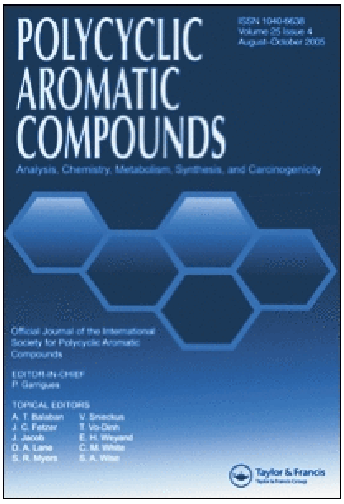
This article was downloaded by: *[National Taiwan University]*
On: *31 August 2009*
Access details: *Access Details: [subscription number 905688740]*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Polycyclic Aromatic Compounds

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647615

## From Overcrowded Polycyclic Aromatic Enes to Semifullerenes

P. Ulrich Biedermann [ab]; Tien-Yau Luh [c]; David T. -C. Wengc [c]; Chi-Hong Kuo [c]; John J. Stezowski [d]; Israel Agranat [a]

[a] Department of Organic Chemistry, the Hebrew University of Jerusalem, Jerusalem, Israel [b] Institut für Organische Chemie, Universität Stuttgart, Stuttgart, Germany [c] Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C [d] Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE, USA

Online Publication Date: 01 January 1996

**To cite this Article** Biedermann, P. Ulrich, Luh, Tien-Yau, Wengc, David T. -C., Kuo, Chi-Hong, Stezowski, John J. and Agranat, Israel(1996)'From Overcrowded Polycyclic Aromatic Enes to Semifullerenes',Polycyclic Aromatic Compounds,8:2,167 — 175

**To link to this Article: DOI:** 10.1080/10406639608048342

**URL:** http://dx.doi.org/10.1080/10406639608048342

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*Polycyclic Aromatic Compounds*, 1996, Vol. 8, pp. 167–175
Reprints available directly from the publisher
Photocopying permitted by license only

# From Overcrowded Polycyclic Aromatic Enes to Semifullerenes

P. ULRICH BIEDERMANN[a,b], TIEN-YAU LUH[c], DAVID T.-C. WENG[c],
CHI-HONG KUO[c], JOHN J. STEZOWSKI[d] and ISRAEL AGRANAT[a]

[a]*Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

[b]*Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*

[c]*Department of Chemistry, National Taiwan University, Roosevelt Road Sect. 4, Taipei, Taiwan 106, R.O.C*

[d]*Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68588, USA*

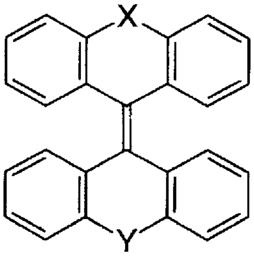
*(Received October 13, 1995; in final form November 22, 1995)*

Overcrowded polycyclic aromatic enes (**1**), e.g., bi-9*H*-fluoren-9-ylidene (**2**) and bi-4*H*-cyclopenta[def]-phenanthren-4-ylidene (**3**) are potential starting materials for the preparation of bowl-shaped fragments of fullerenes. Semiempirical MNDO-PM3 calculations of $C_{26}H_n$ and $C_{30}H_n$ (n = 12, 14, 16) species **2**–**14** are used to analyze energetic and steric effects on the dehydrocyclization and isomerization reactions of these molecules. The out-of-plane bending and pyramidalization in these species are ascribed to intramolecular overcrowding in the fjord and cove regions and to strain introduced by C5 rings in the PAH skeleton. Oxidative photocyclization reactions on Z-2,2′-bridged derivatives of **2** and **3** are briefly outlined.

*Keywords: non-planar PAHs, strain, overcrowding, semiempirical calculations, photocyclization.*

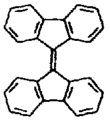
## INTRODUCTION

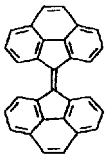
The bistricyclic enes (**1**) enigma[1] has fascinated chemists since the red hydrocarbon

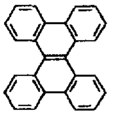


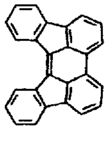
**1**

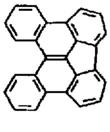
bi-9*H*-fluoren-9-ylidene (**2**) was synthesized six score years ago.[2] Overcrowded polycyclic aromatic enes, e.g., **2** and bi-4*H*-cyclopenta[def]phenanthren-4-ylidene (**3**) are potential starting materials for the preparation of bowl-shaped fragments of fullerenes. Dehydrogenation of **2** and the isomeric dibenzo[g,p]chrysene (**4**) may lead via benz[e]indeno[1,2,3-hi]acephenanthrylene (**5**) and benz[g]indeno[1,2,3,4-mnop]chrysene (**6**), respectively, to diindeno[1,2,3,4-defg; 1',2',3',4'-mnop]chrysene (**7**), while dehydrogenation of **3** and the isomeric tetrabenzo[de, hi, mn, qr]naphthacene (**8**) may lead via diindeno[4,3,2,1-opqr; 4',3',2',1'-avut]picene (**9**) and dibenzo[mn, qr]fluoreno[2,1,9,8,7-defghi]naphthacene (**10**) to diacenaphtho[3,2,1,8-cdefg; 3',2',1',8'-lmnop]chrysene (**11**) and difluoreno[2,1,9,8,7-defghi; 2',1',9',8',7'-mnopqr]naphthacene (**12**), respectively. Semifullerene **11** may also be viewed as circumpentafulvalene.[3] Syntheses of

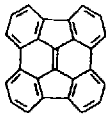

**2**

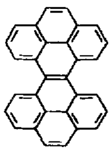

**3**

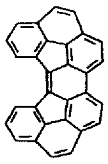

**4**

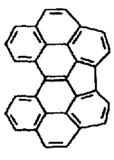

**5**

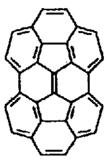

**6**

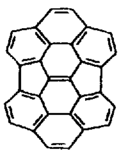

**7**

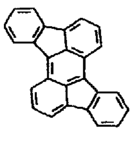

**8**

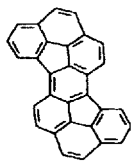

**9**


**10**


**11**


**12**


**13**


**14**

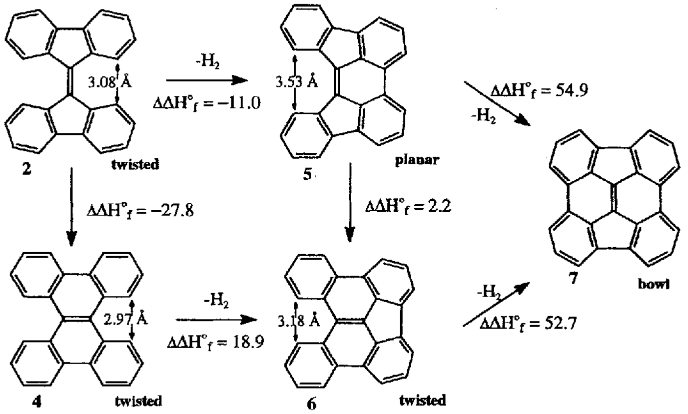
the fullerene fragment **7**, of **12** and of the intermediates **5**, **6**, **9**, and **10** by thermal and catalytic dehydrocyclization have been reported recently.[4] Semifullerene **11** has been synthesized by an alternative route from 1,2,5,6,-tetraoxopyracene.[5]

The present article describes the results of PM3 calculations of $C_{26}H_n$ and $C_{30}H_n$ (n = 12, 14, 16) species including hydrocarbons **2**–**12**, rubicene (**13**),[6] an isomer of **5** and **6**, and dibenzorubicene (**14**), an isomer of **8** and **9**. Syntheses of bridged derivatives of **5** and **8** by oxidative photocyclization of *Z*-2,2'-bridged derivatives of **2**[7] and **3** are also outlined.[8]

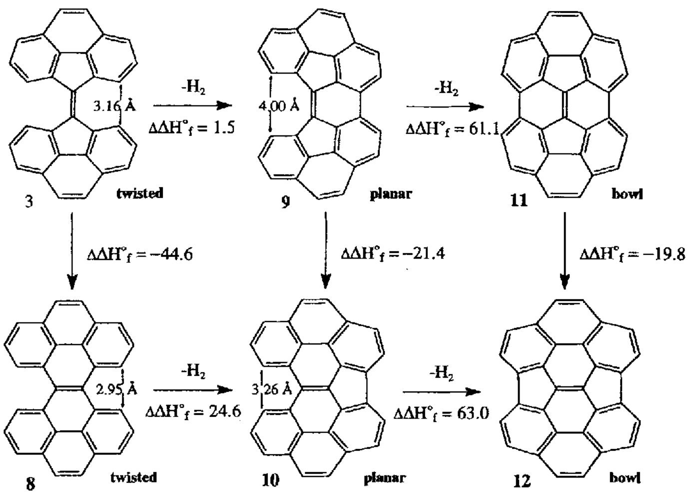
## RESULTS AND DISCUSSION

The calculations of hydrocarbons **2**–**14** were carried out by the quantum mechanical semiempirical MNDO–PM3 method, using MOPAC6.[9] Heat of Formation ($\Delta H_f^\circ$) values are given in kcal/mol; bond lengths, H···H, and C···C distances are given in Å, bond angles and pyramidalization angles $\chi$ are given in degrees.

Bistricyclic enes **2** and **3** adopt twisted conformations with experimental average twist angles (about the central C = C bonds) of 32.5° and 24.7° in the crystalline state, respectively.[10,11] The PM3 calculated twist angles of **2** and **3** are 30.2°[12] and 23.0°. The isomeric compounds **4** and **8** also have twisted conformations, with twist angles of 26.0° and 23.7°, respectively, in their crystal structures.[13,14] The corresponding PM3 calculated twist angles are 25.8° and 24.3°. Schemes 1 and 2 describe the



SCHEME 1 Dehydrocyclizations and isomerizations in the $C_{26}H_n$ series.



SCHEME 2 Dehydrocyclizations and isomerizations in the $C_{30}H_n$ series.

dehydrocyclizations and isomerizations in the $C_{26}H_n$ and $C_{30}H_n$ ($n = 12, 14, 16$) series, respectively, including the reaction enthalpies $\Delta\Delta H_f^\circ$ of the various steps and the distance between the carbon atoms, which will form the new bond.

Double dehydrocyclization of **2** and **4** may lead to a single $C_{26}H_{12}$ species, **7**, while double dehydrocyclization of **3** and **8** may lead to two $C_{30}H_{12}$ species, **11** and **12**. The dehydrogenation of **2** all the way to **7** is thermodynamically less demanding than the dehydrogenation of **3** to **11**. Moreover, the "aromatization" of **2** by dehydrogenation to the planar **5** is highly exothermic, while the corresponding "aromatization" of **3** to the planar **9** is slightly endothermic. On the other hand, the dehydrogenations of **4** into **6** and of **8** into **10** are highly endothermic. In all cases, the second dehydrocyclization

(**5** to **7**, **6** to **7**, **9** to **11** and **10** to **12**) is highly endothermic. In contrast, the isomerization reactions **2** to **4**, **3** to **8**, **9** to **10**, and **11** to **12** are highly exothermic, with the exception of **5** to **6**, which is slightly endothermic. Apart from the energetic criterion the steric situation in the reactants may have an effect on their reactivity. Short non-bonded C···C distances could be advantageous for the reactions **2** to **5** (3.080 Å), **3** to **9** (3.157 Å), **4** to **6** (2.966 Å), **6** to **7** (3.183 Å), and might explain why reaction **10** to **12** (3.264 Å) was observed under FVP conditions while reaction **9** to **11** (3.999 Å) was not.[4]

The results of the PM3 calculations on the compounds **2**–**14** are summarized in Table 1, including the symmetry, heat of formation ($\Delta H_f^\circ$), and some important geometrical parameters. 3D projections of the most important structures are shown in Figures 1 and 2. All calculated structures presented are *bona fide* minima, unless otherwise stated. Figure 3 gives the bond lengths and bond angles of the bowl shaped hydrocarbons **7**, **11**, and **12**, respectively.

The benzenoid PAHs **4** and **8** are significantly more stable than the bistricyclic enes **2** and **3**, respectively ($\Delta H_f^\circ(\mathbf{4}) - \Delta H_f^\circ(\mathbf{2}) = -27.8$ kcal/mol; $\Delta H_f^\circ(\mathbf{8}) - \Delta H_f^\circ(\mathbf{3}) = -44.6$ kcal/mol). Among the $C_{26}H_{14}$ species, the planar **5** is the most stable; compounds **6** and **13** are higher in energy by 2.2 kcal/mol and 8.0 kcal/mol, respectively. Among the $C_{30}H_{14}$ species, the planar **10** is the most stable; compounds **9** and **14** are higher in energy by 21.4 kcal/mol and 28.1 kcal/mol, respectively.

TABLE 1
PM3 calculated structures of compounds 2–14.

| Compound | Conformation | | Symmetry | $\Delta H_f^\circ$ | $\Delta\Delta H_f^\circ$ | |
|---|---|---|---|---|---|---|
| **2** | twisted | | $D_2$ | 140.874 | 0 | twist = 30.2° |
| **2** | anti-folded | | $C_{2h}$ | 145.481 | 4.607 | fold = 20.8° |
| **2** | syn-folded | | $C_{2v}$ | 149.034 | 8.160 | fold = 22.5° |
| **3** | twisted | | $D_2$ | 175.291 | 0 | twist = 23.0° |
| **3** | anti-folded | | $C_{2h}$ | 178.165 | 2.874 | fold = 18.1° |
| **3** | syn-folded | | $C_{2v}$ | 181.499 | 6.208 | fold = 19.4° |
| **4** | twisted | | $D_2$ | 113.115 | 0 | twist = 25.8° |
| **4** | anti-folded | | $C_{2h}$ | 117.279 | 4.164 | fold = 24.8° |
| **5** | planar | | $C_{2v}$ | 129.893 | | |
| **6** | twisted | | $C_2$ | 132.052 | 0 | twist = 11.9° |
| **6** | planar | TS | $C_{2v}$ | 132.458 | 0.406 | |
| **7** | bowl | | $C_{2v}$ | 184.745 | 0 | $\chi = 36.8°$ |
| **7** | planar | TS | $D_{2h}$ | 198.860 | 14.115 | |
| **8** | twisted | | $D_2$ | 130.695 | 0 | twist = 24.3° |
| **8** | anti-folded | | $C_{2h}$ | 134.504 | 3.809 | fold = 22.7° |
| **9** | planar | | $C_{2v}$ | 176.754 | | |
| **10** | planar | | $C_{2v}$ | 155.358 | | |
| **11** | bowl | | $C_{2v}$ | 237.868 | 0 | $\chi = 42.4°$ |
| **11** | anti | | $C_{2h}$ | 288.032 | 50.164 | $\chi = 40.9°$ |
| **11** | | TS | $C_s$ | 292.876 | 55.008 | $\chi = 49.3°/6.9°$ |
| **11** | planar | [a] | $D_{2h}$ | 336.200 | 98.332 | |
| **12** | bowl | | $C_{2v}$ | 218.358 | 0 | $\chi = 40.9°$ |
| **12** | planar | TS | $D_{2h}$ | 267.356 | 48.998 | |
| **13** | planar | | $C_{2h}$ | 137.948 | | |
| **14** | planar | | $C_{2h}$ | 183.486 | | |

[a] second order saddle point with 2 imaginary frequencies.

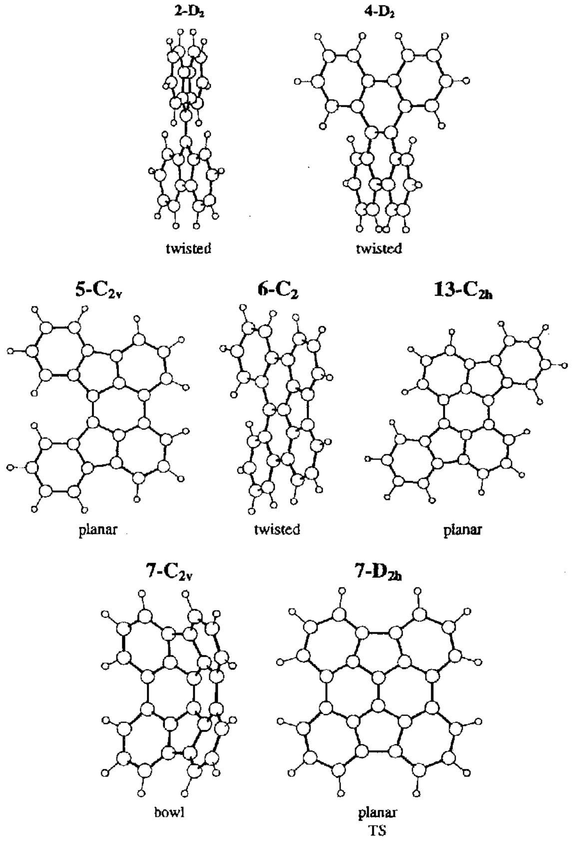


FIGURE 1 Conformations of the $C_{26}H_n$-species.

The bowl-to-bowl inversion of 7 involves a planar $D_{2h}$ transition state; the inversion barrier is 14.2 kcal/mol.[4b]

The most stable conformation of semifullerene **11** has a bowl-shaped $C_{2v}$ geometry. The corresponding $C_{2h}$ *anti*-folded conformation is a local minimum higher in energy by 50.2 kcal/mol. The transition state for the $C_{2h} \rightarrow C_{2v}$ isomerization is a $C_s$ conformation 4.8 kcal/mol above the $C_{2h}$ conformation. Bowl-to-bowl inversion of the $C_{2v}$ conformation proceeds in two steps via the $C_{2h}$ intermediate; the barrier is 55.0 kcal/mol. The planar $D_{2h}$ conformation of **11** is a second order saddle point with a relative energy of 98.3 kcal/mol. (Ab-initio calculations of various conformations of **11** and of bowl-to-bowl inversions in other PAHs with curved surfaces have been reported.[4,5])

The isomeric $C_{30}H_{12}$ compound, **12**, is not a buckminsterfullerene fragment. It is 19.5 kcal/mol more stable than compound **11**. The transition state for bowl-to-bowl inversion of **12** is planar; the inversion barrier is 49.0 kcal/mol.

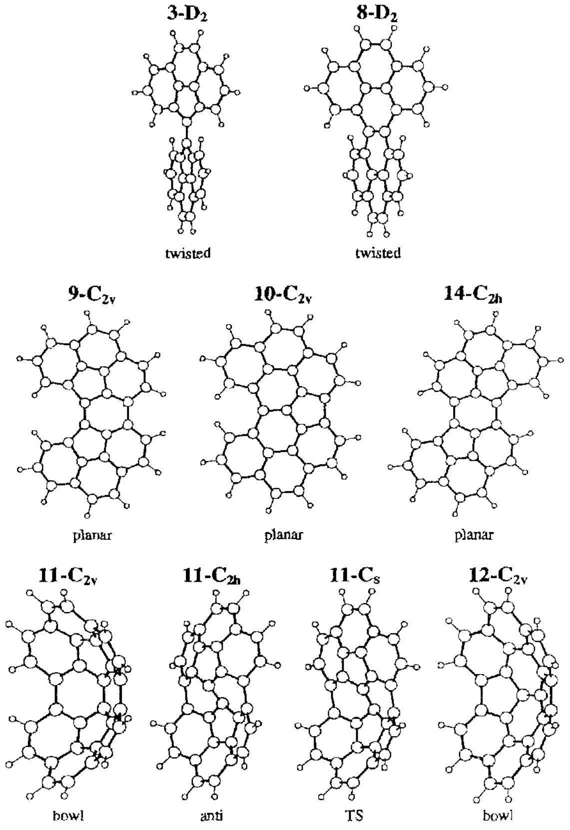


FIGURE 2 Conformations of the $C_{30}H_n$-species.

## Isodesmic Reactions

Table 2 gives the energies (ΔE) of isodesmic reactions related to the species shown in Schemes 1 and 2. Isodesmic reactions (a) and (b) indicate that the intermediate **5** is relatively stable while **7** is highly strained as compared with **9** and **11** respectively. On the other hand reactions (c) and (d) indicate that **10** is more stable than **6**.

## Steric Strain and Overcrowding

Two effects may cause non-planarity of the $C_{26}H_n$ and $C_{30}H_n$ species: intramolecular overcrowding in the fjord and cove regions and in-plain strain. The in-plain strain may qualitatively be evaluated by counting the number of carbon atoms $q$ that belong simultaneously to one 5-membered ring and to two 6-membered rings. The central carbon atom of acenaphthylene is the simplest example. At these carbon atoms the ideal bond angles of the polygons do not add up to 360°. This would lead to

TABLE 2
Energies of isodesmic reactions.

| | Isodesmic Reactions | | | $\Delta\Delta H_f^{\circ}$ |
|---|---|---|---|---|
| (a) | 2 + 7 | ⟶ | 5 + 5 | − 65.8 |
| (b) | 3 + 11 | ⟶ | 9 + 9 | − 59.6 |
| (c) | 4 + 7 | ⟶ | 6 + 6 | − 33.8 |
| (d) | 8 + 12 | ⟶ | 10 + 10 | − 38.3 |

pyramidalization of the carbon centers and/or distortion of the ring angles. A chain of $q = 3$ such carbon atoms is still acceptable for a planar structure, a chain of $q = 5$, as in corannulene, is not. The number of overcrowded regions of compounds **2**–**14** along with the symmetries and conformations and the number $q$ are given in Table 3. The overcrowding in the various $C_{26}H_n$ and $C_{30}H_n$ species (n = 14, 16) is reflected in the short H···H and C···C distances in the fjord and cove regions. Note in particular the very short H···H distances in the planar compounds **5** and **10**, and the slightly twisted compound **6**.

The length of the bonds connecting the two halves of the bowl-shaped molecules are noteworthy: **7**: 1.344 Å (central bond) and 1.471 Å (peripheral bonds); **11**: 1.356 Å (central bond) and 1.462 Å (peripheral bonds); **12**: 1.353 Å (central bond), 1.358 Å (peripheral bonds), and 1.446 Å (inner bonds). Thus, the central bonds are of double bond character and the peripheral bonds (inner bonds in the case of **12**) are more of a single bond character. The strain in the bowl-shaped species **7**, **11** and **12** is manifested in the C-C-C bond angles in their perimeter. The angles in the phenanthrene-type bay region of **7** and **11** are 127.2° and 125.8°, respectively. The angles in the fluorene-type

TABLE 3
Conformations, strain and overcrowding.

| Compound | Symmetry | Conformation | q | Number of Overcrowded Regions | | | Shortest[a] | |
|---|---|---|---|---|---|---|---|---|
| | | | | Fjords | Coves | Bays[b] | C···C | H···H |
| **2** | $D_2$ | twisted | — | 2 | — | 2 | 3.080 | 1.883 |
| **3** | $D_2$ | twisted | 2 + 2 | 2 | — | — | 3.157 | 1.764 |
| **4** | $D_2$ | twisted | — | — | 2 | 2 | 2.966 | 1.848 |
| **5** | $C_{2v}$ | planar | 1 + 1 | 1 | — | 3 | 3.534 | 1.657 |
| **6** | $C_2$ | twisted | 3 | – | 1 | 3 | 3.183 | 1.657 |
| **7** | $C_{2v}$ | bowl | 6 | – | – | 4 | | |
| **8** | $D_2$ | twisted | – | – | 2 | – | 2.953 | 1.847 |
| **9** | $C_{2v}$ | planar | 3 + 3 | 1 | – | 1 | 3.999 | 2.320 |
| **10** | $C_{2v}$ | planar | 3 | – | 1 | 1 | 3.264 | 1.637 |
| **11** | $C_{2v}$ | bowl | 10 | – | – | 2 | | |
| **12** | $C_{2v}$ | bowl | 6 | – | – | 2 | | |
| **13** | $C_{2h}$ | planar | 1 + 1 | – | 2 | 2 | 3.439 | 1.883 |
| **14** | $C_{2h}$ | planar | 3 + 3 | – | 2 | – | 3.843 | 2.549 |
| corannulene | $C_{5v}$ | bowl | 5 | – | – | – | – | – |
| $C_{60}$ | $I_h$ | sphere | 60 | – | – | – | | – |

[a] The H···H and C···C distances given (in Å) are the shortest in the fjords, coves and bays.
[b] The bays include proper (phenanthrene-type) and improper (fluorene-type) bay regions.

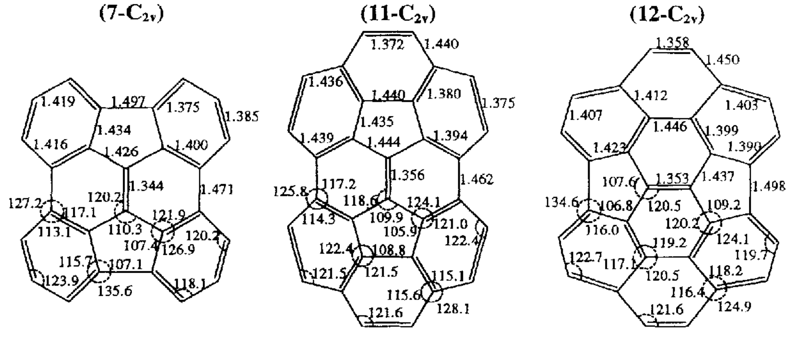
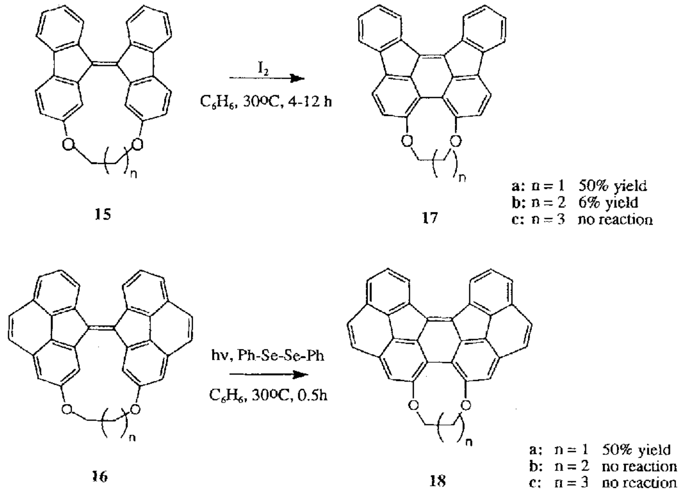


FIGURE 3 Bond lengths and bond angles of 7, 11 and 12.

bay regions of **7** and **12** are 135.6° and 134.6°, respectively. The C-C-C angles at the peri positions of **11** and **12** are 128.1° and 124.9° (for comparison: corannulene, 129.5°). Thus, angle strain is larger in **7** as compared with **11** and **12**. The high values of the pyramidalization angles, $\chi$, of the various bowl-shaped species should be noted: $\chi(C_{2v}\text{-}\mathbf{7}) = 36.8°$, $\chi(C_{2v}\text{-}\mathbf{11}) = 42.4°$, $\chi(C_{2v}\text{-}\mathbf{12}) = 40.9°$; for comparison, $\chi(C_{60}) = 41.8°$,[15] and $\chi(\text{corannulene}) = 33.8°$.[16]

## Syntheses

Scheme 3 describes the dehydrogenation reactions of Z-2,2′-bridged bi-9*H*-fluoren-9-ylidene derivatives **15a–c** and Z-2,2′-bridged bi-4*H*-cyclopenta[def]phenanthren-4-ylidene derivatives **16a–c** by oxidative photocyclizations leading to **17** and **18**. The syntheses of **15a–c** and **16a–c** have been described previously.[7,8] A second oxidative



SCHEME 3 Oxidative Photocyclization.

photocyclization of compounds **17** and **18** to give derivatives of **7** and **11** could not be accomplished. The dramatic decrease in the yields with increasing tether length $n$ suggests steric requirements, e.g., a short $C \cdots C$ non-bonded distance in the reactants is essential for the dehydrogenation. It should be noted that the unsubstituted compound **2** does not undergo oxidative photocyclization.[8]

## CONCLUSIONS

The insertion of 5-membered rings into the framework of benzenoid polycyclic hydrocarbons distorts mainly the bond angles at the $sp^2$ carbon centers from the ideal 120° (angle strain effect), as long as the number $q$ is small and the conformation of the molecule is planar or a shallow bowl. However, at higher $q$ values, with increasing depth of the bowl, pyramidalization of the carbon atoms increases, while the angular strain in the 6-membered rings is reduced.

## REFERENCES

1. G. Shoham, S. Cohen, M. R. Suissa and I. Agranat, in J. J. Stezowski, J. -L. Huang, and M. -C. Shao (editors), *Molecular Structure, Chemical Reactivity and Biological Activity*, Oxford University Press, Oxford, 1988, p. 290.
2. C. de la Harpe and W. A. van Dorp, *Ber. Dtsch. Chem. Ges.*, 8 (1875) 1048.
3. For a review on circulenes, see: K. Yamamoto, H. Matsubara, *J. Synthetic Org. Chem.*, 53 (1995) 318.
4. (a) S. Hagen, U. Nuechter, M. Nuechter and G. Zimmermann, *Tetrahedron Lett.*, 35 (1994) 7013; (b) S. Hagen, U. Nuechter, M. Nuechter and G. Zimmermann, *Polycyclic Aromatic Compounds*, 4 (1995) 209.
5. P. W. Rabideau, A. H. Abdourazak, H. E. Folsom, Z. Marcinow, A. Sygula and R. Sygula, *J. Am. Chem. Soc.*, 116 (1994) 7891.
6. (a) K. F. Lang, H. Buffleb and J. Kalowy, *Chem. Ber.*, 94 (1961) 523; (b) E. Clar, *Polycyclic Hydrocarbons*, Vol. 2, Academic Press, London, 1964, p. 345.
7. Y. C. Yip, X. -J. Wang, D. K. P. Ng, T. C. W. Mak, P. Chiang, and T. -Y. Luh, *J. Org. Chem.*, 55 (1990) 1881.
8. C. -H. Kuo, M. H. Tsau, D. T. C. Weng, G. H. Lee, S. -M. Peng and T. -Y. Luh, P. U. Biedermann and I. Agranat, *J. Org. Chem.*, 60 (1995) 7380.
9. (a) J. J. P. Stewart, *J. Comp. Chem.*, 10 (1989) 221; (b) J. J. P. Stewart, *J. Computer-Aided Molecular Design*, 4 (1990) 1; (c) J. J. P. Stewart, MOPAC 6.00, *QCPE* 455, (1990).
10. (a) N. A. Bailey and S. E. Hull, *Acta Cryst.*, B34 (1978) 3289; (b) J. -S. Lee and S. C. Nyburg, *Acta Cryst.*, C41 (1985) 560.
11. J. J. Stezowski, T. Hildenbrand, M. R. Suissa and I. Agranat, *Struct. Chem.*, 1 (1990) 123.
12. P. U. Biedermann, A. Levy, J. J. Stezowski and I. Agranat, *Chirality*, 7 (1995) 199.
13. F. H. Herbstein, *Acta Cryst.*, B35 (1979) 1661.
14. K. W. Muir and J. M. Robertson, *Acta Cryst.*, B28 (1972), 879.
15. (a) R. C. Haddon, *J. Am. Chem. Soc.*, 112 (1990) 3385. For a PM3 calculation on $C_{60}$ see: (b) J. J. P. Stewart and M. B. Coolidge, *J. Comp. Chem.*, 12 (1991) 1157.
16. PM3 calculation; for experimental value ($\chi = 32.6°$), see reference 15a and J. C. Hanson, C. E. Nordman, *Acta Cryst.*, B32 (1976) 1147.