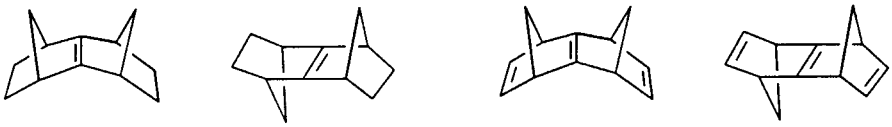
Synthesis of a New System Containing a Pyramidalized Double Bond: Lack of Reactivity of a Strongly Protected Pyramidalized Double Bond

by **Nurullah Saraçoğlu**[a]) and **Metin Balci**[b])*

[a]) Department of Chemistry, Atatürk University, TR-25240 Erzurum
[b]) Department of Chemistry, Middle East Technical University, TR-06531 Ankara

The chemical reactivity of *syn*-**3** was investigated. The experimental results showed that the central double bond of this system is inert toward chemical reactions. To determine the reactivity of this central double bond, we synthesized *syn*- and *anti*-**7** and recorded their photoelectron spectra. Low first-ionization potentials of *syn*- and *anti*-**7** (7.6 eV) clearly indicated that these compounds should be highly reactive.

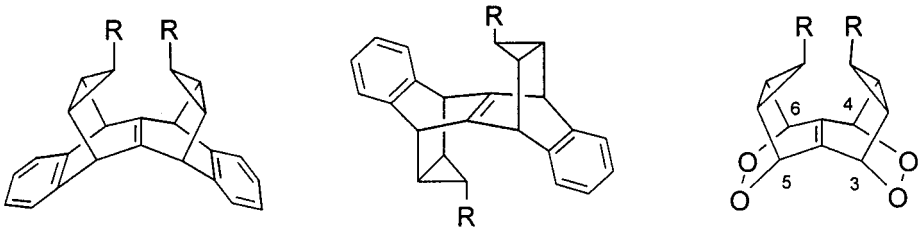
Introduction. – In 1980, *syn*- and *anti*-'sesquinorbornenes' *syn*- and *anti*-**1** and 'norbornatrienes' *syn*- and *anti*-**2** were synthesized independently by *Bartlett* and co-workers [1] and *Paquette* and co-workers [2]. X-Ray studies [3] showed that the π-bonded C-atoms in the *syn* isomer are significantly pyramidalized, with folding angles ranging from 16 to 18°.



syn-**1** *anti*-**1** *syn*-**2** *anti*-**2**

Theoretical work has shown that a trigonal center of a C=C bond pyramidalizes when located in an unsymmetrical environment [4]. When there is an unsymmetrical arrangement of allylic bonds with respect to an alkene, there is a driving force for pyramidalization. *Houk* [5] has postulated that the electron density of the alkene π bond influences the degree of the pyramidalization. The strained ring systems containing pyramidalized C=C bonds are unusually reactive and often unstable [6]. For example, epoxidation of *syn*-**1** with *m*-chloroperbenzoic acid (*m*-CPBA) delivered the *exo*-epoxide within 10 min at $-20°$. Increasing the number of C=C bonds in the *syn*-'sesquinorbornene' skeleton also increases the reactivity of the central C=C bond. Thus, *syn*-**2** is so reactive to triplet oxygen that it must be handled in an inert atmosphere [7].

In recent years, we have been concerned with the synthesis, structure analysis, and chemical properties of pyramidalized alkenes, and have reported the synthesis of *syn*- and *anti*-**3** and of *syn*-**4** [8–12].



syn-**3** *anti*-**3** *syn*-**4**

R = $COOCH_3$

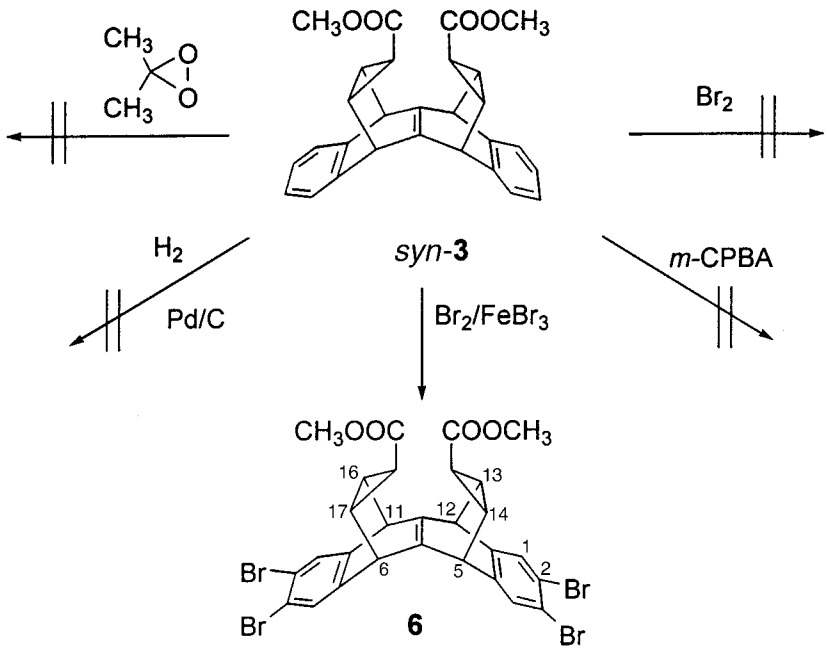
It has been found that, in asymmetric environments, C=C bonds tend to pyramidalize to minimize eclipsing interactions. The results of X-ray analysis [11] showed that compounds in *syn*-structures are pyramidalized, and that the relevant pyramidalization angle varies between 16.4–19.9°, while *anti*-isomers have a planar structure. Most recently, we have shown that there is another factor responsible for the pyramidalization. The change in rehybridization of C(3) and the symmetrically equivalent atoms C(4), C(5), and C(6) in *syn*-**4** causes further pyramidalization [12]. In this paper, we describe the synthesis of dimethyl derivatives of *syn*- and *anti*-**7** and their photoelectron spectra. Furthermore, we will discuss the chemical reactivity of *syn*-**3**.

Results and Discussion. – The synthesis of *syn*-**3** [10] and *anti*-**3** [8] entailed the addition of 2 mol of benzyne to the *cis*-**5** [10] and *trans*-**5** [13], respectively, and took advantage of the cycloheptatriene-norcaradiene equilibrium (see below, *Scheme 2*) [14]. To examine the chemical reactivity, we selected *syn*-**3** as the model compound.

Bromination, hydrogenation, and epoxidation of a C=C double bond are formally three of the simplest reactions typical of unsaturated compounds. However, when epoxidation, bromination, and hydrogenation of *syn*-**3** were attempted, we isolated, in all cases, only unreacted starting material (*Scheme 1*). Besides, we treated *syn*-**3** with Br_2 in the presence of $FeBr_3$ and obtained as the single reaction product, the tetrabromide **6** (*Scheme 1*). NMR Data (*s* for the aromatic H-atoms) and elemental analysis established that **6** contains four Br-atoms at the aromatic rings, which are symmetrically substituted. The exact position of the Br-atoms was determined by analysis of the ^{13}C satellites in the ^{1}H-NMR spectrum. The ^{13}C satellites of aromatic H-atoms appeared as a broad *d* around the main signal with a coupling constant $J(H,C) = 168.9$ Hz. In the case of *para*-substitution by Br-atoms, we should observe further *d* splitting in the ^{13}C satellite signals with *ortho*-coupling [15].

The X-ray crystal-structure analysis of *syn*-**3** shows a pyramidalization angle ϕ of 16.8° [10]. Calculations indicate that pyramidalization has little effect on the energy of HOMO, but that of LUMO is lowered appreciably [16]. This should be reflected in the chemical reactivity of pyramidalized compounds. That we could not observe any reaction with the central C=C bond in *syn*-**3** indicates that the *syn*-structures are so heavily congested that the pyramidalized sp^2-C-atoms are not accessible to any reactant.

Scheme 1



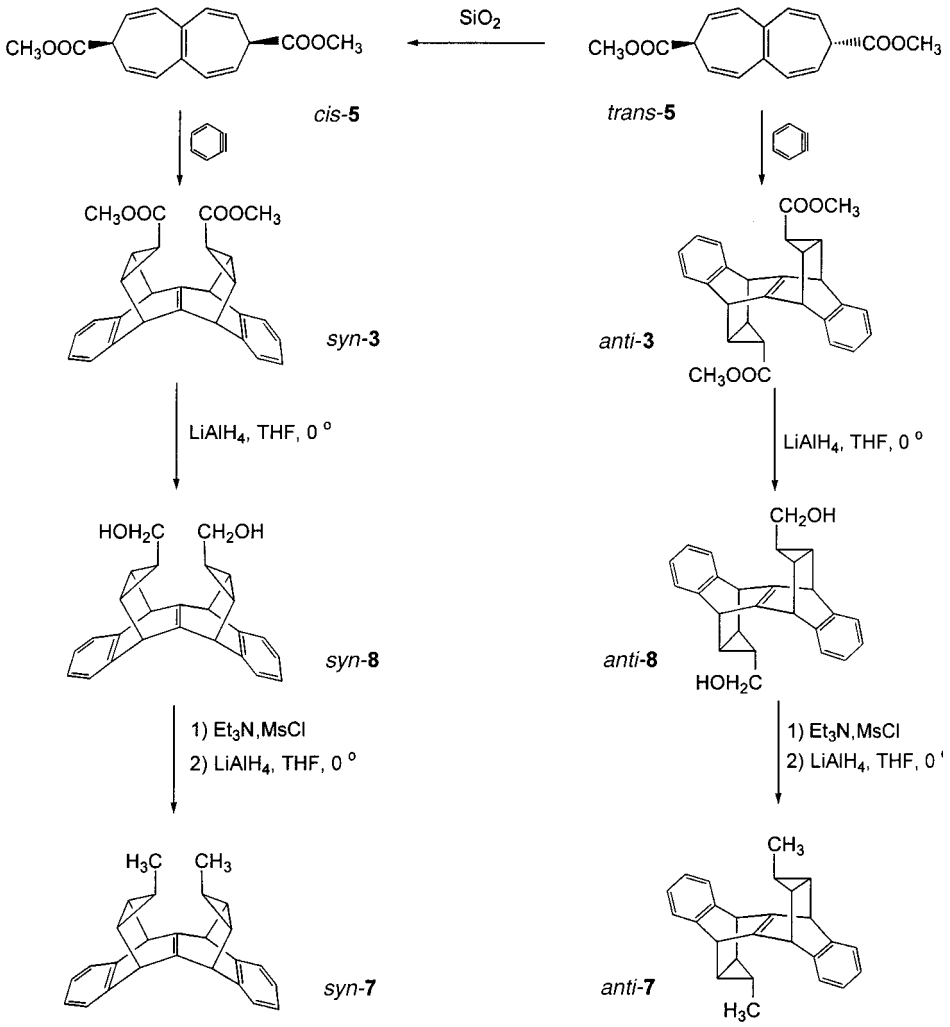
Since we could not compare the chemical reactivity of *syn*-**3** with that of *syn*-**1** and *syn*-**2**, which have similar pyramidalization, we decided to synthesize the methyl derivatives *syn*- and *anti*-**7** and to record their photoelectron spectra, which should give some insight into the reactivity of the pyramidalized C=C bond.

For this purpose we reduced the ester groups in *syn*- and *anti*-**3** to the corresponding alcohols with $LiAlH_4$. Reaction of the obtained diols, *syn*- and *anti*-**8**, with methanesulfonyl chloride (MsCl) in the presence of Et_3N in CH_2Cl_2 furnished the *syn*- and *anti*-dimesylates in 78 and 80% yields, respectively. Finally, treatment of the latter with $LiAlH_4$ in THF at 0° gave the reduced hydrocarbons *syn*- and *anti*-**7**, respectively, as the sole products.

Comparison of the ^{1}H-NMR spectra of *syn*- and *anti*-**7** indicates that the resonance signal of the H-atoms above the central C=C bond of *syn*-**7** is shifted remarkably downfield (1.92 ppm). In contrast, the equivalent H-atoms of *anti*-**7** resonate at −0.42 ppm. The high-field resonance of these H-atoms can be accounted for by their location in the shielding cone of the central C=C bond as well as of the opposite aromatic rings. However, the resonance frequencies of the internal cyclopropane H-atoms in *syn*- and *anti*-**9** [11], where the aromatic rings of *syn*- and *anti*-**7** are replaced by C=C bonds, show also a chemical-shift difference of 1.6 ppm (*Fig. 1*).

Therefore, we attribute the extraordinary shift of the cyclopropane H-atoms (which are also located over the C=C bond) in *syn*-**7** partly to steric compression between these internal cyclopropane H-atoms. Furthermore, it is interesting to note that the bridge H-atoms in *syn*- and *anti*-'sesquinorbornatrienes' *syn*- and *anti*-**2** [3c] do not

Scheme 2



show any remarkable chemical-shift difference (*Fig. 1*). Recently, we have shown that there is a correlation between the chemical shift and the degree of the pyramidalization angle in these compounds [12]. NMR Analysis indicates that *syn*-**7** should have also a similar pyramidalization degree as *syn*-**3**.

The photoelectron (PE) spectra of *syn*- and *anti*-**7** (*Fig. 2*) are quite similar in the sense that there are two bands at 7.6 and 8.2 (8.4) e.V. The first bands (7.6 eV) are well separated from the other strongly overlapping bands at higher energy. These compounds have also other structure moieties, such as the cyclopropane and aromatic rings. A comparison of the ionization potentials of compounds having similar structure moieties [17] (*Fig. 3*) clearly indicates that the first bands in the PE spectra of *syn*-**7** and *anti*-**7** are attributed to an ionization from the central π-bond. *Brown et al.* [18] and

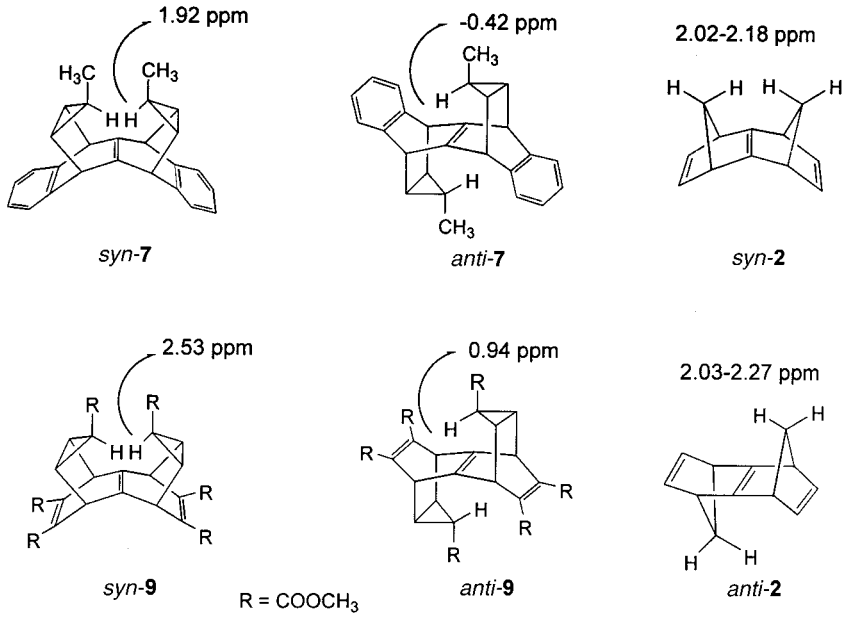


Fig. 1. *H-NMR Resonances of some selected compounds*

Gleiter, Paquette, and co-workers [19] have obtained the PE spectra of 'sesquinorbornanes' *syn-* and *anti-***1** and 'norbornatrienes' *syn-* and *anti-***2**. In each pair, the *anti-*isomer had a slightly lower ionization potential. These authors attributed this result to a larger hyperconjugative interaction between the central π-bond and σ-orbitals in the five-membered ring. The lower first ionization potentials of *syn-* and *anti-***7** (7.6 eV) compared to 'sesquinorbornanes' and 'sesquinorbornatrienes' provides evidence for such an electronic interaction in these systems but also indicates that this effect does not depend on the geometry. Despite the planarity of the C=C bond in *anti-***7**, the first ionization potential of *anti-***7** has the same value as that of the pyramidalized double

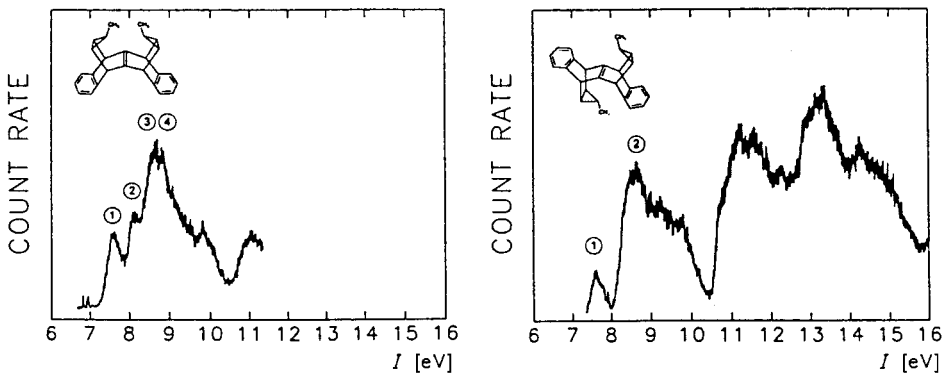


Fig. 2. *Photoelectron spectra of* syn- *and* anti-**7**

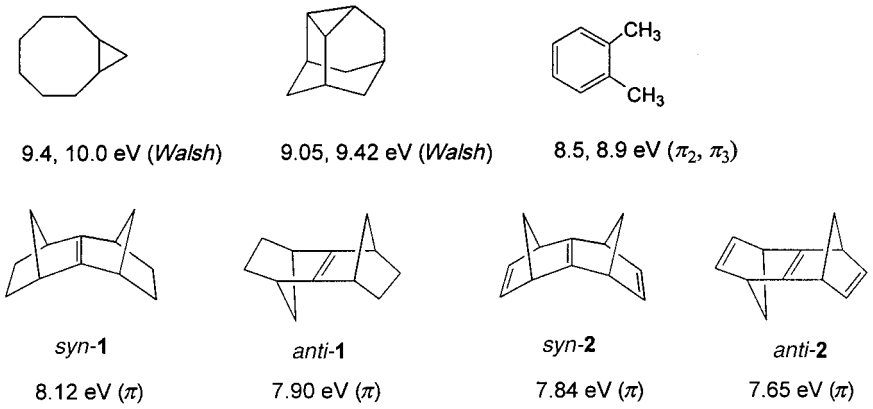


Fig. 3. *First ionization potentials of some selected compounds*

bond in *syn*-**7**. We attribute this result to a larger hyperconjugative interaction between the central π-bond and σ-orbitals of the rings in the *anti*-**7** than in the *syn*-**7**. The first ionization potentials of *syn*- and *anti*-**7** are lower than that of 'sesquinorbornanes' and 'sesquinorbornatrienes'. The reduction in the ionization potentials is generally consistent with the enhanced chemical reactivity. The measured ionization potential of *syn*-**7** indicates that this compound and ester derivative *syn*-**3** should be at least as reactive as the 'sesquinorbornene' and 'sesquinorbornatriene' systems. However, the lack of reactivity can be rationalized in terms of steric shielding of the C=C bond by the adjacent cyclopropane and benzene rings.

The authors are indebted to the Departments of Chemistry (Middle East Technical University and Atatürk University) for financial support of this work. Furthermore, we thank Prof. Dr. *R. Gleiter*, University of Heidelberg, Germany, for recording the photoelectron spectra and Prof. Dr. *W. Adam*, University of Würzburg, Germany, for elemental analyses.

Experimental Part

General. Column chromatography (CC): silica gel *60* (*Merck*). M.p.: *Thomas-Hoover* cap. melting point apparatus. PE Spectra: *PS-18* Spectrometer, *Perkin-Elmer*; at 150°. IR Spectra: KBr pellets; *Perkin-Elmer 377* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR: 200-MHz-*Varian* spectrometer; δ in ppm, $SiMe_4$ as internal standard, J in Hz.

Dimethyl 'syn'*-2,3,8,9-Tetrabromo-5,6,11,12,14,15,17,18-octahydro-13*H,*16*H-*5,12 : 6,11-di*-endo-*cyclopropanaphthacene-15,18-dicarboxylate* (**6**). To a magnetically stirred soln. of *syn*-**3** (55 mg, 0.13 mmol) and $FeBr_3$ (150 mg) in $CHCl_3$ (15 ml), a soln. of Br_2 (285 mg, 1.78 mmol) in $CHCl_3$ (5 ml) was added dropwise during 5 min, and the mixture was stirred for 27 h at r.t. The resulting brown soln. was washed with 20% HCl soln. (2 × 50 ml) and extracted with $CHCl_3$ (150 ml). The org. layers were washed with 10% $NaHCO_3$ soln. (50 ml) and H_2O (50 ml), dried ($MgSO_4$) and evaporated: **6** (70 mg, 73%). Pale yellow crystals from $CHCl_3$/hexane. M.p. >250°. IR (KBr): 2970*w*, 2940*w*, 1715*s*, 1430*s*, 1215*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.19 (*s*, 4 arom. H); 3.99 (*m*, 4 H); 3.68 (*s*, MeO); 2.62 (*t*, ^3J = 3.0, H–C(15), H–C(18)); 1.92 (*m*, H–C(13), H–C(14), H–C(16), H–C(17)). ^{13}C-NMR (50 MHz, $CDCl_3$): 171.9; 147.5; 145.8; 128.1; 120.8; 52.6; 44.1; 29.7; 29.4. Anal. calc. for $C_{28}H_{20}Br_4O_4$: C 45.44, H 2.72; found: C 45.21, H 2.74.

'syn'*-5,6,11,12,14,15,17,18-Octahydro-13*H,*16*H-*5,12 : 6,11-di*-endo-*cyclopropanaphthacene-15,18-dimethanol* (*syn*-**8**). To a vigorously stirred soln. of *syn*-**3** (260 mg, 0.61 mmol) in dry THF (50 ml), $LiAlH_4$ (0.6 g, 15.5 mmol) was added portionwise during 10–15 min at 0°. The mixture was stirred at 0° for 4 h, the H_2O (2 ml) was added dropwise (5 min), and stirring was continued for 30 min. The mixture was filtered through a silica gel

column (15 g), washing with $CHCl_3$ (200 ml). Evaporation gave *syn*-**8** (206 mg, 91%). White powder crystals from MeOH. M.p. 268–270°. IR (KBr): 3320*s*, 3060*w*, 3000*w*, 1455*s*. ^{1}H-NMR (200 MHz, CD_3OD): 6.85–6.57 (*AA′BB′*, 8 arom. H); 3.92 (*m*, H–C(5), H–C(6), H–C(11), H–C(12)); 3.40 (*d*, ^3J = 7.0, 2 CH_2OH); 2.37 (*tt*, ^3J = 7.0, 3.5, H–C(15), H–C(18)); 1.19 (*m*, H–C(13), H–C(14), H–C(16), H–C(17)). ^{13}C-NMR (50 MHz, CD_3OD): 149.6; 147.9; 125.06; 123.3; 64.8; 46.4; 31.7; 27.7. Anal. calc. for $C_{26}H_{24}O_2$: C 84.75, H 6.57; found: C 84.39, H 6.81.

'syn'-*5,6,11,12,14,15,17,18-Octahydro-13*H,*16*H-*5,12 : 6,11-di*-endo-*cyclopropanaphthacene-15,18-dimethanol Bis(methanesulfonate)*. To a soln. of *syn*-**8** (206 mg, 0.56 mmol) and Et_3N (450 mg, 4.5 mmol) in CH_2Cl_2 (100 ml) at 0°, MsCl (0.6 g, 14.7 mmol) in dry CH_2Cl_2 (20 ml) was added dropwise within 30 min. After 8 h stirring at 0°, the reaction was quenched with 5% H_2SO_4 soln. Then H_2O (150 ml) was added, the aq. layer extracted with CH_2Cl_2 (2 × 50 ml), the combined org. layer dried ($MgSO_4$) and evaporated, and the residue crystallized from CH_2Cl_2/Et_2O: 230 mg (78%) of crystalline white powder. M.p. 84–85°. IR (KBr): 3005*m*, 2940*m*, 1460*m*, 1345*s*, 1170*s*. ^{1}H-NMR (200 MHz, $CDCl_3$) 6.88–6.57 (*AA′BB′*, 8 arom. H); 4.09 (*d*, ^3J = 7.1, 2 CH_2O); 3.96 (*m*, H–C(5), H–C(6), H–C(11), H–C(12)); 3.04 (*s*, 2 $MeSO_3$); 2.39 (*tt*, ^3J = 7.1, 3.62, H–C(15), H–C(18)); 1.40 (*m*, H–C(13), H–C(14), H–C(16), H–C(17)). ^{13}C-NMR (50 MHz, $CDCl_3$): 147.5; 147.0; 124.7; 122.8; 72.1; 44.9; 38.2; 27.0 (2 C).

'syn'-*5,6,11,12,14,15,17,18-Octahydro-15,18-dimethyl-13*H,*16*H-*5,12 : 6,11-di*-endo-*cyclopropanaphthacene* (*syn*-**7**). To a vigorously stirred soln. of the bis(methanesulfonate) (230 mg, 0.44 mmol) in dry THF (40 ml) at 0°, $LiAlH_4$ (0.6 g, 15.5 mmol) was added portionwise within 5–10 min. The mixture was then stirred at 0° for 3 h. The mixture was filtered through a silica-gel column (10 g) eluting with $CHCl_3$ (200 ml). Evaporation gave *syn*-**7** (112 mg, 76%). White crystals from CH_2Cl_2/MeOH. M.p. 249–251°. IR (KBr): 3050*w*, 3000*m*, 2930*m*, 1450*s*, 1160. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.85–6.62 (*AA′BB′*, 8 arom. H); 3.88 (*m*, H–C(15), H–C(6), H–C(11), H–C(12)); 1.92 (*tq*, ^3J = 6.2, 3.1, H–C(5), H–C(18)); 1.01 (*m*, 2 Me, H–C(13), H–C(14), H–C(16), H–C(17)). ^{13}C-NMR (50 MHz, $CDCl_3$): 148.7; 146.4; 124.1; 122.3; 45.7; 29.9; 23.1; 17.5. Anal. calc. for $C_{26}H_{24}$: C 92.81, H 7.19; found: C 92.39, H 7.02.

'anti'-*5,6,11,12,14,15,17,18-Octahydro-13*H,*16*H-*5,12 : 6,11-di*-endo-*cyclopropanaphthacene-15,18-dimethanol* (*anti*-**8**). As described for *syn*-**8**, with *anti*-**3**: (570 mg, 1.34 mmol): 420 mg (85%) of *anti*-**8**. White crystalline powder. M.p. >280°. IR (KBr): 3350*s*, 3060*m*, 3000*s*, 1460*s*. ^{1}H-NMR (200 MHz, CD_3OD): 7.21–6.97 (*AA′BB′*, 8 arom. H); 4.00 (*m*, H–C(5), H–C(6), H–C(11), H–C(12)); 3.01 (*d*, ^3J = 6.6, 2 CH_2OH); 1.03 (*m*, H–C(13), H–C(14), H–C(16), H–C(17)); –0.04 (*tt*, ^3J = 6.6, 3.4, H–C(15), H–C(18)). ^{13}C-NMR (50 MHz, CD_3OD): 148.4; 142.0; 125.8; 124.2; 63.94; 46.0; 31.8; 25.0. Anal. calc. for $C_{26}H_{24}O_2$: C 84.75, H 6.57; found: C 84.61, H 6.62.

Bis(methanesulfonate) from anti-**8** (420 mg, 0.56 mmol): white crystalline powder (478 mg, 80%). M.p. 99–99.5°. IR (KBr): 3060*w*, 3005*w*, 2960*m*, 2930*m*, 1460*m*, 1405*m*, 1350*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.24–7.02 (*AA′BB′*, 8 arom. H); 4.05 (*m*, H–C(5), H–C(6), H–C(11), H–C(12)); 3.74 (*d*, ^3J = 7.0, 2 CH_2O); 2.65 (*s*, 2 $MeSO_3$); 1.25 (*m*, H–C(13), H–C(14), H–C(16), H–C(17)); –0.07 (*tt*, ^3J = 7.15, 3.62, H–C(15), H–C(18)). ^{13}C-NMR (50 MHz, $CDCl_3$): 146.2; 141.1; 125.5; 123.8; 71.7; 44.4; 38.2; 28.9; 24.3.

'anti'-*5,6,11,12,14,15,17,18-Octahydro-15,18-dimethyl-13*H,*16*H-*5,12 : 6,11-di*-endo-*cyclopropanaphthacene* (*anti*-**7**). As described for *syn*-**7**, with the bis(methanesulfonate) of *anti*-**8** (468 mg, 0.89 mmol): 270 mg (90%) of *anti*-**7**. White crystals. M.p. 262–263°. IR (KBr): 3050*w*, 3000*m*, 2920*m*, 1450*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.22–7.01 (*AA′BB′*, 8 arom. H); 3.96 (*m*, H–C(5), H–C(6), H–C(11), H–C(12)); 0.84 (*m*, H–C(13), H–C(14), H–C(16), H–C(17)); 0.60 (*d*, ^3J = 6.2, 2 Me); –0.42 (*tq*, ^3J = 3.1, 6.2, H–C(15), H–C(18)). ^{13}C-NMR (50 MHz, $CDCl_3$): 147.4; 140.3; 124.8; 123.2; 45.1; 27.3; 23.1; 16.9. Anal. calc. for $C_{26}H_{24}$: C 92.81, H 7.19; found: C 92.71, H 7.22.

REFERENCES

[1] P. D. Bartlett, A. J. Blakeney, M. Kimura, W. H. Watson, *J. Am. Chem. Soc.* **1980**, *102*, 1383.

[2] L. A. Paquette, R. V. C. Carr, M. C. Böhm, R. Gleiter, *J. Am. Chem. Soc.* **1980**, *102*, 1186; L. A. Paquette, R. V. C. Carr. *J. Am. Chem. Soc.* **1980**, *102*, 7553.

[3] a) J. P. Hagenbuch, P. Vogel, A. A. Pinkerton, A. D. Schwarzenbach, *Helv. Chim. Acta* **1981**, *64*, 1819; b) L. A. Paquette, A. G. Schaefer, J. F. Blount, *J. Am. Chem. Soc.* **1983**, *105*, 3642; c) L. A. Paquette, H. Künzer, K. E. Green, O. de Lucchi, G. Licini, L. Pasquato, G. Valle, *J. Am. Chem. Soc.* **1986**, *108*, 3453.

[4] For a review of pyramidalized double bonds, see W. T. Borden, *Chem. Rev.* **1989**, *89*, 1095.

[5] K. N. Houk, in 'Stereochemistry and Reactivity of Systems Containing π Bonds', Ed. W. H. Watson, Verlag Chemie International, Dearfield Beach, Florida, 1983, p. 1.
[6] G. Wipf, K. Morokuma, *Tetrahedron Lett*. **1980**, *21*, 4445; M. N. Paddon-Row, N. G. Randan, K. N. Houk, *J. Am. Chem. Soc*. **1982**, *104*, 7162; H. Hake, H. Landen, H. D. Martin, D. C. Spellmeyer, *Tetrahedron Lett*. **1989**, *29*, 6601.
[7] L. A. Paquette, H. Künzer, K. E. Green, O. De Lucchi, G. Licini, L. Pasquato, G. Valle, *J. Am. Chem. Soc*. **1986**, *108*, 3453.
[8] A. Menzek, M. Krawiec, W. H. Watson, M. Balci, *J. Org. Chem*. **1991**, *56*, 6755.
[9] A. Menzek, M. Balci, *Aust. J. Chem*. **1993**, *46*, 1613.
[10] A. Menzek, N. Saraçoğlu, M. Krawiec, W. H. Watson, M. Balci, *J. Org. Chem*. **1995**, *60*, 829.
[11] M. Balci, S. A. Bourne, A. Menzek, N. Saraçoglu, W. H. Watson, *J. Chem. Cryst*. **1995**, *25*, 107.
[12] N. Saraçoğlu, A. Menzek, S. Sayan, U. Salzner, M. Balci, *J. Org. Chem*. **1999**, *64*, 6670.
[13] E. Vogel, F. Hogrefe, *Angew. Chem., Int. Ed.* **1974**, *13*, 735.
[14] For a most recent review on the cycloheptatriene-norcaradiene equilibrium, see M. Balci, *Turk. J. Chem*. **1992**, *16*, 42.
[15] H. Günther, M. Görlitz, *Org. Magn. Reson*. **1974**, *6*, 384; M. Balci, A. Menzek, C. Kazaz, *Turk. J. Chem*. **1994**, *18*, 205.
[16] D. A. Hrovat, W. T. Borden, *J. Am. Chem. Soc*. **1988**, *110*, 4710; J. M. Smith, D. A. Hrovat, W. T. Borden, *J. Am. Chem. Soc*. **1993**, *115*, 3816.
[17] R. Gleiter, *Topics Curr. Chem*. **1979**, *86*, 197.
[18] R. S. Brown, J. M. Buschek, K. R. Kopecky, A. J. Miller, *J. Org. Chem*. **1983**, *48*, 3692.
[19] H. Künzer, E. Litterst, R. Gleiter, L. A. Paquette, *J. Org. Chem*. **1987**, *52*, 4740.

Received November 2, 2000