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A DFT study of pyramidalized alkenes: 7-oxasesquinorbornenes and 7,7′-dioxasesquinorbornenes

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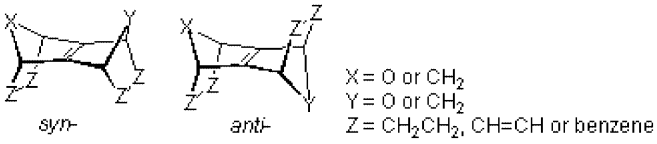
Abstract. DFT calculations of 7′–oxasesquinorbornenes and 7,7′-dioxasesquinorbornenes using the B3LYP/6–31G* method are reported. All the investigated structures (*syn*- and *anti*- derivatives) showed significant non-planarity of the central double bond, with the exception of those *anti*-derivatives possessing symmetrical structures. The influence of the replacement of the methylene groups at position 7- of the norbornene fragment with oxygen and the introduction of second and third (peripheral) double bonds and benzene rings on the molecular and electronic structures of these molecules have also been investigated.



Keywords: Pyramidalized alkenes – DFT calculations – Sesquinorbornenes

Introduction

It is a well-documented fact that norbornenes (bicyclo[2.2.1]hept-2-enes) possess pyramidalized terminal π-bond hydrogens bent towards the *endo*-side [1, 2]. Non-planarity of the central π-bond in *syn*-sesquinorbor[4a,8a]nenes is even more pronounced [3]. The most remarkable examples in the literature are the spiro cyclopentylsesquinorbornene molecule **1** with a record deformation for these systems of internal π-bond of 22.7°[4], *syn*-oxabenzosesquinorbornene **2** (22.1°) and the cage compound **3** (39.0°, B3LYP value) [5]. In contrast to the *syn*-sesquinorbornene derivatives, the corresponding *anti*-isomers have essentially planar central π-bonds, Scheme 1.

While sesquinorbornenes are relatively stable, the introduction of an oxygen atom at the 7-position causes almost all *oxa*-derivatives to be unstable species readily undergoing air oxidation or molecular transformations. Their formation was proven indirectly by trapping experiments [6], variable temperature photoelectron spectroscopy [7, 8], matrix isolation at cryogenic temperatures [9], mass spectrometry etc. It was also found that synthesis of oxa-bridged systems is more difficult than their carbon analogues. For instance, while *syn*-oxasesquinorbornadiene **4** [10] is a stable compound, *syn*-oxasesquinorbornene **5** is quite unstable [11, 12] and attempted syntheses of **6** have failed [13], Scheme 2.

Koch and Holthausen were the first to show that a precise description of the double-bond folding in pyramidalized olefins requires inclusion of valence electron correlation at least at the MP2 level of theory [14]. The same method was subsequently sucessfully used in studying a vast number of pyramidalized olefins by our group [7] and by others [15, 16]. Lately, the density functional theory methods (DFT) have become a very popular choice in studying geometries of large organic molecules containing pyramidalized double bonds [5, 17]. In our previous papers we have successfully used the B3LYP/6-31G* method to study pyramidalized alkenes [7, 18, 19, 20].

In this paper we have addressed the molecular and electronic structures of oxa- and dioxa derivatives of sesquinorbornenes, with a particular focus on the deformation of the central double bond [21]. The consequences of the replacement of a methylene bridge at

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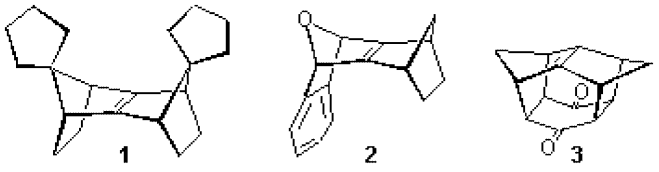
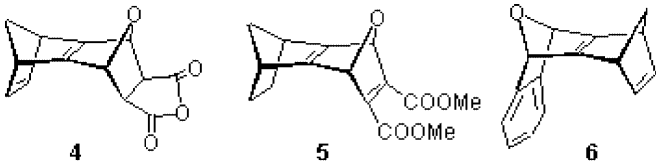


Scheme 1



Scheme 2

position 7 of a norbornene system with oxygen, the introduction of a second and third (peripheral) double bond, as well as the annelation of benzene rings have been herein computationally investigated.

Computational details

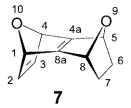
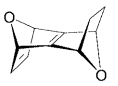
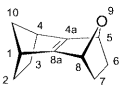
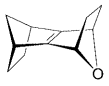
The initial geometry optimizations were performed using the *SPARTAN* [22] and the *Gaussian98* [23] programs employing the *ab initio* RHF/6-31G* basis set [24], without geometrical constraints using the Fletcher-Powell method [25] and default Gaussian convergence criteria. Further optimizations were carried out using density functional theory (DFT) hybrid B3LYP (Becke's 3 parameter functional [26] with the non-local correlation provided by the expression of Lee *et al.* [27]) and the 6-31G* basis set. Frequency calculations verified the identity of each stationary point as a minimum [34]. Only the results of B3LYP/6–31G* (hereafter denoted as B3LYP) will be discussed here unless otherwise noted.

Results and discussion

The calculated bond lengths and angles of optimized structures are given in Tables 1, 2, 3, 4, 5, 6, 7, together with calculated values for the out-of-plane deviations for central and hydrogens attached to the peripheral double bonds. Previously published B3LYP results for alkenes **28** and **29** have also been included for comparison [7]. Table 8 lists the total energies of all studied molecules, as well as energy differences between *syn*- and *anti*-isomers. B3LYP optimized structures are depicted in Figs. 1, 2, 3, 4, 5, 6, 7.

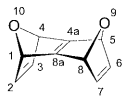
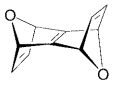
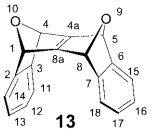
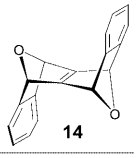
Before discussing extent of nonplanarity in the studied molecules, it is important to note that B3LYP results predict a smaller nonplanarity than the correspoding MP2 calculations [7, 14]. The estimated angles are by 0.5–2.0° smaller than MP2 calculations, whose are, in turn slightly smaller than available X-ray data. However, while underestimating pyramidalization, both

Table 1. Selected B3LYP geometrical data and total energies for molecules **7**–**10**[a]

	 **7**	 **8**	 **9**	 **10**
Bond /Å				
$C_{4a}C_{8a}$	1.343	1.339	1.346	1.341
C_1C_{8a}	1.535	1.543	1.515	1.515
C_1C_2	1.559	1.546	1.571	1.572
C_2C_3	1.333	1.333	1.561	1.564
$C_{4a}C_5$	1.515	1514	1.518	1.518
C_5C_6	1.567	1.568	1.567	1.566
C_6C_7	1.555	1.557	1.558	1.561
C_1X_{10}	1.446	1.458	1.555	1.556
C_5O_9	1.444	1.444	1.446	1.450
C_2C_7	3.503	4.862	3.697	4.936
O_9X_{10}	4.268	4.292	4.277	4.437
Angle /°				
$C_1C_{8a}C_{4a}$	105.2	105.2	108.1	108.2
$C_1C_{8a}C_8$	142.3	143.2	143.0	145.9
$C_8C_{8a}C_{4a}$	105.7	105.8	105.7	105.8
$C_1X_{10}C_4$	95.9	94.8	94.6	94.6
$C_5O_9C_8$	97.1	97.1	97.0	96.7
$C_1C_2H_2$	125.4	125.3	-	-
$C_1C_2C_3$	105.2	105.3	-	-
Φ_1	21.9	20.0	15.5	3.0
Φ_2	1.5	5.0		

[a] Φ_1=out-of-plane deviation for central π-bond
Φ_2=out-of-plane deviation for terminal π-bond

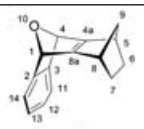
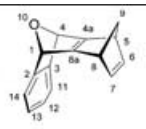
Table 2. Selected B3LYP geometrical data and total energies for molecules **11**–**14**[a]

	 **11**	 **12**	 **13**	 **14**
Bond /Å				
$C_{4a}C_{8a}$	1.340	1.332	1.342	1.336
C_1C_{8a}	1.582	1.538	1.529	1.531
C_1C_2	1.562	1.556	1.542	1.541
C_2C_3	1.331	1.331	1.406	1.407
C_1O_{10}	1.447	1.452	1.453	1.456
C_2C_7	3.550	4.982	3.585	4.923
C_2O_9	4.510	4.187	4.519	4.176
O_9O_{10}	4.243	4.357	4.242	4.367
C_2C_{14}	-	-	1.380	1.380
$C_{11}C_{12}$	-	-	1.410	1.410
$C_{12}C_{13}$	-	-	1.391	1.391
Angle /°				
$C_1C_{8a}C_{4a}$	105.3	105.4	105.8	105.9
$C_1C_{8a}C_8$	142.5	149.1	143.1	148.2
$C_1O_{10}C_4$	95.9	95.6	96.8	96.6
$C_1C_2C_3$	105.2	105.3	-	-
$C_1C_2H_2$	125.3	125.2	-	-
Φ_1	22.0	0.0	19.4	0.0
Φ_2	2.0	3.8		

[a] Φ_1=out-of-plane deviation for central π-bond
Φ_2=out-of-plane deviation for terminal π-bond

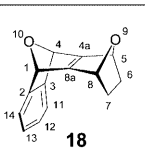
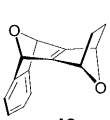
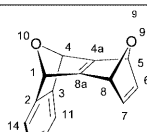
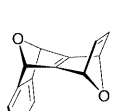
B3LYP and MP2 calculated bond lengths and bond angles are very close to the experimental values. In this study, we have come to the same conclusions.

Table 3. Selected B3LYP geometrical data and total energies for molecules **15**–**17**[a]

	 **15**	**16**	 **6**	**17**
Bond /Å				
$C_{4a}C_{8a}$	1.346	1.340	1.344	1.338
C_1C_{8a}	1.531	1.533	1.528	1.529
C_1C_2	1.542	1.539	1.543	1.543
C_2C_3	1.408	1.408	1.409	1.408
C_8C_{8a}	1.512	1.513	1.527	1.536
C_5C_6	1.573	1.573	1.55	1.546
C_6C_7	1.560	1.562	1.335	1.336
C_5C_9	1.554	1.556	1.566	1.571
C_1O_{10}	1.453	1.460	1.452	1.455
C_9O_{10}	4.296	4.418	4.288	4.387
C_2C_{14}	1.381	1.380	1.380	1.380
$C_{11}C_{12}$	1.410	1.410	1.411	1.411
$C_{12}C_{13}$	1.392	1.392	1.391	1.391
Angle /°				
$C_1C_{8a}C_{4a}$	105.7	105.8	105.7	105.9
$C_1C_{8a}C_8$	141.5	144.7	141.1	144.7
$C_8C_{8a}C_{4a}$	108.1	108.3	107.7	107.7
$C_5C_9C_8$	94.6	94.7	93.0	92.7
$C_1O_{10}C_4$	96.8	96.2	97.8	96.7
$C_5C_6C_7$	-	-	107.7	107.7
$C_5C_6H_6$	-	-	122.3	124.4
Φ_1	18.9	9.5	20.1	10.8
Φ_2			2.3	3.6

[a]Φ_1=out-of-plane deviation for central π-bond
Φ_2=out-of-plane deviation for terminal π-bond

Table 4. Selected B3LYP geometrical data and total energies for molecules **18**–**21**[a]

	 **18**	 **19**	 **20**	 **21**
Bond /Å				
$C_{4a}C_{8a}$	1.434	1.338	1.342	1.336
C_1C_{8a}	1.530	1.533	1.528	1.529
C_1C_2	1.542	1.538	1.543	1.543
C_2C_3	1.407	1.407	1.406	1.409
$C_{4a}C_5$	1.516	1.516	1.534	1.542
C_5C_6	1.567	1.567	1.561	1.551
C_6C_7	1.556	1.559	1.331	1.332
C_2C_{14}	1.381	1.380	1.380	1.379
$C_{11}C_{12}$	1.410	1.409	1.411	1.411
$C_{12}C_{13}$	1.392	1.392	1.391	1.391
C_1O_{10}	1.452	1.461	1.451	1.455
C_5O_9	1.444	1.445	1.445	1.454
O_9O_{10}	4.259	4.352	4.262	4.338
C_7O_{10}	4.530	3.960	4.495	4.377
C_2C_7	3.556	4.905	3.477	4.922
Angle /°				
$C_1C_{8a}C_{4a}$	105.7	105.8	105.8	105.9
$C_1C_{8a}C_8$	143.1	146.6	141.7	146.8
$C_8C_{8a}C_{4a}$	105.7	105.9	105.2	105.3
$C_5O_9C_8$	97.1	96.1	95.9	95.3
$C_1O_{10}C_4$	96.9	97.1	96.9	96.8
$C_5C_6H_7$	-	-	125.3	125.3
$C_5C_6C_7$	-	-	105.2	105.3
Φ_1	19.6	10.8	22.8	11.4
Φ_2			2.6	4.5

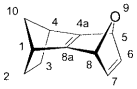
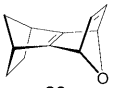
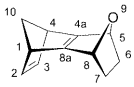
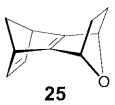
[a]Φ_1=out-of-plane deviation for central π-bond
Φ_2=out-of-plane deviation for terminal π-bond

First, we will focus our attention on the energetics of *syn*/*anti* pairs of isomers. An inspection of the energy differences between *syn*- and *anti*-isomers (collected in Table 8) reveals that, although more bent, in all cases *syn*-isomers are thermodynamically more stable by 5.9 to 15.9 kJ/mol. The smallest energy difference was found in the *syn*/*anti* pair **28**/**29**, and the largest difference in the *syn*/*anti* pair **24**/**25**. The magnitude of the calculated *syn*/*anti* energy gap does not correlate well with the extent of out of plane deviation.

Next we focus our attention on the changes in double bond folding across the studied family of molecules. Let us consider the effect of gradual replacement of the CH_2 bridges with oxygen atoms in the sesquinorbornene moiety first. Our DFT calculations indicate that the replacement of one methylene bridge in *syn*-sequinorbornene **30** by oxygen to make **9** causes only a small increase in olefinic non-planarity (from 15.1° to 15.5°, see Tables 1 and 7).[⊥] A related prediction of the same kind was made by Gleiter and Spanget-Larsen [28] for *syn*-dioxasesquinorbornene **28** using EHT calculations. However, the double bond in the corresponding symmetrical *anti*-sesquinorbornene **31** is planar, while *anti*-7-oxasesquinorbornene **10** (where 7-oxanorbornene fragment is bent *endo*- in respect to the methylene bridge, Fig. 1) possesses a slightly nonplanar central double bond (3.0°). Replacement of the methylene bridges in **9** and **10** to give dioxasesquinorbornenes **28** and **29**, respectively, produced essentially no further change in pyramidalization for **28** (by only 0.3°) while the symmetrical *anti*- isomer **29** is completely flat) (Table 7, Fig. 7).

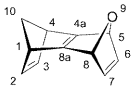
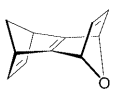
Structural consequences were calculated for the inclusion of etheno bridge(s) into these sesquinorbornyl compounds. For exampe, the replacement of the ethano bridge in dioxa molecule **28** with a double bond in diene **7** caused a significant increase in double bond non planarity (from 15.8° to 21.9°) (Table 1, see also Fig. 1). Furthermore, when yet another double bond was introduced in diene **7** to form dioxasesquinorbornatriene **11**, only a small further increase of 0.1° (to a value of 22°) was predicted (Table 2, Fig. 2), in accordance with previously published results of Gleiter and Spanget-Larsen for *syn*-sesquinorbornatriene [28]. A relatively small pyramidalization angle was rationalized by repulsive interactions on the *endo* side, involving three ethylene π orbitals. Essentially same geometrical effects on nonplanarity of olefinic bond were experimentally observed by Paquette *et al*. in *syn*-sesquinorbornadiene [29] and *syn*-sesquinorbornatriene [30]. We can also see that *anti*-alkene **29** and *anti*-triene **12** have symmetrical structures and planar central olefinic bonds, diene **8** has

Table 5. Selected B3LYP geometrical data and total energies for molecules **22**–**25**[a]

	 **22**	 **23**	 **24**	 **25**
Bond /Å				
$C_{4a}C_{8a}$	1.345	1.341	1.344	1.338
C_1C_{8a}	1.512	1.512	1.529	1.536
C_1C_2	1.572	1.574	1.554	1.547
C_2C_3	1.559	1.561	1.336	1.336
$C_{4a}C_5$	1.534	1.544	1.515	1.516
C_5C_6	1.560	1.547	1.567	1.567
C_6C_7	1.333	1.333	1.556	1.560
C_1C_{10}	1.553	1.554	1.566	1.570
C_5O_9	1.446	1.457	1.445	1.447
C_2C_7	3.520	4.878	3.559	4.941
O_9C_{10}	4.305	4.377	4.305	4.410
O_9C_{10}	4.589	4.504	4.591	4.046
$C_{10}C_7$	4.978	3.788	4.525	4.337
Angle /°				
$C_1C_{8a}C_{4a}$	108.1	107.9	107.7	107.7
$C_1C_{8a}C_8$	140.8	142.4	141.0	145.8
$C_8C_{8a}C_{4a}$	105.2	105.8	105.7	105.9
$C_1C_{10}C_4$	94.7	92.9	93.0	92.8
$C_5O_9C_8$	95.9	98.1	97.0	96.9
$C_1C_2H_2$	-	124.6	124.4	124.4
$C_1C_2C_3$	-	107.6	107.5	107.6
$C_5C_6H_7$	125.4	-	-	-
$C_5C_6C_7$	105.2	-	-	-
Φ_1	21.2	17.0	20.5	6.6
Φ_2	1.8	1.1	1.3	3.5

[a]Φ_1=out-of-plane deviation for central π-bond
Φ_2=out-of-plane deviation for terminal π-bond

Table 6. Selected B3LYP geometricaldata and total energies for molecules **26**, **27**[a]

	 **26**	 **27**
Bond /Å		
$C_{4a}C_{8a}$	1.342	1.335
C_1C_{8a}	1.526	1.533
C_1C_2	1.557	1.549
C_2C_3	1.335	1.336
$C_{4a}C_5$	1.533	1.538
C_5C_6	1.562	1.558
C_6C_7	1.331	1.332
C_1C_{10}	1.566	1.570
C_5O_9	1.447	1.451
C_2C_7	3.628	4.970
O_9C_{10}	4.274	4.407
$C_{10}C_7$	4.609	4.133
C_2O_9	4.535	4.251
Angle /°		
$C_1C_{8a}C_{4a}$	107.8	107.8
$C_1C_{8a}C_8$	141.5	146.7
$C_8C_{8a}C_{4a}$	105.2	105.4
$C_1C_{10}C_4$	93.0	92.8
$C_5O_9C_8$	95.8	95.7
$C_1C_2H_2$	124.3	124.4
$C_1C_2C_3$	107.5	107.6
$C_5C_6H_7$	125.3	125.3
$C_5C_6C_7$	105.2	105.2
Φ_1	20.1	3.2
Φ_2	1.6	3.2
Φ_3	2.4	3.7

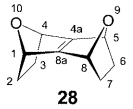
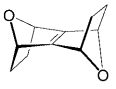
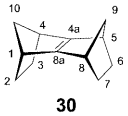
[a]Φ_1=out-of-plane deviation for central π-bond
Φ_2=out-of-plane deviation for the C_2C_3 terminal π-bond
Φ_3=out-of-plane deviation for the C_6C_7 terminal π-bond

an unsymmetrical structure and an unexpectedly large deformation angle of 20.0° (where 7-oxanorbornadiene fragment is bent *endo*- in respect to the 7-oxanorbornene moiety, Table 1, Figure 1). This is by far the largest pyramidalization angle calculated for *anti*- sesquinorbornenes that has come to our attention during this study.

A comparison of X-ray crystallographic data for molecule **15** with the B3LYP calculated structure has revealed that the DFT method employed here significantly underestimates central bond non-planarity (by 3.3°, the experimental value is 22.1°, the theoretical is 18.9°), which is presumably due to the crystal packing effect [31]. Interestingly, there is a much better agreement between calculated and experimental bond lengths. The experimentally determined double bond length was found to be 1.339 Å, while the calculated value was shorter by only 0.007 Å.

The incorporation of a benzene ring or an alkene adjacent to the oxanorbornene moiety increases nonplanarity of central olefinic bond of sesquinorbornenes. For instance, in the dioxa series the internal alkene in **28** has an out of plane bending of 15.8° and this angle increases to 19.6° in benzo compound **18**. Incorporation of an etheno bridge causes even larger pyramidalization

Table 7. Selected B3LYP geometrical data and total energies for molecules **28**–**31**[a]

	 **28**	 **29**	 **30**	**31**
Bond /Å				
$C_{4a}C_{8a}$	1.343	1.337	1.348	1.344
C_1C_{8a}	1.518	1.517	1.516	1.518
C_1C_2	1.566	1.566	1.572	1.571
C_2C_3	1.558	1.560	1.561	1.566
C_1X_9	1.445	1.449	1.555	1.556
C_2C_7	3.689	4.495	3.704	4.931
X_9X_{10}	4.244	4.383	4.311	4.490
$X_{10}C_7$	4.584	4.203	4.655	4.213
Angle /°				
$C_1C_{8a}C_{4a}$	105.7	105.9	108.0	108.1
$C_1C_{8a}C_8$	144.8	148.3	141.1	143.8
$C_5X_9C_8$	97.0	97.1	94.5	94.5
Φ_1	15.8	0.0	15.1	0.0

[a]Φ_1=out-of-plane deviation for central π-bond

Table 8. B3LYP total energies and *syn–anti* energy differences for molecules **6-31**

syn–		*anti–*		
Molecule	E_{tot}/a.u.	Molecule	E_{tot}/a.u.	Rel.energy/kJ/mol
7	–537.386021	**8**	–537.381602	11.7
9	–502.751994	**10**	–502.748220	10.0
11	–536.124895	**12**	–536.119592	13.8
13	–843.462063	**14**	–843.457443	12.1
15	–655.163625	**16**	–655.158134	14.2
6	–653.911401	**17**	–653.906436	13.0
18	–691.054657	**19**	–691.049459	13.8
20	–689.794512	**21**	–689.788928	14.6
22	–501.494714	**23**	–501.489617	13.4
24	–501.502879	25	–501.496880	15.9
26	–500.241747	**27**	–500.236636	13.4
28	–538.643080	**29**	–538.640770	5.9
30	–406.859186	**31**	–406.855129	10.5

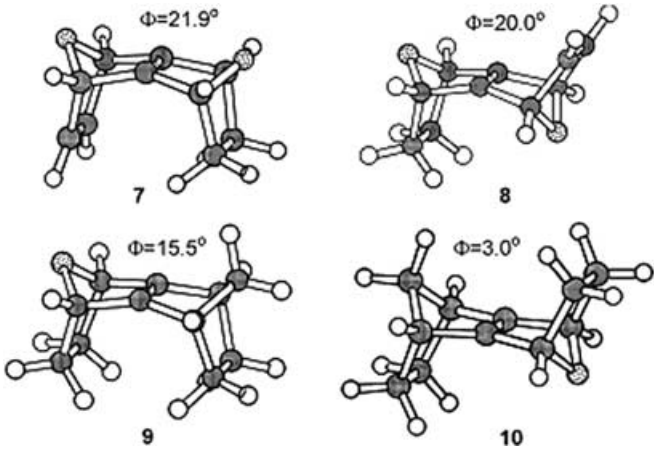


Fig. 1. B3LYP optimized structures and deformation angles (φ) of compounds **7**–**10**

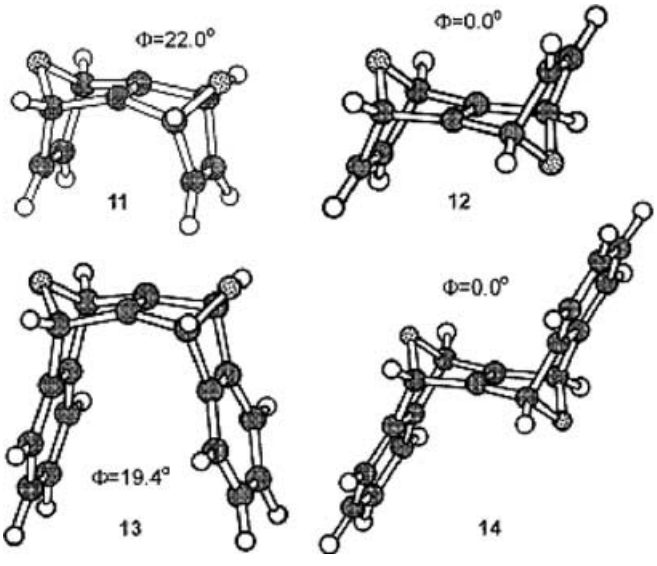


Fig. 2. B3LYP optimized structures and deformation angles (φ) of compounds **11–14**

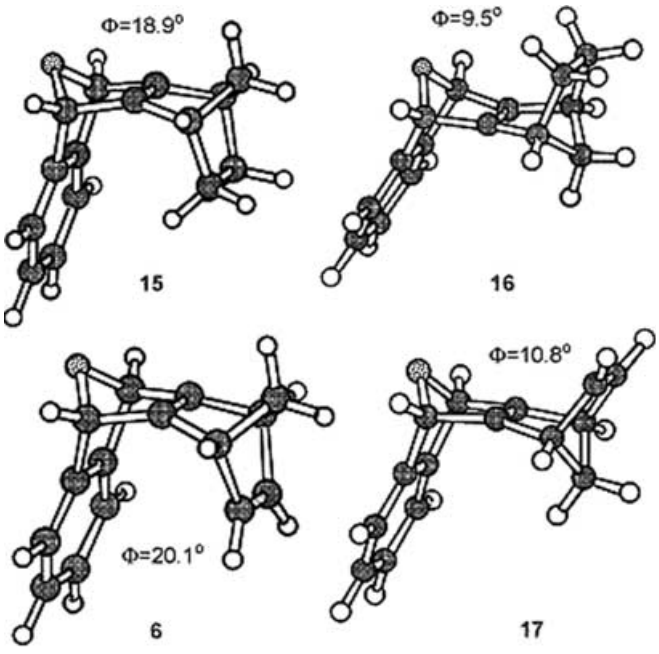


Fig. 3. B3LYP optimized structures and deformation angles (φ) of compounds **6**, **15**–**17**

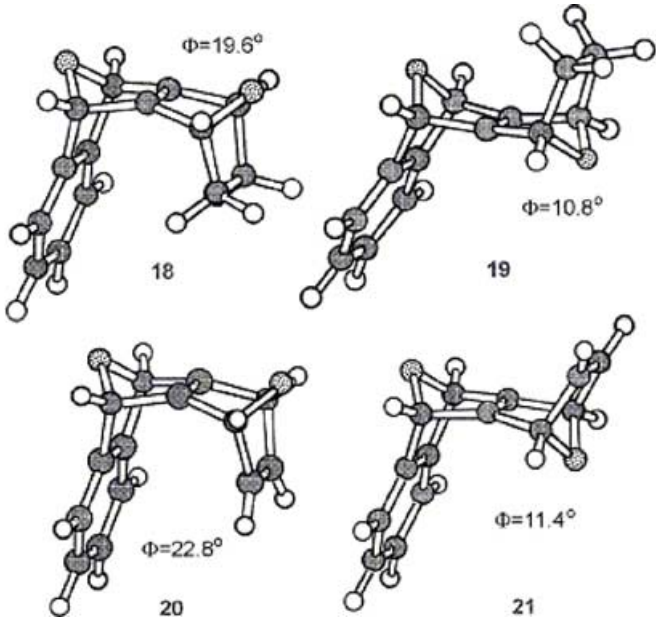


Fig. 4. B3LYP optimized structures and deformation angles (φ) of compounds **18**–**21**

than incorporation of a benzene ring. Thus B3LYP calculation of **18** predicts a large double bond distortion, which is by 2.3° smaller than the value predicted for the corresponding dioxasesquinorbornadiene **7** possessing an etheno bridge (Table 4, Fig. 4). As in the case of the introduction of the second etheno bridge in triene **11**, when the second benzene ring was incorporated to form dibenzotriene **13**, there was no further pyramidalization

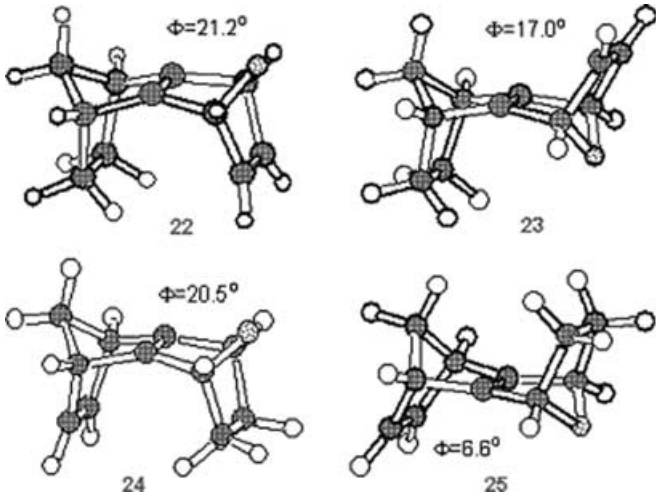


Fig. 5. B3LYP optimized structures and deformation angles (φ) of compounds **22**–**25**

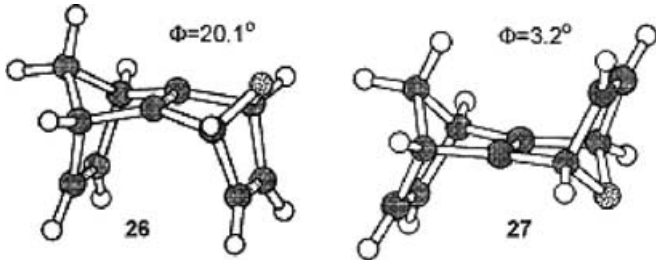


Fig. 6. B3LYP optimized structures and deformation angles (φ) of compounds **26** and **27**

increase, indeed a slight decrease was predicted (up to 19.4°). Olefinic out of plane bending in the *anti* derivatives **14** (consisting of two identical subunits) and **19** (consisting of two unequal subunits) follows trends described earlier, i.e., *anti*-dibenzotriene **14** has a planar structure (Fig. 2), while *anti*-dioxabenzodiene **19** showed a 10.8° bending toward the etheno bridge (Table 4).

It is also interesting to note that the non-planarity of the central double bond increases on going from dioxabenzodiene **18** to dioxabenzotriene **20** (Table 4, Fig. 4). The non-planarity value increased by 3.2° to a value of 22.8°. This value is the largest deformation angle calculated for molecules in this study and cannot be explained by the repulsive π interactions postulated by Gleiter. This is further corroborated by results for **7**/**11** (21.9° and 22.0°) or **18**/**13** pairs of molecules (22.8° and 19.4°). Similarly, a decrease in extent of bending was found in going from oxabenzodiene **15** to oxabenzotriene **6** (Table 3).

In the oxasesquinorbornene series, the introduction of a peripheral double bond in *syn*-oxasesquinorbornene **9** to form diene **22** (where the alkene is located in the oxanorbornene moiety) was predicted to have more pyramidalization than in the case of the isomeric diene

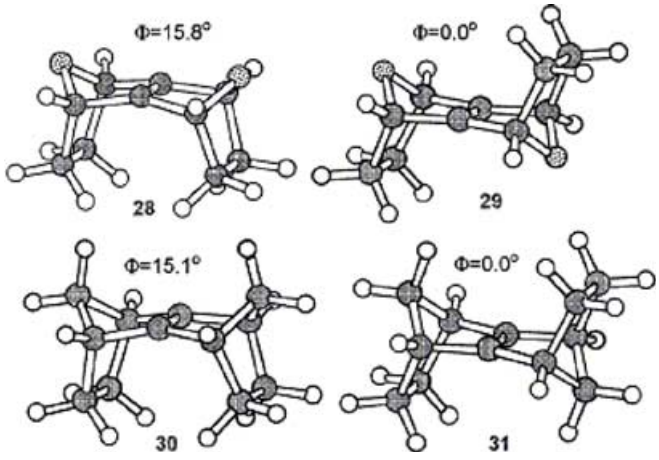


Fig. 7. B3LYP optimized structures and deformation angles (φ) of compounds **28**–**31**

24 (where the alkene is located in the norbornene moiety) (21.2° vs. 20.5°, respectively, Table 5). When a third double bond was introduced in either diene **22** or diene **24**, to form s*yn*-oxasesquinorbornatriene **26**, a small decrease in the angle Φ was found (by 1.1° and 0.4°, respectively), i.e. the same diminishing trend as predicted earlier for dioxasesquinorbornatriene **11** by Gleiter (Table 6).

It is interesting to mention that the calculations also predict nonplanarity of the terminal double bonds in these compounds. Olefinic protons are deviated towards the *endo*- direction between 1.3° (molecule **24**) and 5.0° (molecule **8**). These values correlate well with available X-ray results [32]. Furthermore, it was found that there is slightly larger terminal π-bond nonplanarity in the 7-oxanorbornene moiety than in norbornene (for instance, in triene **26**, the 7-oxanorbornadiene terminal π-bond hydrogens are bent by 2.1°, while in the norbornadiene side hydrogens are bent by 1.3°). A larger value for angle Φ was also found in the terminal double bond of *syn*-benzodioxatriene **20** as compared with *syn*-dioxatriene **11** (2.6° and 2.0°, respectively). A similar result was obtained for their *anti*- counterparts **21** and **12** (4.5° and 3.8°, respectively, Tables 2 and 4).

The central π-bonds of the unsymmetrical *anti*-molecules also deviate from planarity. Non-planarity angles have values between 3.2° (**27**) and 11.4° (**21**), in most cases significantly smaller than in the corresponding *syn*-derivatives, as expected, due to the cancellation effects of the two norbornene moieties operating in opposite directions.

Finally, other characteristic structural parameters of studied molecules were examined. For instance, the length of the central double carbon-carbon bonds, shortens with diminishing pyramidalization (increased bonding). The largest deviation from planarity was computed for compound **11** (22.0°) which has a $C_{4a}C_{8a}$ bond distance of 1.340 Å, and the least for alkene **12** (planar) with $C_{4a}C_{8a}$ bond length of 1.332 Å. For molecule **4** an X-ray $C_{4a}C_{8a}$ bond distance of 1.388 Å

was found, which correlated well with our theoretical predictions.

There is good agreement between calculated and experimentally determined COC angles. The COC X-ray angles are around 96° [33] with all calculated values for $C_1O_{10}C_4$ angles are within a range of 95.3° to 98.1° (the smallest angle is in the molecule **21**, and the largest is in molecule **23**). Interestingly, the bond angles do not follow the trends of changes in central double bond folding.

Another characteristic of the calculated geometries worthy of note is the bridge C_1O_{10} bond length, which vary from a value of 1.444 Å (molecule **7**) to 1.461 Å (molecule **19**). These values correlate well the with experimentally determined distance of 1.448 Å in molecule **4**. Again, no correlation of bond length and out of plane deviation was found.[⊥]

Conclusions

B3LYP/6–31G* calculated geometries of the described molecules are in good agreement with available experimental data, while the extent of deformation is underestimated (by 2.2°). Furthermore, it appears that:

a. replacement of the 7-methano bridge(s) with oxygen has very small influence on the increased pyramidalization angle of the central double bond;
b. replacement of one ethano bridge with an etheno or benzene ring causes a significant increase in the deformation of the central double bond;
c. introduction of an etheno bridge causes larger deviation than introduction of a benzene ring;
d. introduction of two peripheral double bonds (or benzene rings) does not further increase nonplanarity of the central double bond;
e. symmetrical *anti*- structures are planar, while others are bent, but to a lesser extent than their *syn*-counterparts;

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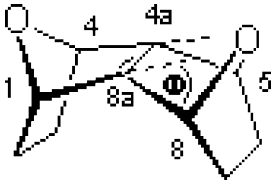
References

1. Carrupt PA,Vogel P (1985) J Mol Struct (THEOCHEM) 124:9
2. Borden WT (1989) Chem Rev 89:1095; Luef W, Keese R (1991) Topics in Stereochemistry 20:231
3. IUPAC name for sesquinorbornene: tetracyclo[6.2.1.1$^{3.6}$0$^{2.7}$] dodec-2(7)-ene, the numbering system used in this paper does not follow IUPAC rules
4. Paquette LA, Shen CC, Krause JA (1989) J Am Chem Soc 111:2351; Shen CC, Paquette LA (1990) J Am Chem Soc 112:1159
5. Griesbeck AG, Deufel T, Hohlneicher G, Rebentisch R, Steinwascher J (1998) Eur J Org Chem 1759
6. Kitamura T, Kotani M, Yokoyama T, Fujiwara Y (1999) J Org Chem 64:680
7. Antol I, Eckert-Maksić M, Margetić D, Maksić ZB, Kowski K, Rademacher P (1998) Eur J Org Chem 1403
8. Eckert-Maksić M, Margetić D, Rademacher P, Kowski K (1993) Tetrahedron Lett 34:6951
9. Eckert-Maksić M, Margetić D, Sander W (unpublished)
10. Kobayashi T, Suda H, Takase H, Iriye R, Kato H (1995) Bull Chem Soc Jpn 68:3269
11. Hagenbuch JP, Stampfli B, Vogel P (1981) J Am Chem Soc 103:3934
12. Hagenbuch JP, Vogel P, Pinkerton AA, Schwarzenbach D (1981) Helv Chim Acta 64:1818
13. Atasoy B, Bayramoglu F, Hökelek T (1994) Tetrahedron 50:5753
14. Holthausen MC, Koch W (1993) J Phys Chem 97:10021
15. Williams RV, Edwards WD, Gadgil VR, Colvin ME, Seidl ET, van der Helm D, Hossain MB (1998) J Org Chem 63:5268
16. Mastrykov VS, Chen K-H, Allinger NL (2001) J Phys Chem A 105:8562
17. Camps P, Font-Bardia M, Méndez M, Pérez F, Pujol X, Solans X, Vásquez S, Vilalta M (1998) Tetrahedron 54:4679
18. Margetić D, Warrener RN, Tiekink ERT (1998) Article 064. In: Rzepa HS, Kappe O (eds) "Electronic Conference on Heterocyclic Chemistry 98". Imperial College Press, ISBN-981-02-3549-1; see also http://www.ch.ic.ac.uk/ectoc/echet98
19. Margetić D, Warrener RN, Butler DN (1999) The Sixth Electronic Computational Chemistry Conference (ECCC6), paper 39, http://www.chemie.uni-regensburg.de/ECCC6/
20. Williams RV, Colvin ME, Tran N, Warrener RN, Margetić D (2000) J Org Chem 2000 65:562
21. For a review on pyramidalization see Borden WT (1988) Chem Rev 89:1095
22. Spartan v. 5.0, (1997) Wavefunction, Inc. 18401 Von Karman Avenue, Suite 370, Irvine, CA, 92612
23. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb, MA, Cheeseman JR, Zakrzewski VG, Montgomery Jr. JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian 98, Revision A.5. Gaussian Inc., Pittsburgh PA
24. The RHF/6–31G* results are not included in discussion, in general this basis set produces structures with Φ angles smaller by 2–3° when compared to B3LYP/6–31G*
25. Fletcher R, Powell MJD (1963) Comput J 6:163
26. Becke AD (1993) J Chem Phys 98:1372
27. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785
28. Spanget-Larsen J, Gleiter R (1983) Tetrahedron 39:3315
29. Paquette LA, Green KE, Gleiter R, Schafer W, Gallucci JC (1984) J Am Chem Soc 106:8232; Bartlett PD, Combs Jr. GL (1984) J Org Chem 49:625
30. Paquette LA, Kunzer H, Green KE, De Lucchi O, Licini G, Pasquato L, Valle G (1986) J Am Chem Soc 108:3453
31. Koch W, Holthausen MC (2000) A Chemist's Guide to Density Functional Theory, Wiley, Weinheim
32. Bartlett PD, Combs Jr. GL, Thi-Le A-X, Watson WH, Galloy J, Kimura M (1982) J Am Chem Soc 104:3131
33. Eckert-Maksić M, Novak-Doumbouya N, Kiralj R, Kojić-Prodić B (2000) J Chem Soc, Perkin Trans 2 1483

[⊥] Out of plane deviation for central π-bond (Φ) is defined as a dihedral angle between $C_1C_{8a}C_{4a}C_4$ and $C_8C_{8a}C_{4a}C_5$ planes



34. Upon a reviewer's suggestion, we looked closely at the central double bond stretching frequencies and found that in all *syn*-/*anti*- pairs of molecules the *syn*- (i.e. more pyramidalized) isomer, as a general rule, has vibration by 10–15 cm^{-1} smaller than corresponding *anti*- (less pyramidalized) isomer. The same result was reported previously by Brown *et al*. for *syn*-/*anti*-sesquinorbornenes **30** and **31** [35]

35. Brown RS, Buschek JM, Kopecky KR, Miller AJ (1983) J Org Chem 49:3692