7-Oxanorbornene cycloadducts. X-Ray, molecular orbital and photoelectron spectroscopic study †

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Structural (X-ray and MP2(fc)/6-31G*) features of 1,4:5,8-diepoxynaphthalenes **1** and **2** are reported. The extent of *endo* bending of the olefinic hydrogens is estimated from the calculated structures and compared with the X-ray data. The computed out-of-plane angles are 7.6 and 6.8° in **1** and **2**, respectively. Photoelectron spectroscopic data of diepoxynaphthalenes **1** and **2** and their higher analogue **3** are discussed and interpreted in terms of through-space and through-bond interaction of the oxygen lone pairs and their interactions with the olefinic π-orbital.

Introduction

7-Oxanorbornene cycloadducts are continuing to attract considerable attention as building blocks of highly interesting molecules such as polarofacial spacers[1] and macrocycles with extended π-conjugation.[2] No less important is their role in preparing sterically rigid polar macrocycles of interest in host–guest chemistry.[3–9] High stereospecificity in such reactions is to a great extent predisposed by the nonplanarity[10] of the double bond incorporated into the significantly strained framework of the starting cycloadducts. Recent X-ray studies performed on a variety of 7-oxanorbornene derivatives and their bisadducts revealed that substituents at the olefinic carbon atoms deviate from planarity by 1.0° to 22.1°.[11–17] However, accurate experimental data about the geometry of the double bond in 7-oxanorbornene derivatives unsubstituted on the double bond, are not available[11,15] as yet, in spite of their obvious importance for understanding intrinsic properties of the parent system. Moreover, most of the previous theoretical studies have been limited to empirical force field,[18,19] semiempirical or *ab initio* model calculations using small basis sets,[19–22] which were amply demonstrated to be inadequate for reliable description of the nonplanar double bonds.[23]

In this paper we would like to report on the molecular and electronic structure of recently prepared cycloadducts **1–3**,[24,25]
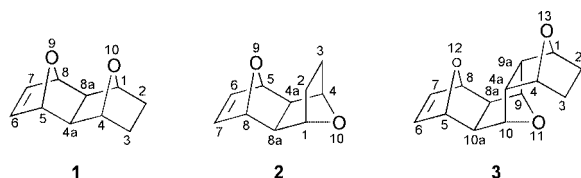
which all possess potentially nonplanar double bonds. Our primary goal in studying structural features of these compounds was to evaluate the extent of deviation of olefinic hydrogen atoms from planarity in the 7-oxanorbornene subunit. This was carried out by employing high level MP2(fc)/
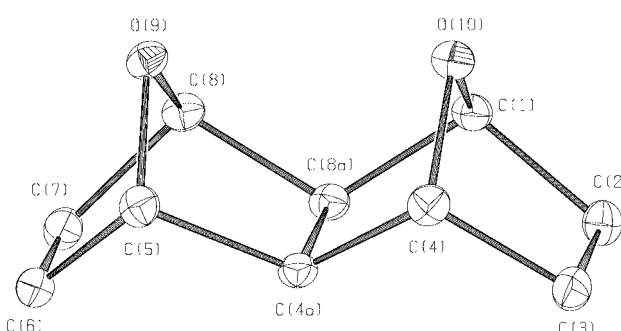
Fig. 1 ORTEP plot of **1** with atom numbering (scaled at the 30% probability level).

6-31G* calculations[26] and also by the X-ray determination of structures of diepoxides **1** and **2** at 100 K. It should be stressed that Holthausen and Koch,[23] using the MP2(fc)/6-31G* level of theory, obtained an almost exact agreement with the experimentally determined pyramidalization in *exo,exo*-norborn-5-ene-2,3-dicarboxylic anhydride.[27] Applicability of this theoretical method to other strained systems with nonplanar double bonds, including those composed of 7-oxanorbornene subunits, has been also discussed by us[28] and other research groups.[29]

Similarly, investigations of the electronic structure of 7-oxanorbornene derivatives have been the subject matter of several previous photoelectron spectroscopic studies.[30–34] The aim of PE investigation of epoxides **1–3** presented here was to extend our earlier work directed toward understanding the ability of rigid polycyclic spacers to transmit long range π-electron and lone pair interactions.

Results and discussion

Structural features

ORTEP plots[35] of a single molecule of compounds **1** and **2** are shown in Figs. 1 and 2. Selected bond lengths and bond angles are listed in Table 1. Both molecules in the crystal structure exhibit an approximate mirror symmetry, with the non-crystallographic mirror plane passing through M(C(2)–C(3)), M(C(4a)–C(8a)), M(C(6)–C(7)), O(9) and O(10), where M represents the midpoint of the respective bond. The largest difference between pseudosymmetry related bonds is observed

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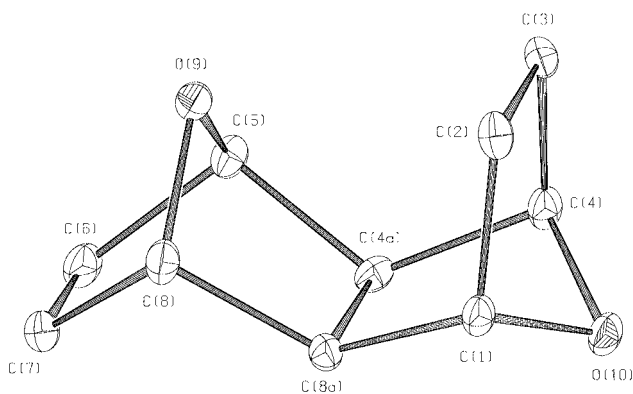*J. Chem. Soc., Perkin Trans. 2*, 2000, 1483–1487 **1483**

Fig. 2 ORTEP plot of **2** with atom numbering (scaled at the 30% probability level).

for the C(5)–C(6) and C(7)–C(8) bonds in *exo,exo*-diepoxide **1** which differ by 0.011(3) Å. The other pseudosymmetry related C–C bonds differ by ≤0.008 Å, while the differences in the pseudosymmetry related C–O bonds are in the range 0.004–0.009 Å. Differences between pseudosymmetry related bond angles are ≤0.8 and ≤0.9° for bisadducts **1** and **2**, respectively. Olefinic hydrogen atoms in *exo,exo*-diepoxide **1** are displaced towards the *endo* face of the molecule by 9(2) and 7(2)°. Interestingly, the olefinic hydrogens in *endo,exo*-diepoxide **2** are found to be considerably twisted, with deviation angles of 11(2) and 5(3)° (in the *endo* direction). Although the significance of these values is questionable, due to uncertainties in locating precise positions of hydrogen atoms in crystals, which is inherent to the X-ray analysis, they are in the direction (*endo*) found in structurally related molecules.[11–17] They are also in good agreement with the deviation angles calculated at the MP2(fc)/6-31G* level of theory, which are available as supporting information in Table S1.

The molecular conformations of bisadducts **1** and **2** are described by selected torsion angles listed in Table 1, and by Cremer and Pople parameters.[36] Each of the six-membered rings adopts a *boat* conformation, with average deviations from the ideal θ and φ angles of 0.2 and 0.4°, respectively. The five-membered rings are in an *envelope* conformation, with an average deviation from the ideal φ angle of 0.5°. The overall geometry of the tetracyclic framework in bisadducts **1** and **2** is, in general, comparable to other known structures.[11–13,15–17] For instance, the C–C bond distances emanating from the central bridge appear to be slightly longer in the 7-oxanorbornene ring than in the fully saturated part of the molecule. This is exactly what would be expected on the basis of hyperconjugative interaction between the double bond π-electrons and σ-MOs describing allylic C–C bonds. Another common feature concerns tilting of the oxygen bridge in the unsaturated ring away from the double bond, which is indicative of repulsion between the lone pair electrons of O(9) and the π-electrons of C(6)=C(7).[11–13,15] Finally, the non-bonding contacts O(9)···O(10) are 2.787(3) and 3.885(5) Å in diepoxides **1** and **2**, respectively, thus allowing considerable through-space interaction of the oxygen lone pairs in the *exo,exo*-diepoxide **1**.

Comparison of the calculated structural parameters (MP2(fc)/6-31G*) with the experimental data (Tables S1 and 1, respectively) reveals satisfactory agreement, particularly if experimental errors are taken into account. The largest discrepancy is observed for the C(6)=C(7) bond which appears to be longer by ~0.02 Å relative to the experimental value. A result of considerable interest in theoretically predicted structures is given by *endo*-deviation of hydrogen atoms around the double bond of 7.6 and 6.8° in diepoxides **1** and **2,** respectively, which is very close to the value found in norbornene (7.9°).[23] Assuming that the accuracy of calculations is the same in oxa-derivatives as in related hydrocarbons, one can conclude that replacement of the CH$_2$ bridges in norbornene by oxygen atoms does not

Table 1 Bond lengths, bond angles and selected torsion angles of **1** and **2** obtained by X-ray structure analysis

Compound	1	2
Bond length/Å		
C(5)–C(6)	1.525(3)	1.525(5)
C(7)–C(8)	1.514(3)	1.523(5)
C(4a)–C(5)	1.556(3)	1.555(4)
C(8)–C(8a)	1.551(3)	1.547(5)
C(4a)–C(8a)	1.565(3)	1.573(5)
C(4)–C(4a)	1.536(3)	1.542(4)
C(1)–C(8a)	1.531(3)	1.538(5)
C(3)–C(4)	1.534(3)	1.526(5)
C(1)–C(2)	1.536(3)	1.529(5)
C(2)–C(3)	1.551(3)	1.553(5)
C(6)–C(7)	1.325(3)	1.322(5)
C(5)–O(9)	1.440(2)	1.451(4)
C(8)–O(9)	1.444(3)	1.443(4)
C(4)–O(10)	1.439(2)	1.452(4)
C(1)–O(10)	1.448(3)	1.457(4)
Bond angle/°		
C(4a)–C(5)–C(6)	105.6(2)	105.1(3)
C(7)–C(8)–C(8a)	105.3(2)	105.7(3)
C(5)–C(4a)–C(8a)	100.7(1)	100.6(2)
C(4a)–C(8a)–C(8)	100.6(2)	100.9(2)
C(4)–C(4a)–C(5)	117.3(2)	120.5(3)
C(1)–C(8a)–C(8)	117.2(2)	120.8(3)
C(4)–C(4a)–C(8a)	100.9(2)	101.4(2)
C(1)–C(8a)–C(4a)	101.3(2)	100.6(2)
C(3)–C(4)–C(4a)	108.5(2)	113.4(2)
C(2)–C(1)–C(8a)	108.3(2)	113.2(2)
C(2)–C(3)–C(4)	101.1(2)	101.9(3)
C(1)–C(2)–C(3)	101.6(2)	101.0(3)
C(5)–C(6)–C(7)	105.2(2)	105.6(3)
C(6)–C(7)–C(8)	106.0(2)	105.9(3)
C(6)–C(5)–O(9)	101.4(2)	101.3(2)
C(7)–C(8)–O(9)	101.4(2)	101.2(2)
C(4a)–C(5)–O(9)	102.4(1)	102.2(2)
C(8a)–C(8)–O(9)	102.7(2)	102.4(2)
C(4a)–C(4)–O(10)	103.9(1)	100.7(2)
C(8a)–C(1)–O(10)	103.5(2)	101.2(2)
C(3)–C(4)–O(10)	102.0(2)	101.8(3)
C(2)–C(1)–O(10)	101.8(2)	102.4(2)
C(5)–O(9)–C(8)	95.9(2)	96.0(2)
C(1)–O(10)–C(4)	96.6(2)	96.0(2)
Torsion angle/°		
C(6)–C(5)–C(4a)–C(8a)	−70.0(2)	−70.5(3)
C(4a)–C(8a)–C(8)–C(7)	70.8(2)	−69.8(3)
C(5)–C(4a)–C(8a)–C(8)	0.4(2)	0.3(3)
C(1)–C(8a)–C(4a)–C(4)	−0.5(2)	−0.1(3)
C(3)–C(4)–C(4a)–C(8a)	−74.5(2)	−71.9(3)
C(2)–C(1)–C(8a)–C(4a)	73.4(2)	72.7(3)
C(1)–C(2)–C(3)–C(4)	0.6(2)	1.0(3)
C(5)–C(6)–C(7)–C(8)	−0.2(2)	−0.6(3)
C(8a)–C(4a)–C(5)–O(9)	−35.7(2)	−34.9(3)
C(4a)–C(8a)–C(8)–O(9)	−35.0(2)	35.7(3)
C(8a)–C(4a)–C(4)–O(10)	−33.5(2)	−36.0(3)
C(4a)–C(8a)–C(1)–O(10)	−34.1(2)	36.2(3)
C(2)–C(3)–C(4)–O(10)	−35.5(2)	−35.9(2)
C(3)–C(2)–C(1)–O(10)	−34.2(2)	−34.2(3)
C(7)–C(6)–C(5)–O(9)	−32.8(2)	31.9(3)
C(6)–C(7)–C(8)–O(9)	−32.4(2)	33.0(3)

influence significantly the nonplanarity of the double bond. It should also be noted that the bond angles, as well as the torsion angles, including the tilting of the oxygen bridges, are in almost exact agreement with experiment. The same holds for the non-bonded O(9)···O(10) distances, which are 2.749 and 3.867 Å in diepoxides **1** and **2**, respectively.

Photoelectron spectra

The He(I) photoelectron spectra of cycloadducts **1**–**3** are shown in Fig. 3, whereas the measured vertical ionization energies are given in Table 2. Assuming the validity of Koopmans'

Table 2 Comparison between measured vertical ionization energies (E_{iv}) and calculated (HF/STO-3G) orbital energies of **1**–**3**

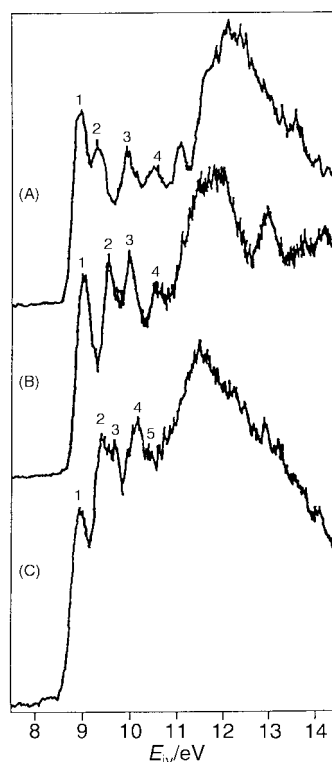| Compound	Peak	E_{iv}/eV	Assignation	$-\varepsilon$/eV
1 (C_s)	1	9.00	$\pi(27a')$	8.12
	2	9.40	$n_O^-(26a')$	8.64
	3	10.10	$n_O^+(25a')$	9.33
	4	10.80	$\sigma(17a'')$	10.18
2 (C_s)	1	9.10	$\pi(27a')$	8.10
	2	9.70	$n_O^-(26a')$	8.95
	3	10.10	$n_O^+(25a')$	9.23
	4	10.70	$\sigma(17a'')$	10.52
3 (C_s)	1	8.95	$\pi(38a')$	8.14
	2	9.45	$n_O(37a')$	8.65
	3	9.69	$n_O(36a')$	9.12
	4	10.16	$n_O(35a')$	9.25
	5	10.40	$\sigma(24a'')$	10.33

Fig. 3 He(I) photoelectron spectra of (A) **1**, (B) **2** and (C) **3**.

approximation,[37] the ionization energies are assigned to specific molecular orbitals. Due to the size of *endo,exo,endo,exo*-triepoxide **3**, orbital energies of all three molecules are calculated by employing the HF/STO-3G procedure.

According to the calculations, the first ionization band in all three photoelectron spectra is assigned to the ionization from π-MO. Its energy is by 0.44 and 0.34 eV lower in diepoxides **1** and **2**, respectively, than in 7-oxabicyclo[2.2.1]hept-2-ene.[30] Analysis of the corresponding HF/STO-3G wave function reflects considerable admixture of the σ_{C-C}-ribbon orbitals, as well as significant admixture of the oxygen lone pairs. A similar decrease in the first ionization energy is encountered on passing from the bisadducts to triepoxide **3**, indicating that enlargement of the molecular frame has a stronger effect on the π-system than the added oxygen bridge. It should be noted, however, that the observed degree of destabilization is significantly smaller than on passing from the parent 7-oxanorbornene to the diepoxides **1** or **2**.

Assignment of the second and the third ionization events in the photoelectron spectra of bisadducts **1** and **2** is also straightforward. They correspond to the ionization from the orbitals of predominant 2p oxygen lone pair character with the out-of-

phase linear combination (with respect to the central bridge) lying above its in-phase counterpart. HF/STO-3G MO calculations predict a slightly larger contribution of the oxygen lone pair residing on the unsaturated ring for both molecular orbitals in **1**. The same holds for the n_O^- linear combination in **2**, whereas the opposite is true for the n_O^+ linear combination. It should be also noted that the n_O^- linear combinations in both compounds exhibit coefficients at olefinic carbon atoms. Furthermore, both MOs exhibit significant incorporation of σ_{C-C}-ribbon MOs of appropriate symmetry. The experimentally observed larger n_O^-,n_O^+-energy difference in *exo,exo*-diepoxide **1** is reproduced computationally and is indicative of cooperative action of through-space and through-bond orbital interactions. The same trend was observed earlier in the structurally related 7-oxanorbornane[31] and 7-oxanorbornene[33] bisadducts.

Finally, band 4 in the photoelectron spectra of both bisadducts **1** and **2** is assigned to the ionization from the 17a″ skeletal σ-MO, in accordance with computational results.

Contrary to bisadducts **1** and **2**, assignment of the higher energy bands in the photoelectron spectrum of trisadduct **3** is less straightforward, due to the presence of strongly overlapping ionization bands. Based on comparison with the HF/STO-3G calculated MO energies, the second band with the two close lying maxima is assigned to two ionization events, each of them being associated with MOs (37a′ and 36a′) of predominantly lone pair character. Similarly, the two maxima within the third band are related to the MO of lone pair character (35a′) and the σ-skeletal MO (24a″).

Conclusions

By combining X-ray analysis and *ab initio* MP2(fc)/6-31G* calculations it is shown that structural features of diepoxides **1** and **2** are dominated by hyperconjugative interaction of the double bond and the σ-MOs describing allylic C–C bonds. The folding of the double bond in bisadducts **1** and **2**, predicted by MP2(fc)/6-31G* calculations and X-ray structural data, as well as the tilting of oxygen bridges in the unsaturated part of the adducts, are explained by electrostatic interaction between the oxygen lone pair and the double bond. Considerable mixing of the lone pair orbitals with the skeletal σ-MOs is confirmed by measuring and interpreting photoelectron spectra of the studied molecules.

Experimental

Computational methods

In studying structural features of diepoxides **1** and **2** calculations were carried out using the GAUSSIAN 92 programme package.[38] Geometries of compounds **1** and **2** were fully optimized within C_s symmetry at the MP2(fc) level of theory utilizing the 6-31G* basis set.[39]

In order to help assignment of the measured He(I) photoelectron spectra, MO energies of all three molecules were calculated at the restricted Hartree–Fock level of theory employing the STO-3G basis set.[39]

Experimental details

^{1}H and ^{13}C NMR spectra were obtained using a Varian Gemini 300 spectrometer. Infrared spectra were recorded using Perkin-Elmer FTIR 1725X or Perkin-Elmer M297 infrared spectrometers. High resolution mass spectra were measured using an Extrel FTMS 2001 DD mass spectrometer. Melting points were determined using a Kofler apparatus (ENH) and were uncorrected. HPLC analyses were performed using a Waters Associates HPLC instrument with a 30 cm μ-porasil column, using hexane–ethyl acetate (4 : 1) as eluent.

PE spectra of diepoxides **1** and **2** were recorded on a Perkin-Elmer PS 18 spectrometer and that of triepoxide **3** on a

Table 3 Crystal data and summary of experimental details and refinement for **1** and **2**

	1	2
Chemical formula	$C_{10}H_{12}O_2$	$C_{10}H_{12}O_2$
Formula weight	164.20	164.20
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/a$
$a/\text{Å}$	7.8726(5)	6.517(7)
$b/\text{Å}$	5.3580(4)	18.98(1)
$c/\text{Å}$	18.8596(6)	6.754(8)
$\beta/°$	93.633(4)	107.16(6)
$V/\text{Å}^3$	793.92(9)	798(1)
T/K	100(3)	100(3)
Z	4	4
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$		0.9
$\mu(\text{Cu-K}\alpha)/\text{cm}^{-1}$	7.6	
No. of measured reflections/R_{int}	1647/0.0551	1878/0.0423
No. of sym. indep. reflections	1153	1123
Observed criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R(F^2)$	0.0486	0.0611
$wR(F^2)$	0.1297	0.1884
$w, P = [(F_{o,o})^2 + 2F_c^2]/3$	$w^{-1} = \sigma(F_o^2)^2 + (0.0805P)^2 + 0.27P$	$w^{-1} = \sigma(F_o^2)^2 + (0.0896P)^2 + 0.18P$

Leybold-Heraeus UPG 200 spectrometer, at 65, 30 and 75 °C, respectively. The spectra were calibrated with Xe and Ar. All three samples were purified by HPLC prior to measurements.

Compounds **1** and **2** were prepared according to the procedure described in ref. 25. Compound **3** was also isolated as a byproduct from the mixture obtained by electrolytic bisdecarboxylation of *exo,exo-* and *exo,endo*-1,2,3,4,4a,5,6,7,8,8a-decahydro-1,4:5,8-diepoxynaphthalene-2,3-dicarboxylic acids and *exo,endo,exo,endo*-1,2,3,4,4a,5,6,7,8,8a,9,9a,10,10a-tetradecahydro-1,4:5,8:9,10-triepoxyanthracene-2,3-dicarboxylic acid. Following the procedure described earlier,[25] column chromatography on silica gel of the isolated product mixture with hexane–ethyl acetate (3 : 1) as the eluent yielded pure *endo,exo*-diepoxynaphthalene **2**,[25] followed by a mixture of *exo,exo*-diepoxynaphthalene **1**[25] and *endo,exo,endo,exo*-triepoxyanthracene **3**. Fractional crystallization of the later fraction from DCM afforded analytically pure triepoxide **3**, mp 262–263 °C; $M^+_{found} = 232.1098$, $M^+_{calc.} = 232.1094$; $v_{max}(\text{KBr})/\text{cm}^{-1}$ 3076 (=C–H), 1630 (C=C), 836 (C–O); δ_H(300 MHz; CDCl$_3$; Me$_4$Si) 1.47 (2H, m, *exo*-2-H, *exo*-3-H), 1.68 (2H, m, *endo*-2-H, *endo*-3-H), 2.39 (2H, m, 8a-H, 10a-H), 2.57 (2H, m, 4a-H, 9a-H), 4.16 (2H, m, 9-H, 10-H), 4.48 (2H, m, 1-H, 4-H), 4.63 (2H, s, 5-H, 8-H), 6.40 (2H, s, 6-H, 7-H); δ_C(300 MHz; CDCl$_3$; Me$_4$Si) 26.44 (t, 2-C, 3-C), 48.93 (d, 8a-C, 10a-C), 51.07 (d, 4a-C, 9a-C), 75.18 (d, 9-C, 10-C), 76.42 (d, 1-C, 4-C), 78.78 (d, 5-C, 8-C), 138.19 (d, 6-C, 7-C).

X-Ray analysis §

Compounds **1** and **2** were crystallized from *n*-hexane with a few drops of ethyl acetate. The crystal data and a summary of the experimental details and refinement of **1** and **2** are listed in Table 3. The Lorentz and polarization corrections were performed by HELENA.[40] The structures were solved by direct methods using the programme SHELXS86[41] and refined on the F^2 values with the programme SHELX97.[42] The positions of hydrogen atoms were deduced from difference Fourier maps and were refined isotropically. Atomic scattering factors were those from the SHELX97[42] programme.

§ CCDC reference number 188/249. See http://www.rsc.org/suppdata/p2/b0/b001267j/ for crystallographic files in .cif format.

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