Tetrahedron Vol. 37, No. 21, pp 3671 to 3679, 1981
Printed in Great Britain

0040-4020/81/213671-09$02.00/0
Pergamon Press Ltd

POLYETHERS

STRUCTURAL ANALYSIS OF THE 1,4,5,8-TETRAOXADECALINS AND 2,2'-BIS(1,3-DIOXOLANE) BY PHOTOELECTRON SPECTROSCOPY, MOLECULAR MECHANICS AND MOLECULAR ORBITAL CALCULATIONS

FLEMMING S. JØRGENSEN, LEIF NØRSKOV-LAURITSEN, ROALD BOE JENSEN and GUSTAV SCHROLL

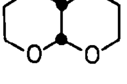
Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

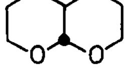
(*Received in UK* 5 *May* 1981)

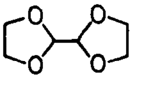
Abstract—The photoelectron (PE) spectrum of *cis*-1,4,5,8-tetraoxadecalin exhibits in contrast to most polyoxa compounds an extremely well resolved low energy part due to large 'through-bond' interactions between the oxygen lone pairs and the ideally oriented C–C bonds. The 'through-bond' interactions of the *cis*- as well as the unknown *trans*-1,4,5,8-tetraoxadecalin are discussed based on simple perturbation molecular orbital theory and PRDDO molecular orbital calculations. Additionally the PE spectrum of 2,2'-bis (1,3-dioxolane) is reported.

Molecular mechanics (MM1 and MM2) and molecular orbital (PRDDO) calculations of the different conformations of the 1,4,5,8-tetraoxadecalin and 2,2'-bis(1,3-dioxolane) systems allow the absence of the *trans*-1,4,5,8-tetraoxadecalin, and the *cis-trans* energy difference in the series decalin, 1,8-dioxadecalin and 1,4,5,8-tetraoxadecalin systems to be explained.

Conformational analysis of oxygen containing compounds has often been successfully analysed by considering the replacement of a methylene group[1–4] by an O atom. From this point of view the *cis*- and *trans*-1,4,5,8-tetraoxadecalins **1** and **2** constitute an interesting pair of isomers. Originally they were postulated to be products from the condensation of ethylene glycol and 2,3-dichloro-1,4-dioxane.[5–7] Later they were characterized as *cis*-1,4,5,8-tetraoxadecalin[8] **1** and 2,2'-bis(1,3-dioxolane) **3** by X-ray crystallography and NMR spectroscopy.[9–15] Several workers have since attempted to prepare the *trans*-tetraoxadecalin **2** and to explain the absence of this isomer.[16]


1


2


3

We present a molecular mechanics study of the two isomeric tetraoxadecalins **1** and **2**, and the bisdioxolane **3** using Allinger's force fields MM1 and MM2.[17–21] Secondly, the PE spectra of **1** and **3** reveal a remarkable difference between these two structural isomers. The electronic structures of the three compounds are discussed based on simple perturbation MO arguments and confirmed by MO calculations using the PRDDO method.[22,23]

Molecular structures

The molecular mechanics (force field) method has proved a very efficient tool in conformational analysis.[24–26] The calculation of structures and energies (conformation energies and heats of formation) of a great variety of compounds is accomplished with high accuracy.[24–26] The most versatile molecular mechanics program available today is undoubtedly the Allinger MM1 force field[17,18] (1973 version), which has been applied to hydrocarbons as well as several heteroatom containing systems including oxygen compounds.[17–19,26,27] For alcohols and ethers the MM1 method was found to give reasonably good structures and energies, although not as good as for hydrocarbons.[17–19] MM2 is an improved version of MM1 yielding better results for alcohols and ethers with respect to conformational energies and heats of formation.[21]

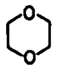
We performed the geometry optimizations with MM1 and when the MM2 version was available, we reoptimized all the structures and found the MM1 and MM2 geometries to be very similar. We only report the MM1 structures as they were employed in the MO calculations.

Before turning to the bicyclic polyoxa systems **1–3** we applied the molecular mechanics method to the simple cyclic ethers, oxane (tetrahydropyran) **4** and 1,4-dioxane **5**. For oxane **4** the agreement between the calculated and the experimentally determined structures is excellent,[28] and for 1,4-dioxane **5** only the C–O–C bond angle seems to be too large by 3° (*cf* Table 1).[30] It should be noticed that MM1 shows the dioxane ring slightly more puckered (ϕ_{av}) than the oxane ring in accordance with experiment.[31]

The structure of *cis*-1,4,5,8-tetraoxadecalin **1** as calculated by MM1 (and MM2) is in reasonable agreement with that determined by X-ray[9] (*cf* Fig. 1a and Table 2) although some discrepancies exist. The calculated bond lengths generally are too short by 0.03–0.04 Å; all bond angles agree within 1°, except for the C2–01–C9 and C6–05–C10 bond angles, which are calculated to be 6° too large.

As expected MM1 (and MM2) fails to reproduce the differences in the C–O bond lengths as a function of the conformation of the acetal moiety (*cf* the anomeric effect).[32,33] This problem could be overcome by some minor modifications in the force field parameters,[34] but

Table 1. Structural data for oxane 4 and 1,4-dioxane 5 as calculated by molecular mechanics (MM1) and as determined by electron diffraction. Bond lengths in Å and angles in degrees

			r(CO)	r(CC)	<COC	<CCO	ϕ_{av}[a]
4		MM1	1.410	1.531[b]	110.0	111.7	57.2
		ED[c]	1.420	1.531[b]	111.5	111.8	56.4
5		MM1	1.409	1.530	109.4	110.6	58.2
		ED[d]	1.423	1.523	112.5	109.2	57.9[e]

a. See ref. 31 for definition of ϕ_{av}, the average torsion angle.

b. C-C bond lengths are equal.

c. Ref. 29.

d. Ref. 30.

e. Taken from Ref. 31.

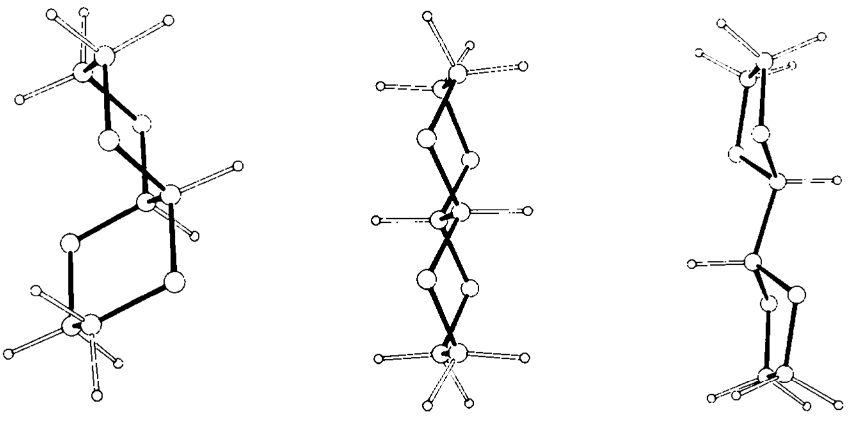
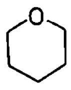
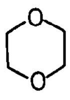

(a) (b) (c)

Fig. 1. ORTEP representation of the molecular mechanics (MM1) determined minimum energy conformation of : (a) *cis*-1,4,5,8-tetraoxadecalin 1, (b) *trans*-1,4,5,8-tetraoxadecalin 2, and (c) 2,2'-bis (1,3-dioxolane) 3.

even without these modifications the MM1 method gives energetic and conformational results for the simplest acetal, dimethoxymethane 6, which are comparable to *ab initio* calculations.[35,36]


4


5

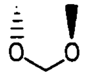
$CH_3OCH_2OCH_3$

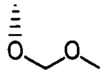
6

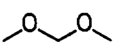
We thus conclude that the MM1 and MM2 methods are able to produce structures of compounds with one or more O atoms in good agreement with experimental structures.

The structure of *trans*-1,4,5,8-tetraoxadecalin 2 is interesting by virtue of its *anti, anti* oriented C-O-C-O-C acetal fragments (Fig. 1b). The central C-O bond lengths as calculated by molecular mechanics are slightly shorter than the corresponding ones in the *cis* compound 1 (see Table 2). This is in accordance with *ab initio* calculations,[35] although the reason for this shortening is not clear. Maybe more important is the compression of the O-C-O angles in 2 relative to 1. Still, it is not a large effect, probably due to the constraints imposed by the bicyclic nature of the compounds. In dimethoxymethane 6 the O-C-O bond angles as calculated by MM1 are 111.8°, 108.6° and 105.6° for the *gauche, gauche*; *gauche, anti* and *anti, anti* conformations, respectively.[36]

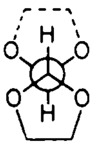
6

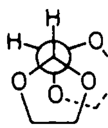

g^+,g^+


g^+,a


a,a

Special problems arise for the 2,2'-bis(1,3-dioxolane) 3, which in the solid state exists in an *anti* form 3a with a center of inversion[10] and in solution as an equilibrium between the *anti* form 3a and a *gauche* form 3g, the latter predominating.[37]


3a


3g

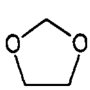
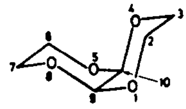
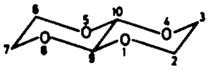

7

Table 2. Molecular mechanics (MM1) calculated and X-ray determined structural data for *cis*- and *trans*-1, 4, 5, 8-tetraoxadecalin (**1** and **2**). Bond lengths in Å and angles in degrees

		1-9	1-2	2-3	3-4	4-10	9-10	1-9-8	2-1-9	1-2-3	2-3-4	3-4-10
 1	MM1[a]	1.407	1.409	1.531	1.409	1.404	1.520	108.9	119.4	110.7	110.4	109.8
	X-ray[b]	1.400 1.416	1.450 1.442	1.510 1.517	1.445 1.436	1.430 1.428	1.529	108.3 107.1	113.4 113.2	109.8 110.0	110.1 110.4	109.3 110.5
 2	MM1[c]	1.405	1.411	1.533	1.411	1.405	1.532	107.4	109.5	111.0	111.0	109.5

a. The torsion angles ϕ(7-8-9-1) and ϕ(8-9-1-2) are 179.3° and 65.8°, respectively.

b. Taken from Ref. 9. Two values due to non-exact C_2 symmetry.

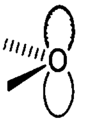
c. The torsion angles ϕ(7-8-9-1) and ϕ(8-9-1-2) are 178.6° and 179.0°, respectively.

The conformation of the dioxolane rings in the solid state are neither envelope nor half-chairs, but somewhere in-between.[10,38] Our molecular mechanics calculations find the *anti* form **3a** to be more stable than the *gauche* form **3g**. In both conformers the O–C–C–O fragment in the dioxolane rings is planar (see Fig. 1c), contrary to X-ray results of **3**.[10] Using start geometries for **3** without any symmetry restrictions, with a non-zero torsional angle about the O–C–C–O part and even identical to the crystal structure in all cases led to C2 envelope coformations after optimization.

Whether the molecular mechanics method generally is poor in handling 1,3-dioxolanes **7** cannot be judged solely on the above results, as crystal forces may be responsible for the conformation of the dioxolane rings in **3** in the solid phase.

Electronic structures

The lone pairs on the O atom in ethers are often described as two localized orbitals with a tetrahedral arrangement,[39–41] and this has been used in explaining the *rabbit ear* and *gauche* effects.[42,43]



$n_O(\pi)$

$n_O(\sigma)$

Another way of describing the O lone pairs is as two energetically nonequivalent lone pairs, a π type and a σ type.[39–41] Assuming the validity of Koopman's theorem,[44,45] the lowest ionization energy of ethers corresponds to the $n_O(\pi)$ lone pair, which can be represented by a non-bonding oxygen 2p orbital placed perpendicular and therefore antisymmetric to the C–O–C plane. The orbital associated with the $n_O(\sigma)$ lone pair is placed in the C–O–C plane and can best be described as an sp^2 orbital, as it contains a considerable amount of 2s character.[39–41] The $n_O(\sigma)$ lone pair is located at a higher ionization energy than the more localized $n_O(\pi)$ lone pair.

The PE spectrum of oxane **4**[46,47] contains a single low energy ionization at 9.48 eV, which undoubtedly corresponds to the $n_O(\pi)$ lone pair. The next higher ionization energy was found at 10.90 eV and has been assigned to the $n_O(\sigma)$ lone pair.[46,47]

A PRDDO MO calculation of oxane **4** using the previously discussed MM1 optimized structure[48] locates the $n_O(\pi)$ orbital at -9.07 eV and the $n_O(\sigma)$ orbital at -10.05 eV.

The PE spectrum of 1, 4-dioxane **5**[46,47] exhibits three low energy ionizations of which only the two lowest originally were assigned. In 1, 4-dioxane **5** the chair form of the molecule places the C–C bonds in such a way relative to the O lone pairs that interactions between these orbitals and the σ_{cc} and the σ_{cc}^* orbitals are close to optimal.[30] According to Sweigart and Turner[46] the lowest ionization energy at 9.43 eV corresponds to a combination of the $n_O(\pi)$ lone pair orbitals destabilized by out-of-phase interaction with σ_{cc} orbitals. The following value at 10.65 eV has been interpreted as a combination of the $n_O(\pi)$ lone pair orbitals stabilized by in-phase interaction with σ_{cc}^* orbitals. Kobayashi and Nagakura[47] interpreted the PE spectrum of **5** by means of CNDO/2 calculations, but due to the tendency of the latter method to destabilize σ type orbitals relative to π type orbitals their interpretation may only be correct for the two lowest ionization energies.

A PRDDO MO calculation of 1, 4-dioxane **5** reveals that the electronic structure of the compound can be explained easily as arising from interaction between the σ_{cc} orbitals and combinations of both types of O lone pairs. The PRDDO results (*cf* Fig. 2 and Table 3) show that the HOMO[50] and H-1 orbitals are out-of-phase combinations of the σ_{cc} orbitals and combinations of the $n_O(\pi)$ and $n_O(\sigma)$ lone pairs, respectively. The H-2 and H-3 orbitals correspond to those combinations of the lone pairs which cannot interact with the σ_{cc} orbitals due to different symmetry. The HOMO and H-2 orbitals are the π type lone pairs and the split between them ($\Delta\epsilon = 1.63$) can be taken as a measure of the σ_{cc} interaction. The split between the σ type lone pairs (H-1 and H-3) amounts to 1.98 eV, both values in good agreement with the experimentally observed numbers ($\Delta IE = 1.86$ eV and $\Delta IE = 2.26$ eV, respectively). This leads to an orbital ordering $1A_g < 2A_g < 1B_u < 2B_u$ for dioxane **5**.[51]

A recent *ab into* study[52] has shown in close agreement with our results that the electronic structure of 1, 4-

Table 3. Experimental and PRDDO MO calculated data for 1,4-dioxane 5

IE[a]	IE[b]	ΔIE		ε[c]	Δε	Symmetry[d]	Orbital type[e]	electron density[f] O-atoms (2s:2p)[g]	electron density[f] CH-atoms
9.43	9.41		HOMO	-8.68		$1A_g$	$n_+(\pi)-\sigma_{cc}$	0.77 (3:97)	0.22
10.65	10.60	1.86	H-1	-10.16	1.68	$2A_g$	$n_+(\pi)-\sigma_{cc}$	0.62 (19:81)	0.36
	11.27	2.26	H-2	-10.31	1.98	$1B_u$	$n_-(\pi)$	0.82 (5:95)	0.13
	12.86		H-3	-12.14		$2B_u$	$n_-(\sigma)$	0.85 (18:82)	0.10

a. Ionization energies (eV); taken from Ref. 46.

b. Ionization energies (eV); taken from Ref. 47.

c. Orbital energies (eV).

d. Symmetry within the C_{2h} point group.

e. $n_+(\pi)$ corresponds to an in-phase combination of the $n_O(\pi)$ lone pairs; $n_-(\sigma)$ to an out-of-phase combination of the $n_O(\sigma)$ lone pairs; σ_{cc} to a combination of the σ_{cc} orbitals and so on.

f. The electron density is defined as $\sum c_i^2$, where c_i is the atomic orbital coefficient.

g. The ratio between the oxygen 2s and 2p atomic orbital coefficients.

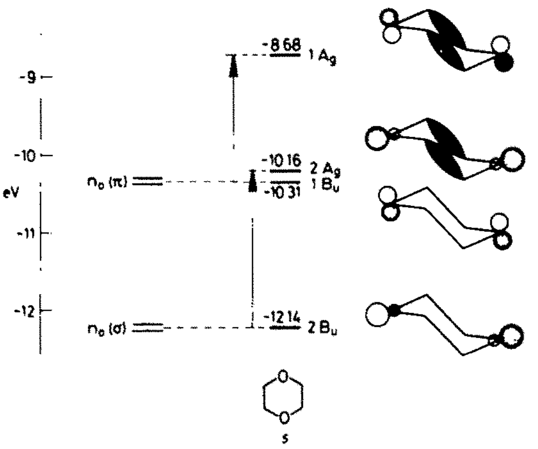
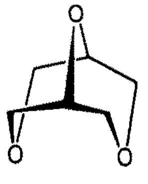


Fig. 2. PRDDO MO correlation diagram for 1,4-dioxane 5. The arrows indicate the "through-bond" destabilization of the oxygen lone pairs. For further explanation see text and Table 3.

dioxane 5 best can be described as a 'through-bond' phenomenon.[53]

In 3,7,9-trioxabicyclo[3.3.1]nonane **8** the "through-bond' destabilization of two of the three O lone pair combinations are even larger than in 1,4-dioxane 5 (ΔIE = 2.00 eV resp. ΔIE = 1.74 eV).[54] The destabilization in **8** has been explained as out-of-phase interactions between combinations of the two O lone pairs and combinations of the four σ_{cc} orbitals in a way similar to that described above for 1,4-dioxane 5.[54]



8

The PE spectrum of *cis*-1,4,5,8-tetraoxadecalin **1** (Fig. 3) contains four well resolved bands below 12 eV, which is quite unusual for polyethers.[46,54–58] The maxima of the four peaks are located at 9.22, 9.98, 10.66 and 11.40 eV, the latter accompanied by a shoulder at 11.64. The corresponding areas suggest that each of the first three bands corresponds to a single ionization and the fourth to two or three ionizations.[59] The shapes of the bands in the PE spectrum of the *cis*-tetraoxadecalin **1** suggest that the HOMO of the molecule is more delocalized than the H-1 and H-2 orbitals, and therefore gives rise to a broader peak than the two latter ones, which seem to be mainly localized on the O atoms.[60]

As shown the frontier orbitals of molecules like 1,4-dioxane 5 and 3,7,9-trioxabicyclo[3.3.1]nonane **8** can be derived by combinations of the $n_O(\pi)$ O lone pairs and suitable σ_{cc} orbitals, and the same can be done for *cis*-1,4,5,8-tetraoxadecalin **1**, which can be viewed as two 1,4-dioxane units with a common C–C bond (see Fig. 1a). It is possible to combine the $n_O(\pi)$ lone pairs to give two symmetric ($n_O(1A)$ and $n_O(2A)$) and two antisymmetric (n_O(1B) and n_O(2B)) combinations with respect to the C_2 symmetry of the *cis*-tetraoxadecalin molecule. Analogously, the three σ_{cc} orbitals can be combined into two symmetric (σ_{cc}(1A) and σ_{cc}(2A)) and one antisymmetric (σ_{cc}(B)) orbital (Fig. 4). Interaction between the lone pair and σ_{cc} combinations leads to destabilization of the three of the lone pair orbitals. The n_O(1A) orbital will be destabilized by interaction with both the σ_{cc}(1A) and σ_{cc}(2A) orbitals. The n_O(2A) and n_O(1B) orbitals can interact with the σ_{cc}(1A) and σ_{cc}(B) orbitals, respectively, but the symmetric case seems to lead to a smaller destabilization than the antisymmetric case. Hence the 1:1:1 picture observed for the *cis*-1,4,5,8-tetraoxadecalin molecule **1** (see Fig. 3) can be described easily using a simple PMO molel, which predicts the ordering of the frontier orbitals to be 1A < 1B < 2A < 2B.

A PRDDO MO calculation of *cis*-1,4,5,8-tetraoxadecalin based on the MM1 optimized geometry

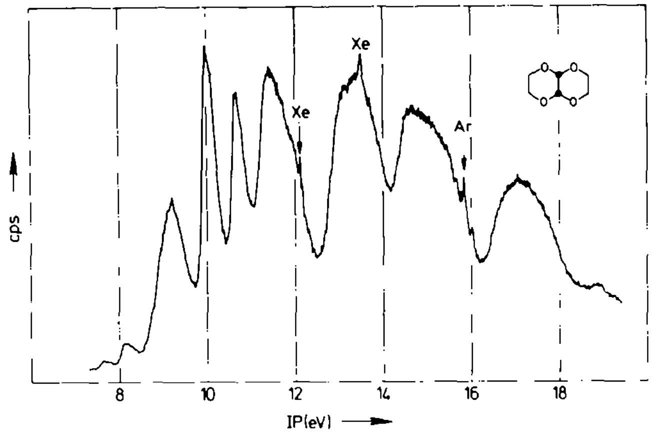


Fig. 3. Photoelectron spectrum of *cis*-1, 4, 5, 8-tetraoxadecalin 1.

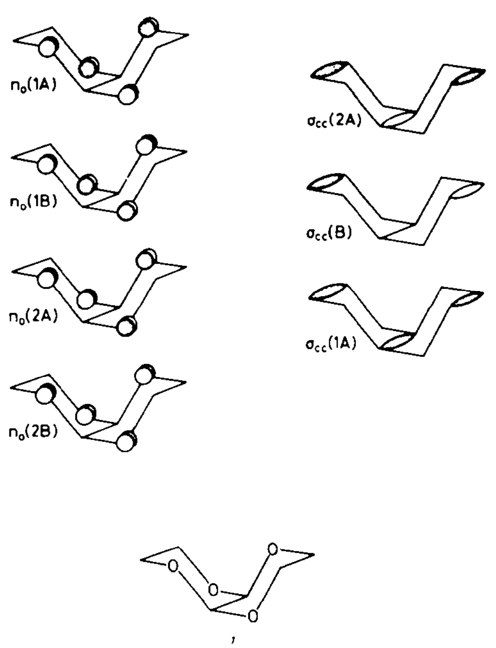


Fig. 4. The four $n_O(\pi)$ lone pair combinations and the three σ_{cc} combinations for *cis*-1, 4, 5, 8-tetraoxadecalin 1. For further explanation see text.

confirms the above interpretation. The PRDDO results (Fig. 5 and Table 4) show the HOMO to be predominantly the n_O(1A) orbital, but with considerable amount of σ_{cc} character. The H-1 and H-2 orbitals are the n_O(1B) and n_O(2A) orbitals containing less σ character than the HOMO in agreement with the broad appearence of the first band in the PE spectrum of 1 (Fig. 3) compared to the following two bands.

The σ type lone pairs on the O atoms can be combined in a similar way and interaction with the σ orbitals leads to an analogous picture (see Table 4 and Fig. 5). The H-3 and H-4 orbitals are the combinations of the σ type lone pairs, which show the largest coefficients on the C atoms, whereas the remaining combinations are nearly unaffected.

The size of the "through-bond" interaction may be defined as the difference between the most destabilized lone pair orbital (the HOMO) and the lone pair orbital which cannot interact with the σ orbitals for symmetry reasons. This leads to $\Delta\epsilon = 2.76$ eV (see Table 4) for the $n_O(\pi)$ lone pairs corresponding to an experimental $\Delta IE = 11.64 - 9.22 = 2.42$ eV. The calculated split for the $n_O(\sigma)$ lone pairs corresponds to $\Delta\epsilon = 2.14$ eV (see Table 4). The "through-bond" interactions in *cis*-1, 4, 5, 8-tetraoxadecalin 1 are therefore larger than in both 1, 4-dioxane 5 and 3, 7, 9-trioxabicyclo[3.3.1]nonane 8, and to our knowledge the largest observed for any O compound.

Plotting of the experimentally determined ionization energies (IE_{obs}) against the eigenvalues ($-\epsilon$) calculated by the PRDDO method for oxane 4, 1, 4-dioxane 5, and *cis*-1, 4, 5, 8-tetraoxadecalin 1 (see Fig. 6) yields the relationship:

$$IE_{pred} = -0.917\,\epsilon + 1.50\,\text{eV}$$

(correlation coefficient 0.933), which confirms the validity of Koompmans' theorem for these compounds.[61]

The *trans*-1, 4, 5, 8-tetraoxadecalin 2 having C_{2h} symmetry can be viewed like the *cis* isomer as composed of two 1, 4-dioxane units fused together (see Fig. 1b), which suggests that large "through-bond" effects may be present in this molecule as observed for the *cis* isomer 1. A PRDDO MO calculation of the *trans*-tetraoxadecalin 2 confirms this and the destabilization of the combinations of the $n_O(\pi)$ and $n_O(\sigma)$ O lone pairs leads to a comparable pattern for the *cis* and *trans* isomers (Fig. 5 and Table 5). The HOMO of 2 is located at −8.33 eV, which is even lower than the HOMO of 1 ($\epsilon = -8.44$ eV). The "through-bond" split for the *trans* isomer 2 is equal to the value of the *cis* isomer 1 ($\Delta\epsilon = 2.76$ eV, see Table 5).

Finally we wish to discuss the PE spectrum of 2, 2′-bis(1, 3-dioxolane) 3 (see Fig. 7), which exhibits one broad low energy band with maximum at 9.32 eV. The following band displays two maxima at 10.24 eV and 10.46 eV, and a shoulder on the high energy side estimated at 10.7–10.9 eV. The corrected areas of the two bands suggest that the low energy band corresponds to a single ionization and the large band to four ionizations.[59] The PE spectrum of 3 is not straightforward to interpret, but it may be anticipated that at least one of the lone pair combinations may be destabilized by interaction with the σ_{cc} orbital of the central band.

The PRDDO calculations of both the *anti* 3a and the *gauche* 3g forms of the bisdioxolane do not show a HOMO placed well above the following orbitals, al-

Table 4. Experimental and PRDDO MO calculated data for *cis*-1,4,5,8-tetraoxadecalin **1**

						electron density^g	
IE^a	ΔIE^b		ε^c	Δε	Symmetry^f	O-atoms (2s:2p)^g	CH-atoms
9.22	2.42	HOMO	-8.44	2.76^d	1A	0.74 (0:100)	0.22
9.98	1.66	H-1	-9.74	1.46^d	1B	0.76 (0:100)	0.18
10.66	0.98	H-2	-10.31	0.89^d	2A	0.79 (4:96)	0.12
10.40		H-3	-10.67	2.14^e	2B	0.63 (21.79)	0.32
		H-4	-11.09	1.72^e	3A	0.69 (12:88)	0.17
11.64	0.00	H-5	-11.20	0.00^d	3B	0.79 (6:94)	0.11
12.5		H-6	-12.43	0.38^e	4A	0.77 (17.83)	0.08
		H-7	-12.81	0.00^e	4B	0.80 (17:83)	0.10

a. Ionization energies (eV); this work.

b. The differences for the IE's, which correspond to the differences for the ε's (see footnote d).

c. Orbital energies (eV).

d. The difference between the basis combination of the $n_O(\pi)$ lone pairs (H-5) and the three destabilized combinations (HOMO, H-1 and H-2).

e. The difference between the basis combination of the $n_O(\sigma)$ lone pairs (H-7) and the three destabilized combinations (H-3, H-4 and H-6).

f. Symmetry within the C_2 point group.

g. See Table 3, footnotes f and g.

Table 5. PRDDO MO calculated data for *trans*-1,4,5,8-tetraoxadecalin **2**

				electron density^e	
	ε^a	Δε	Symmetry^d	O-atoms (2s:2p)^e	CH-atoms
HOMO	-8.33	2.76^b	1A$_g$	0.80 (0:100)	0.20
H-1	-9.97	1.12^b	1A$_u$	0.80 (0:100)	0.20
H-2	-10.21	2.60^c	2A$_g$	0.68 (12:88)	0.28
H-3	-10.28	0.81^b	1B$_u$	0.76 (5:95)	0.24
H-4	-11.09	0.00^b	1B$_g$	0.84 (0:100)	0.14
H-5	-11.57	1.24^c	2A$_u$	0.52 (31:69)	0.38
H-6	-12.31	0.50^c	2B$_g$	0.80 (25:75)	0.14
H-8^f	-12.81	0.00^c	2B$_u$	0.76 (18:82)	0.22

a. Orbital energies (eV).

b. The difference between the basis combination of the $n_O(\pi)$ lone pairs (H-4) and the three destabilized combinations (HOMO, H-1 and H-3).

c. The difference between the basis combination of the $n_O(\pi)$ lone pairs (H-8) and the three destabilized combinations (H-2, H-5 and H-6).

d. Symmetry within the C_{2h} point group.

e. See Table 3, footnotes f and g.

f. The H-7 orbital is a σ type orbital.

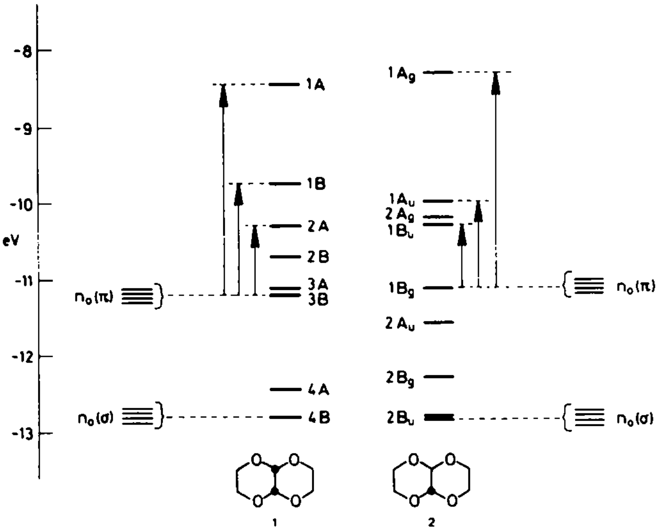


Fig. 5. PRDDO MO correlation diagram for *cis*- and *trans*-1, 4, 5, 8-tetraoxadecalin (**1** and **2**). The arrows indicate the "through-bond" destabilization of the oxygen lone pairs. For further explanation see text and Tables 4 and 5.

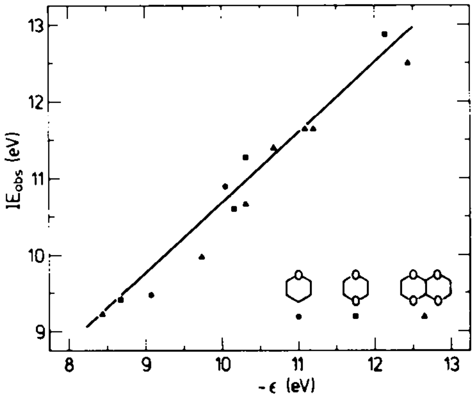


Fig. 6. Plot of the experimentally determined ionization energies (IE_{obs}) vs the PRDDO calculated MO energies (ϵ). All values in eV.

though the HOMO in fact is an orbital with considerable amount of σ_{cc} character from the central C–C bond as mentioned above.

Whether the failure of the PRDDO calculations to yield a high lying HOMO for the bisdioxolane is due to the use of inappropriate geometries of the 1, 3-dioxolane rings in **3** has not been subjected to any detailed studies.

Relative energies

All attempts to prepare the *trans*-1, 4, 5, 8-tetraoxadecalin **2** have until now been unsuccessful, which may be due to the fact that all syntheses have been carried out under conditions leading to isomerization, either in the final product or in some intermediate species.[16] Likewise if the *cis*-isomer or the bisdioxolane **3** are equilibrated by means of acid a mixture of the two compounds is obtained without any trace of the *trans*-isomer **2**.[62] This suggests that the *trans*-1, 4, 5, 8-tetraoxadecalin **2** is thermodynamically less stable than the two other isomers (**1** and **3**) and synthetic approaches to the *trans*-isomer must avoid any conditions that may lead to isomerization.

The relative energies of the two tetraoxadecalines and the two conformers of the bisodioxolane are collected in Table 6. The pseudorotation in 1, 3-dioxolane is estimated to 0.13 kcal/mol,[63,64] which means that although the molecular mechanics calculated conformations of the 1, 3-dioxolane rings in the bis-dioxolane **3** may be wrong the relative energy of this isomer compared to the *cis*- and *trans*-tetraoxadecalines is not much affected.

Both the MM1 and MM2 calculaions show the *cis*-tetraoxadecalin **1** to be 3–4 kcal/mol more stable than the *trans*-tetraoxadecalin **2** and 4–5 kcal/mol more stable than the bisdioxolane **3**. This is far from agreement with the results of the equilibration of **1** and **3**, and the absence of **2**. In the original parameterization of MM1 to alcohols and ethers the largest error between the calculated and experimental heats of formation was found for 1, 3-dioxolane **7** (3.63 kcal/mol),[19] so apparently both force fields have a problem in calculating energies of 1, 3-dioxolanes properly.

The PRDDO energies reflect the experimental facts very well. The *cis*-tetraoxadecalin and the bisdioxolane are nearly equally strained, whereas the *trans*-tetraoxadecalin is about 5 kcal/mol more strained. Thus under equilibrium conditions the *trans*-tetraoxadecalin cannot be expected to be present in detectable amounts.

For the hydrocarbon analogue, decalin **9** the *trans*-isomer is more stable than the *cis*-isomer by about 3 kcal/mol.[65] The 1, 8-dioxadecalin system **10**[66] can be viewed as a decalin skeleton in which a single acetal unit has been incorporated. This alters the relative energies of the *cis*- and *trans*-isomers, so the *trans*-isomer is now only about 0.2 kcal/mol less stable than the *cis*-isomer.[67,68] In the 1,4,5,8 - tetraoxadecalin system (**1, 2**) another acetal unit has been incorporated and this leads to a further favouring of the *cis*-isomer (see Table 6).

In the 1, 8-dioxadecalin **10** and 1, 4, 5, 8-tetraoxadecalin (**1, 2**) systems the conformations of the acetal moieties

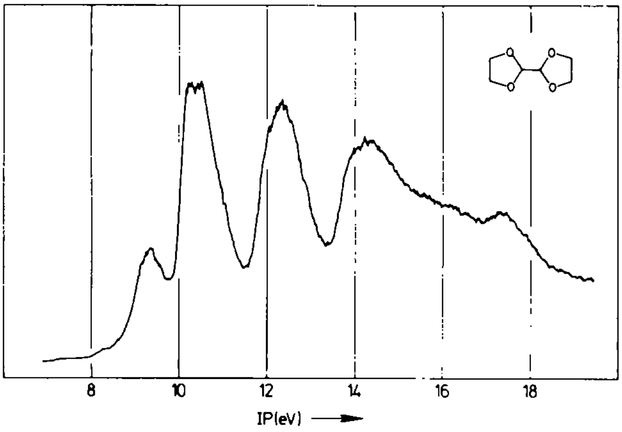


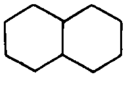
Fig. 7. Photoelectron spectrum of 2, 2'-bis(1, 3-dioxolane) 3.

Table 6. Energies for the 1, 4, 5, 8-tetraoxadecalin and the 2, 2'-bis(1, 3-dioxolane) systems as calculated by molecular mechanics (MM1 and MM2) and MO methods (PRDDO). In kcal/mol

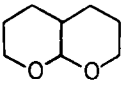
		1,4,5,8-tetraoxadecalin		2,2'-bis(1,3-dioxolane)	
		cis	trans	gauche	anti
MM1	D = 1.0[a]	0.00	3.95	6.78	5.15
	D = 2.2	0.00	3.50	5.85	5.02
MM2	D = 1.0	0.00	3.39	5.57	4.79
	D = 2.2	0.00	3.05	4.49	4.31
PRDDO		0.00	5.50	0.37	1.00

a. Dielectric constant employed in dipole-dipole interaction term.

are *anti, gauche* in the *cis*-conformation and *anti, anti* in the *trans*-conformation (see Figs. 1a, 1b). The difference in energy between these two conformations of the simple model compound, dimethoxymethane **6** is 2.5 kcal/mol and 3.4 kcal/mol as calculated by MM1 and PRDDO, respectively.[36,69] This preference for the *gauche* arrangement in acetals is known as the "anomeric" effect.[32,33]



9



10

A rationalization of this is that the *trans*-isomer is destabilized relative to the *cis*-isomer by about 3 kcal/mol by the introduction of each acetal unit, because this fragment is fixed in the less favorable *anti, anti* conformation, This simple explanation does not account for the possible 1, 4-dioxa interactions in the 1, 4, 5, 8-tetraoxadecalin system, but these interactions are expected to be weaker than the 1, 3-dioxa interactions.[4]

EXPERIMENTAL

cis-1,2,5,8-Tetraoxadecalin **1** and 2, 2'-bis(1,3-dioxolane) **3** were prepared as described[70] and separated by preparative gas chromatography.

The PE spectra were recorded on a PS-18 spectrometer (Perkin-Elmer) with a He(I) source and calibrated with a mixture of agron and xenon introduced into the target chamber simultaneously with the sample. The recording temps for **1** and **3** were 35-36° and 20°, respectively; the experimental resolution was 30 meV. The reported ionization energies are averages of four determinations.

The MM1 program is the QCPE version,[71] whereas copies of the MM2 and PRDDO programs kindly were provided by N.L. Allinger (University of Georgia) and T. A. Halgren (City University of New York), respectively, and made available for us by J. P. Snyder (University of Copenhagen).

Acknowledgements—We are grateful to the Danish Natural Science Research Council for support enabling the purchase of a photolectron spectrometer and for financial support to FSJ (11-0105) as well as to L. Henriksen (University of Copenhagen) for stimulating discussions.

REFERENCES

[1] W. L. F. Armarego, *Stereochemistry of Heterocyclic Compounds*. Part II. Wiley-Interscience, New York (1977).

[2] F. G. Riddell, *The Conformational Analysis of Heterocyclic Compounds*. Academic Press, London (1980).

[3] J. B. Lambert and S. I. Featherman, *Chem. Rev.* **75**, 611 (1975).

[4] J. Dale, *Tetrahedron* **30**, 1684 (1974).

[5] J. Böeseken, F. Tellegen and P. Cohen-Henriquez *Rec. Trav. Chim.* **50**, 909 (1931).

[6] E. Caspi, Th. A. Wittstruck and D. M. Piatak, *J. Org. Chem.* **27**, 3183 (1962).

[7] O. Hassel and C. Rømming, *Acta, Chem. Scand.* **10**, 136 (1956). The compound investigated actually was the *cis*-isomer.

[8] The systematic name of the 1,4,5,8-tetraoxadecalin system is 2,5,7,10-tetraoxabicyclo[4.4.0]decane. The names *p*-dioxino[2,3-b]-*p*-dioxin and 1,4,5,8-naphtodioxane have been used earlier.

[9] B. Fuchs, I. Goldberg and U. Shmueli, *J. Chem. Soc. Perkin II*, 357 (1972).

[10] S. Furberg and O. Hassel, *Acta Chem. Scand.* **4**, 1584 (1950).

[11] C. Altona and E. Havinga, *Tetrahedron* **22**, 2275 (1966).

[12] R. R. Fraser and C. Reyes-Zamora, *Can. J. Chem.* **45**, 1012 (1967).

[13] B. Fuchs, *Tetrahedron Letters* 3571 (1969).

[14] B. Fuchs, *Ibid.* 1747 (1970).

[15] Y. Auerbach, M. Sprecher and B. Fuchs, *Ibid.* 5207 (1970).

[16] B. Fuchs, Y. Auberbach and M. Specher, *Tetrahedron* **30**, 437 (1974).

[17] N. L. Allinger, M. T. Tribble, M. A. Miller and D. H. Wertz, *J. Am. Chem. Soc.* **93**, 1637 (1971).

[18] D. H. Wertz and N. L. Allinger, *Tetrahedron* **30**, 1579 (1974).

[19] N. L. Allinger and D. Y. Chung, *J. Am. Chem. Soc.* **98**, 6798 (1976).

[20] N. L. Allinger, *Ibid.* **99**, 8127 (1977).

[21] N. L. Allinger, S. H.-M. Chang, D. H. Glaser and H. Hönig, *Israel J. Chem.* **20**, 51 (1980).

[22] T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.* **58** 1569 (1973).

[23] T. A. Halgren, D. A. Kleier, J. H. Hall jr., L. D. Brown and W. N. Lipsomb, *J. Am. Chem. Soc.* **100**, 6595 (1978).

[24] N. L . Allinger, *Adv. Phys. Org. Chem.* **13**, 1 (1976).

[25] O. Ermer, *Structure and Bonding* **27** 161 (1976).

[26] U. Burkert, *J. Comput. Chem.* **1**, 192 (1980).

[27] U. Burkert, *Tetrahedron* **33**, 2237 (1977); **35**, 691, 1945 (1979).

[28] The present calculations are compared with the recently published structure of oxane **4**,[29] which was not available when MM1 originally was parametrized to oxygen compounds.[19]

[29] H. E. Breed, G. Gundersen and R. Seip, *Acta Chem. Scand.* **A33**, 225 (1979).

[30] M. Davis and O. Hassel, *Ibid.* **17**, 1181 (1963).

[31] For definition of ϕ_{av} see C. Romers, C. Altona, H. R. Buys and E. Havinga, *Topics in Stereochemistry* (Edited by E. L. Eliel and N. L. Allinger), Vol. 4, p. 39. Wiley-Interscience, New York (1969).

[32] *Anomeric Effect. Origin and Consequences* (Edited by W. A. Szarek and D. Horton), ACS Symposium Series, Vol. 87, American Chemical Society, Washington, D. C. (1979).

[33] S. Wolfe, W.-H. Whangbo and D. J. Mitchell, *Carbohydr. Res.* **69**, 1 (1979) and Refs therein.

[34] C. Ceccarelli, J. R. Ruble and G. A. Jeffrey, *Acta Cryst.* **B36**, 861 (1980).

[35] G. A. Jeffrey J. A. Pople, J. S. Binkley and S. Vishveshwara, *J. Am. Chem. Soc.* **100**, 373 (1978).

[36] F. S. Jørgensen, University of Copenhagen, Thesis.

[37] F. Chastrette, M. Chastrette, J. C. Duplan and J. P. Delmau, *Tetrahedron* **27**, 5579 (1971).

[38] C. Altona and A. P. M. van der Veek, *Ibid.* **24**, 4377 (1968).

[39] W. L. Jorgensen and L. Salem, *The Organic Chemist's Book of Orbitals*, pp. 42–43. Academic Press, New York (1973).

[40] S. Wolfe, A. Rauk, L. M. Tel and I. G. Csizmadia, *J. Chem. Soc.* B, 136 (1971).

[41] O. Eisenstein, N. T. Anh, Y. Jean, A. Devaquet, J. Cantacuzene and L. Salem, *Tetrahedron* **30**, 1717 (1974).

[42] E. L. Eliel, *Svensk Kem. Tidskr.* **81**, 22 (1969).

[43] S. Wolfe, *Acc. Chem. Res.* **5**, 102 (1972).

[44] T. Koopmans, *Physica* **1**, 104 (1934).

[45] J. W. Rabelais, *Principles of Ultraviolet Photoelectron Spectroscopy* pp. 99–103. Wiley-Interscience, New York (1977).

[46] D. A. Sweigart and D. W. Turner, *J. Am. Chem. Soc.* **94**, 5599 (1972).

[47] T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Japan* **46**, 1558 (1973).

[48] We have used the MM1 fully optimized structure of all the compounds **1**–**5** for the PRDDO MO calculation. See Ref. 49 for a discussion of this procedure.

[49] N. L. Allinger and S. Profeta, jr., *J. Comput. Chem.* **1**, 181 (1980).

[50] For simplicity HOMO, H–1, ... refer to the highest occupied orbital, the next highest occupied and so on.

[51] For an explanation of the symbols, see Table 3, footnote *e*.

[52] D. Gonbeau, M. Loudet and G. Pfister-Guillouzo, *Tetrahedron* **36**, 381 (1980).

[53] R. Gleiter, *Angew. Chem.* **86**, 770 (1974), *Ibid.* Int. Ed. **13**, 696 (1974), R. Hoffmann, *Acc. Chem. Res.* **4**, 1 (1971).

[54] R. Gleiter, M. Kabayashi, N. S. Zefirov and V. A. Palyalin, *Dokl. Akad. Nauk. SSSR* (Chem) **235**, 347 (1977); English translation **235**, 396 (1977).

[55] M. H. Palmer and J. D. Nisbet, *J. Mol. Struct.* **67**, 65 (1980).

[56] M. Kajitani, A. Sugimori, N. Sato, K. Seki, H. Inokuchi and Y. Harda, *Bull. Chem. Soc. Japan* **52**, 2199 (1979).

[57] T. H. Gan, J. B. Peel and G. D. Willet, *Chem. Phys. Lett.* **51**, 464 (1977).

[58] R. S. Brown and R. W. Marcinko, *J. Am. Chem. Soc.* **100**, 5584 (1978).

[59] See Ref. 45, pp. 38–43.

[60] See Ref. 45, pp. 347–350.

[61] E. Heilbronner and A. Schmelzer, *Nouv. J. Chim.* **4**, 23 (1980).

[62] K. O. Nielsen, University of Copenhagen, private communication. The equilibration requires quite vigorous conditions.

[63] P. A. Baron and D. O. Harris, *J. Mol. Spectr.* **49**, 70 (1974).

[64] A. C. Legon, *Chem. Rev.* **80**, 231 (1980) and refs therein.

[65] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*. Academic Press, London (1970).

[66] The 1,8-dioxadecalin system may also be named 2,10-dioxabicyclo[4.4.0]decane or hexahydro–2H, 5H-pyrano[2,3-b]-pyran.

[67] G. Descotes, M. Lissac, J. Delmau and J. Duplan, *C. R. Acad. Sci. Paris*. Ser. C. **267**, 1240 (1968).

[68] Y. Bahurel, M. Lissac-Cahu, G. Descotes, M. Gelin, J. Delmau and J. Duplan, *Bull. Soc. Chim. Fr* 4006 (1970).

[69] The corresponding energy difference for **6** calculated by *ab initio* methods amounts to 5.09 kcal/mol using standard geometries.[35]

[70] U. Faass and H. Hilgert, *Chem. Ber.* **87**, 1343 (1954).

[71] MM1, Quantum Chemical Program Program Exchange Program No. 318 University of Indiana, Bloomington, Indiana.