ANTI,ANTI ACETALS

PHOTOELECTRON SPECTROSCOPY OF *trans*-1,8-DIOXADECALINS

### FLEMMING S. JØRGENSEN and LEIF NØRSKOV-LAURITSEN
Department of General and Organic Chemistry, The H. C. Ørsted Institute,
University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

Summary The *anti,anti* acetals *trans*-1,8-dioxadecalin and *trans*-1,8-dioxa-4,5-dithia-
decalin have been studied by photoelectron spectroscopy, and the electronic structure of the
anti,anti acetal moiety was further elucidated by molecular orbital calculations on di-
methoxymethane and visualized by stereoscopic drawings of the frontier orbitals

The simplest acetal, dimethoxymethane (1) exists in the gas phase in a *gauche,gauche* conforma-
tion,[1] which by theoretical methods has been estimated to be 3-10 kcal/mol more stable than the
anti,anti conformation with its all-*trans* arrangement of the molecular skeleton [2] The preference for
the *gauche,gauche* relative to the *anti,anti* conformation in acetals, the so-called "anomeric effect",[3]
has been attributed to stabilizing $n_O \rightarrow \sigma^*_{CO}$ orbital interactions [4]

Although very few examples of *anti,anti* acetals are known,[5] we consider the *anti,anti* conformation
to be the "normal" one, not only because it is the preferred conformation for acyclic alkanes, but also
because it is the acetal conformation where $n_O \rightarrow \sigma^*_{CO}$ interactions are absent

The conformation about the C-O bonds, and hence the orientation of the oxygen lone pairs, has
been shown strongly to influence the reactivity of acetals, cf the stereochemically controlled reactions
studied by Deslongchamps *et al* [6]

gauche, gauche   1   anti, anti

2

3
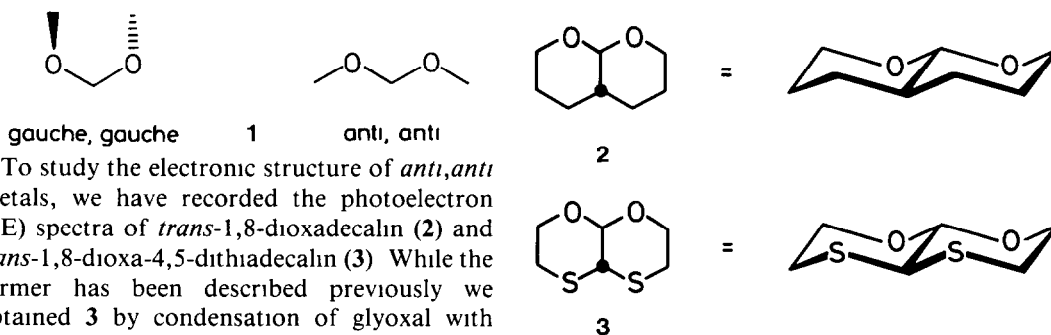
To study the electronic structure of *anti,anti*
acetals, we have recorded the photoelectron
(PE) spectra of *trans*-1,8-dioxadecalin (2) and
trans-1,8-dioxa-4,5-dithiadecalin (3) While the
former has been described previously we
obtained **3** by condensation of glyoxal with
mercaptoethanol [7]

Before turning to these molecules we want to discuss the electronic structure of dimethoxymethane
(1) in the energetically most favourable *gauche,gauche* conformation as well as in the *anti,anti*
conformation, the latter being the one encountered in *trans*-1,8-dioxadecalin (2) and
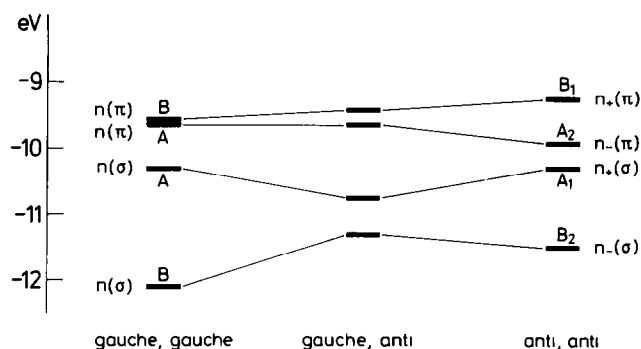*trans*-1,8-dioxa-4,5-dithiadecalin (3)

Fig 1 Molecular orbital correlation diagram for the *gauche,gauche*, *gauche,anti* and *anti,anti* conformations of dimethoxymethane (1) based on PRDDO data

By joint application of PE spectroscopy and nonempirical PRDDO molecular orbital calculations[8] it was found that the frontier orbitals of dimethoxymethane (1) were two closely spaced (ΔIE_{obs} = 0 24 eV) oxygen π type lone pair combinations, followed by an oxygen σ type lone pair combination [9]

Alteration of the conformation about the C-O bonds in 1 from the above-mentioned *gauche,gauche* to *anti,anti* causes an increase in the energy gap between the frontier orbitals according to PRDDO calculations (Figure 1), thus indicating a stronger interaction between the oxygen π type lone pairs in the latter case

We have generated three-dimensional stereoscopic contour drawings[10] of the frontier orbitals of dimethoxymethane (1) in the *anti,anti* conformation (Figure 2), and inspection of these drawings reveals that the HOMO is the in-phase combination of the oxygen 2p lone pairs with a large (18 %) antibonding contribution from the $\pi(CH_2)$ orbital Contrary to this the out-of-phase combination (H-1) contains only a minor antibonding contribution, in this case from the $\pi(CH_3)$ orbitals

It can therefore be concluded that the frontier orbital picture for dimethoxymethane 1 changes from 2 1 (*gauche,gauche*) to 1 1 1 (*anti,anti*), due to "through-bond" coupling[11] via the intervening
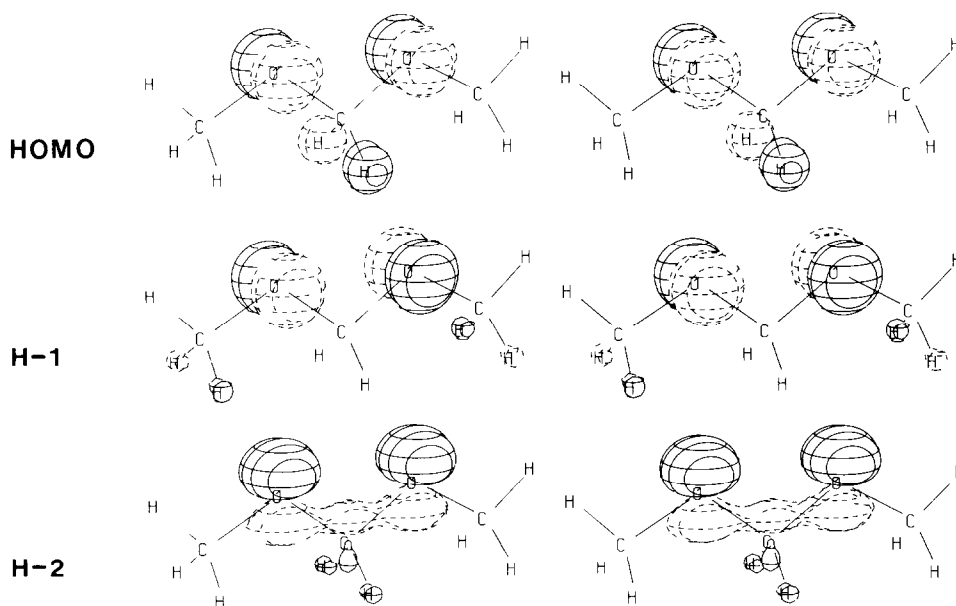

Fig 2 Stereoscopic contour drawings of the frontier orbitals of dimethoxymethane (1) in the *anti,anti* conformation

methylene group, and that the energy gap between the two lowest ionizations from being nearly zero ($\Delta\epsilon_{calc}$ = 0 02 eV) for the *gauche,gauche* conformation increases to a considerable value ($\Delta\epsilon_{calc}$ = 0 69 eV) in the case of the *anti,anti* conformation

In the two *trans*-1,8-dioxadecalins **2** and **3** the acetal moiety has been forced to adopt an *anti,anti* conformation due to the rigid *trans*-decalin framework The PE spectrum of *trans*-1,8-dioxadecalin (**2**) (Figure 3) exhibits two well resolved low-energy ionizations at 9 08 eV and 9 93 eV corresponding to the two oxygen 2p lone pair combinations The difference between these two lowest ionization energies (ΔIE_{obs} = 0 85 eV) is the largest observed for acetals,[12] apparently in good agreement with the PRDDO calculations on dimethoxymethane (**1**) such that the energy gap increases on going from *gauche,gauche* to *anti,anti*

We have previously shown that the C-C bonds (C2-C3, C6-C7 and C9-C10) in the related 1,4,5,8-tetraoxadecalin system are nearly ideally oriented for "through-bond" interactions with the lone pairs in the 1- and 8-positions, and that the PE spectrum of *cis*-1,4,5,8-tetraoxadecalin best can be interpreted by a "through-bond" model [13]

Similarly, the observed energy gap in 1,8-dioxadecalin (**2**) can be explained by destabilization of the in-phase and out-of-phase oxygen 2p lone pair combinations by interactions with lower lying filled σ(C-C) orbitals, the in-phase combination being destabilized more than the out-of-phase combination The band shapes of **2** (cf Figure 3) lend support to this interpretation with the first peak being broad, indicating a considerable contribution of σ type orbitals and the second peak being sharp as is typical for "pure" lone pair ionizations [14]

The interpretation is further confirmed by the PE spectrum of *trans*-1,8-dioxa-4,5-dithiadecalin (**3**) (Figure 3), which contains three low energy bands with the one at lowest energy corresponding to two ionizations This band (maximum at 8 91 eV and a shoulder at 8 62 eV) can be assigned to the two sulfur lone pair combinations [15]

The following two bands at 9 79 eV and 10 44 eV can therefore be assigned to the oxygen 2p lone pair combinations The energy difference between these ionizations (ΔIE_{obs} = 0 65 eV) is smaller than the corresponding difference in **2**, suggesting that the "through-bond" interactions in the 1,8-dioxa-decalin and 1,8-dioxa-4,5-dithiadecalin systems are slightly different [16]

Being the first *anti,anti* acetal studied by PE spectroscopy the *trans*-1,8-dioxadecalin (**2**) shows the same large energy gap between the two oxygen lone pair combinations as calculated for the *anti,anti* form of dimethoxymethane (**1**)

Nevertheless, we would like to stress that the origin of these splits is different the lone pair combinations in **2** being destabilized by interaction with σ(C-C) orbitals and in **1** by interaction with the π(CH$_2$) orbital
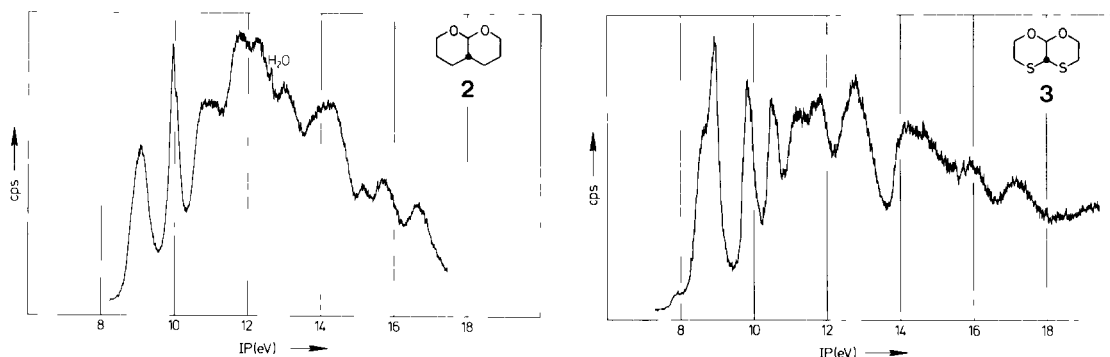

Fig 3 Photoelectron spectra of *trans*-1,8-dioxadecalin (**2**) and *trans*-1,8-dioxa-4,5-dithiadecalin (**3**)

References and Notes

1   E E Astrup, *Acta Chem Scand* **27**, 3271 (1973) Throughout this paper *gauche,gauche* refers to the *gauche(+),gauche(+)* conformation, which is the preferred one for dimethoxymethane and other acyclic acetals The *gauche(+),gauche(-)* and *anti,gauche* conformations have been ignored in the present study

2   G A Jeffrey, J A Pople, J S Binkley and S Vishveshwara, *J Am Chem Soc* **100**, 373 (1978), D G Gorenstein and D Kar, *J Am Chem Soc* **99**, 672 (1977), D G Gorenstein, J B Findlay, B A Luxon and D Kar, *J Am Chem Soc* **99**, 3473 (1977), C van Alsenoy, L Schafer, J N Scarsdale, J O Williams and H J Geise, *J Mol Struct* **86**, 111 (1981)

3   R U Lemieux and S Koto, *Tetrahedron* **30**, 1933 (1974), "Anomeric Effect Origin and Consequences", (Eds W A Szarek and D Horton), *ACS Symposium Series*, **87**, American Chemical Society, Washington D C , 1979

4   S Wolfe, M -H Whangbo and D J Mitchell, *Carbohydr Res* **69**, 1 (1979), S David, O Eisenstein, W J Hehre, L Salem and R Hoffmann, *J Am Chem Soc* **95**, 3806 (1973)

5   Jackson-Meisenheimer complexes R Destro, C M Gramaccioli and M Simonetta, *Acta Cryst* **B24**, 1369 (1968), G G Messmer and G J Palenik, *Acta Cryst* **B27**, 314 (1971), H Ueda, N Sakabe, J Tanaka and A Furusaki, *Bull Chem Soc Jap* **41**, 2866 (1968) Bicyclic systems R Norrestam, K Bock and H Thøgersen, *Acta Cryst* **B37**, 1689 (1981), C -D Zheng, J -Z Qin, Y -X Gu and Q -T Zheng, *Wu Li Hsueh Pao (Acta Physica Sinica)* **30**, 242 (1981) Quinone bisacetals L Nørskov-Lauritsen, S Larsen, M G Ettlinger and J W Jaroszewski, *Acta Cryst* **B38**, 0000 (1982)

6   P Deslongchamps, D D Rowan, N Pothier, T Sauve and J K Saunders, *Can J Chem* **59**, 1105 (1981), P Deslongchamps, *Heterocycles* **7**, 1271 (1977) and references therein

7   *trans*-1,8-Dioxadecalin (2) G Descotes, M Lissac, J Delmau and J Duplan, *C R Acad Sci Paris* **C267**, 1240 (1968) and Y Bahurel, M Lissac-Cahu, G Descotes, M Gelin, J Delmau and J Duplan, *Bull Soc Chim Fr* , 4006 (1970)
    trans-1,8-Dioxa-4,5-dithiadecalin (3) To be published

8   T A Halgren and W N Lipscomb, *J Chem Phys* **58**, 1569 (1973), T A Halgren, D A Kleier, J H Hall Jr , L D Brown and W N Lipscomb, *J Am Chem Soc* **100**, 6595 (1978) The authors would like to express their gratitude towards T A Halgren and J P Snyder for setting up the program in Copenhagen

9   F S Jørgensen, *J Chem Res (S)*, 212 (1981)

10 The contour drawings have been generated by W L Jorgensen's molecular orbital plot program (QCPE no 340) See W L Jorgensen and L Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, 1973

11 R Hoffmann, *Acc Chem Res* **4**, 1 (1971)

12 a D A Sweigart and D W Turner, *J Am Chem Soc* **94**, 5599 (1972)
    b F S Jørgensen, unpublished results

13 F S Jørgensen, L Nørskov-Lauritsen, R B Jensen and G Schroll, *Tetrahedron* **37**, 3671 (1981)

14 See references in ref 13 The band shapes of the *trans*-1,8-dioxadecalin (2) are nearly identical to those of *cis*-1,4,5,8-tetraoxadecalin reported in ref 13

15 See sulfur lone pair ionization energies for 1,4-oxathiane (n_S = 8 67 eV) and 2,4-dithiapentane (n_S = 8 67 and 8 92 eV) in ref 12a and C Guimon, M -F Guimon and G Pfister-Guillouzo, *Tetrahedron Lett* , 1413 (1975), respectively

16 Preliminary MNDO calculations on 3 suggest some mixing of the oxygen and sulfur orbitals, that could account for the discrepancy