227. Cyclic Acetals.
Structural Analysis of 1,3-Dioxepine and Related Compounds

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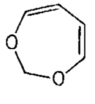
The He(I) PE spectra of 1,3-dioxepine (**1**) and the related bicyclic acetals 1,3,7,7-tetramethyl-2,11-dioxabicyclo[4.4.1]undeca-3,5-dien-10-one (**2**) and 1,3,7,7-tetramethyl-10-methylidene-2,11-dioxabicyclo[4.4.1]undeca-3,5-diene (**3**) have been recorded and analyzed. Interpretation of the PE data indicate strong orbital interactions between the diene and acetal moieties in **1**. Different conformations have been evaluated by a joint MMP2 molecular mechanics and *ab initio* molecular orbital analysis, which shows **1** to prefer a slightly boat-shaped conformation with the diene part being planar and the CH_2 group placed considerably out-of-plane. The bicyclic acetals **2** and **3** show a frontier orbital picture similar to **1** superimposed with the characteristics of the C=O and C=C groups, respectively. The crystal structure of the keto-acetal **2** was determined by an X-ray analysis.

Introduction. – Stereoelectronic effects are important in determining both the molecular structure and the reactivity of organic compounds. Especially for molecules containing two or more heteroatoms with non-bonding electron pairs (lone pairs) the structural behavior is often controlled by conformation-dependent destabilizing four-electron interactions, which can be investigated experimentally by photoelectron (PE) spectroscopy [1] [2]. Likewise for molecules containing lone pairs as well as suitably located antibonding orbitals conformational-dependent stabilizing two-electron interactions are possible and may affect the stability and reactivity of the system [3] [4]. Thus, the preference for the *gauche* arrangement around the C–O bonds in acetals, the so-called 'anomeric effect' [3–6], has been attributed to stabilization of the O lone pair into an antiparallel antibonding C–O orbital ($n_O \rightarrow \sigma^*_{CO}$) [7], and the reactivity of acetals (hydrolysis, ozonolysis *etc.*) has been shown to depend heavily on the conformation around the C–O bonds, the preferred arrangement being the O lone pair antiparallel to the reacting bond [4] [8]. Despite this, the amount of theoretical and experimental work reported on the electronic structure of acetals is rather limited [7–13]. Only few acetals have been studied by PE spectroscopy and nearly all these were simple acetals, which contained no other functional groups [11–13].

In the course of our structural work on acetals [13], we have studied the cyclic, conjugated acetal 1,3-dioxepine (1,3-dioxa-4,6-cycloheptadiene; **1**) [14] together with the two related bicyclic acetals 1,3,7,7-tetramethyl-2,11-dioxabicyclo[4.4.1]undeca-3,5-dien-10-one (**2**) and 1,3,7,7-tetramethyl-10-methylidene-2,11-dioxabicyclo[4.4.1]undeca-3,5-diene (**3**) [15], which besides the dioxepine moiety also contains a C=O group and a C=C bond, respectively. The interpretation of the PE spectra is supported by *ab initio* SCF MO calculations [16]. For **1**, a joint molecular mechanics (MMP2) [17] and MO analysis has been performed.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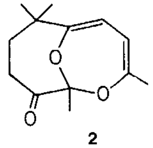
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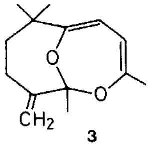
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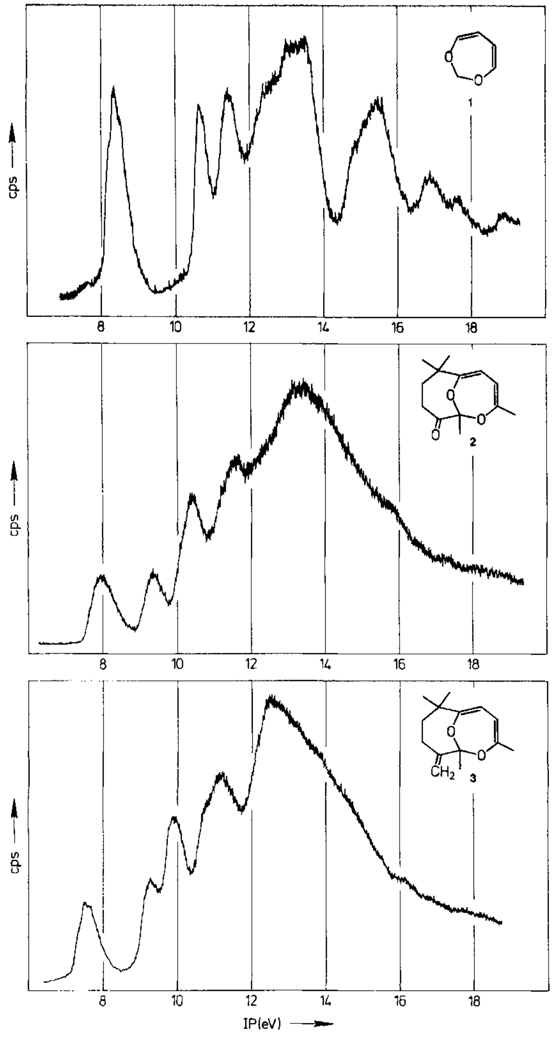

Fig. 1. *PE spectra of* **1**–**3**

1,3-Dioxepine (1). – The PE spectrum of **1** is depicted in *Fig. 1* and exhibits three low-energy peaks, whose intensities after correction for the variation in spectrometer resolution ($I_{corr} = I_{obs}/E_{kin}$) [18] have a ratio close to 1:1:1, indicating each bond to correspond to a single ionization *(cf. Table 1)*.

Table 1. *Vertical Ionization Energies (IE_v) for* **1**–**3**, *Determined by PE Spectroscopy*[a])

Band	**1**		**2**		**3**	
	IE_v	Rel. area[b])	IE_v	Rel. area[b])	IE_v	Rel. area[b])
1	8.33	1.0	7.93	1.0	7.48	1.0
2	10.63	1.0	9.35	0.9	9.27	1.1
3	11.41	1.2	10.35	2.1	9.88	2.2
4	13.0[c])	5.1	11.2 sh 11.49	3.1	10.69 sh 11.17	5.0
5	15.5[c])	4.2				

[a]) Energies in eV; sh = shoulder. [b]) The relative area is the ratio between the corrected intensities = observed intensities/kinetic energies (see the text). [c]) Broad bands, see *Fig. 1*.

The 1,3-dioxepine (**1**) molecule can be regarded as composed of a butadiene and an acetal fragment and its electronic structure can be derived by evaluation of the interactions between the frontier orbitals of these fragments according to the PMO theory [19]. For the planar C_{2v} conformation of **1** the molecular orbital correlation diagram is shown in *Fig. 2*.

The relevant basis orbitals of the diene fragment are the antisymmetric (π_2) and symmetric (π_1) π-type orbitals. Their separation depends heavily on the conformation around the C(2)–C(3) diene bond, but for planar or close-to-planar *cisoid*-dienes the π,π separation is expected to be close to 2.5 eV [1] [20].

The 1,3-dioxa or acetal fragment contributes with an in-phase and an out-of-phase combination of both the O π-type (O_{2p}) lone pairs [$n_+(\pi)$ and $n_-(\pi)$, respectively] and the O σ-type lone pairs [$n_+(\sigma)$ and $n_-(\sigma)$, respectively]. Normally, an in-phase combination is

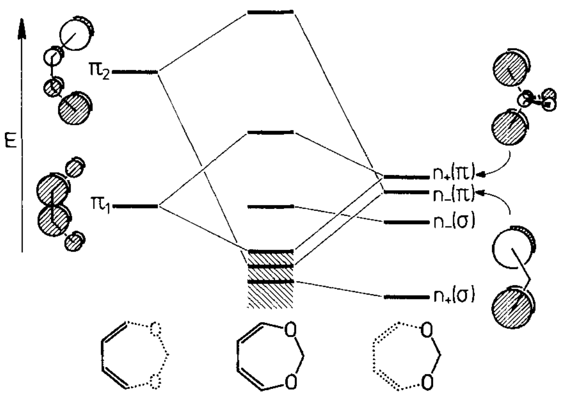

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Fig. 2. *Molecular-orbital interaction diagram for the combination of the diene and acetal moieties in* **1**. The shapes of the π-type orbitals are visualized by circles reflecting the size of the atomic-orbital coefficients.

placed below the out-of-phase combination [21], but in this case the inverted order is more likely for the π-type combinations due to destabilation of the $n_+(\pi)$ combination by interaction with the lower-lying π_{CH_2} orbital [22].

The π_1 and $n_+(\pi)$ orbitals both transform as B_1 and the π_2 and $n_-(\pi)$ orbitals as A_2. The symmetry-allowed interactions may be similar in magnitude, since an interaction is proportional to the overlap between the orbitals (larger coefficients on the terminal diene C-atoms in π_2 than in π_1) and inversely proportional to the difference in basis orbital energies ($B_1 < A_2$). Thus, the highest-occupied orbitals of **1** in the C_{2v} form are the out-of-phase combinations of the π-type orbitals, π_2–$n_-(\pi)$ and π_1–$n_+(\pi)$ followed by a σ-type lone pair, $n_-(\sigma)$.

The search for possible minimum energy conformations of **1** was done using the MMP2 part of *Allinger*'s MM2(82) molecular mechanics program [17] [23] [24], which recently has been reparametrized for acetals [25]. To perform the MMP2 calculations on **1**, one additional torsional parameter for the C_{sp^2}–O–C_{sp^3}–O moiety was needed. This was assumed identical to the value for the C_{sp^2}–O–C_{sp^3}–C_{sp^3} moiety ($V_3 = 0.40$ kcal/mol) [26].

Application of the MMP2 method to **1** yielded only two minima with the C_s conformation placed 10.4 kcal/mol lower in energy than the C_2 conformation. The planar (C_{2v}) form of the molecule is energetically placed above both these conformations and it is not a minimum on the potential surface (*cf. Table 2*).

Table 2. *MMP2 and* ab-initio-*Calculated Energies for* **1**

Conformation		C_s	C_{2v}	C_2
MMP2 Relative energy	[kcal/mol]	0.0	12.3	10.4
ab initio (4-31G)				
Total energy	[au]	–341.976	–341.964	–341.967
Relative energy	[kcal/mol]	0.0	7.2	5.7
Orbital energies[a]	[eV]	– 8.0 (11a″)	– 8.1 (2a$_2$)	– 8.7 (14a)
		–11.5 (15a′)	–10.8 (3b$_1$)	–10.9 (12b)
		–13.3 (10a″)	–13.3 (9b$_2$)	–12.5 (11b)
		–13.5 (14a′)	–13.7 (2b$_1$)	–13.3 (13a)
		–13.9 (13a′)	–13.7 (12a$_1$)	–14.1 (10b)

[a] The symmetries of the MO's are quoted in parenthesis.

The C_s conformation is boat-shaped with the 'stern' (the diene C(5)–C(6) bond) and the 'bow' (the acetal C-atom, C(2)) tilted 18° and 62°, respectively, relative to the main plane of the molecule (C(4)–C(5)–C(6)–C(7), *cf. Fig. 3*). The torsional angles around the O(1)–C(2) and C(2)–O(3) bonds are calculated as ±74°, *i.e.* a *gauche*(+), *gauche*(–) arrangement, which is a relatively favored acetal conformation [3] [22]. The boat shape of the molecule forces the torsional angle around the C(4)–C(5) double bond to be distorted by +22°.

In the C_2 conformation the diene unit is considerably twisted (+33°), the double bond (C(4)–C(5)) is slightly distorted (+12°) and the torsional angle about the O(3)–C(4) bond assumes a value of –76°. The acetal fragment exhibits a somewhat flattened *gauche*(+), *gauche*(+) arrangement with torsional angles on +43° about the O(1)–C(2) and C(2)–O(3) bonds.

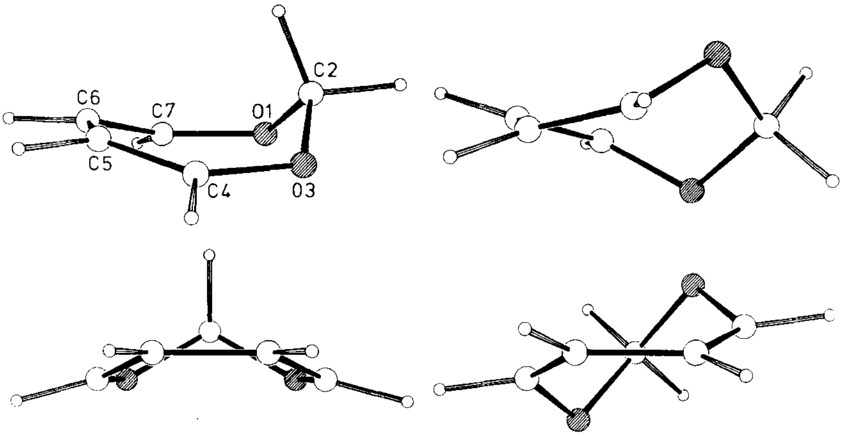
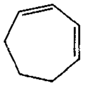


Fig. 3. *Computer-generated drawings of the* C_s (left) *and* C_2 (right) *conformations of* **1**

Using the MMP2-optimized structures of **1** we then performed *ab initio* 4-31G MO calculations [16]. The total energy *(cf. Table 2)* determined for the C_s form, is 5.7 kcal/mol below the energy for the C_2 form, in agreement with the MMP2 results.

For the parent seven-membered ring system, 1,3-cycloheptadiene (**4**), several experimental and theoretical studies with contradictory conclusions have been reported [27], but both electron diffraction [28] and microwave spectroscopy [27] agree on the molecular structure of **4** being a C_s form with only the CH_2 group tilted 73° out-of-plane with the rest of the molecule. Recent MMP2 and *ab initio* studies of **4** find the C_s form to be favoured by 2.07 kcal/mol [29] and 2.5 kcal/mol [30], respectively, relative to the C_2 form.



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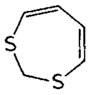

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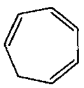

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Boat conformations similar to the C_s conformation of 1,3-dioxepine (**3**) *(cf. Fig. 3)* have also been observed for the sulfur analog 1,3-dithiepine (**5**), which by X-ray crystallography has been shown to adopt a C_s boat conformation with 'stern' and 'bow' values being 3° and 73°, respectively [31]. Other seven-membered ring systems, *e.g.* 1,3,5-cycloheptatriene (**6**) [32], have shown similar behavior.

Finally, the frontier orbital picture obtained from the *ab initio* study confirms the previously discussed PMO considerations. Comparison of the *ab initio* energy levels of the C_s and C_2 forms *(cf. Table 2)* with the PE data does not allow a definite answer concerning the preferred molecular conformation.

Molecular Structure of the Bicyclic Acetals 2 and 3. – Both the bicyclic acetals **2** and **3** are examples of *anti-Bredt* compounds, *i.e.* bridgehead olefins, which often are assumed to be relatively strained [33]. But in the C system being relevant for comparison with **2** and **3**, the bicyclo[4.4.1]undec-1-ene system [34], molecular mechanics calculations estimate the 'olefinic strain' to be close to zero[1]), which means that no extra strain is added by the introduction of the double bond in the 1-position of the bicyclo[4.4.1]undecane framework [35].

To obtain more detailed information about the overall conformation of **2** and **3** as well as distortions caused by the presence of a dioxepine moiety in such a relatively rigid bicyclic framework, we have determined the molecular structure of the keto-acetal **2** by X-ray crystallography.

X-Ray Analysis of 2. – The crystals of **2**, $C_{13}H_{18}O_3$, are orthorhombic, space group $P2_12_12_1$, with cell dimensions $a = 7.872(2)$ Å, $b = 12.015(6)$ Å, $c = 12.250(4)$ Å, $Z = 4$, d(calc) = 1.274 g/cm^3. A total of 4070 reflections were collected at 105 K (*Enraf-Nonius CAD-4*, graphite monochromator, Mo$K\alpha$ radiation, $\omega/2\theta$, $1.0° < \theta < 37.5°$). Data reduction yielded 2510 independent reflections with $I > 2\sigma(I)$. Final refinement gave $R = 0.045$ and $R_w = 0.051$. Further details, tables of atomic coordinates and thermal parameters as well as tables of bond lengths, bond angles and torsional angles have been submitted as *Supplementary Material*.

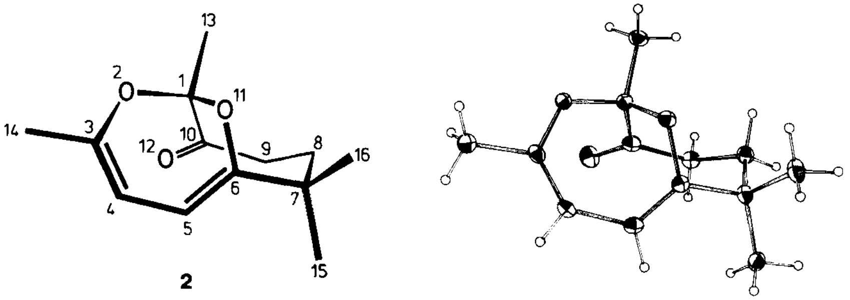

Fig. 4. *ORTEP* [49] *drawing of the molecular structure of* **2**. Thermal ellipsoids are drawn at the 50% probability level and H-atoms represented by spheres.

Examination of the torsional angles and the three-dimensional representation *(Fig. 4)* reveal that in **2** the dioxepine ring is somewhat distorted compared with the boat conformation suggested for **1**. The diene unit is twisted by 21° and the acetal conformations can be considered as being a distorted (+95°, −55°) *gauche*(+), *gauche*(−) conformation. The acetal bond lengths differ by 0.010(2) Å, and the difference is in qualitative agreement with theoretical considerations. A stereoelectronic effect like the 'anomeric effect' involving stabilizing $n_O \rightarrow \sigma^*_{CO}$ interactions has a twofold torsional dependence with a minimum contribution for an orthogonal (90°) arrangement, and deviation from this arrangement increases the $n_O \rightarrow \sigma^*_{CO}$ interactions and the C–O bond is shortened [36]. Accordingly, the C(1)–O(2) bond (1.413(2) Å) associated with a torsional angle of −55° is shorter than the C(1)–O(11) bond (1.423(2) Å) with the torsional angle of +95°.

A search of the *Cambridge Structural Database* (January 1984 version with 40,489 entries [37]) revealed only three molecules containing the 1,3-dioxepine ring system. Two of these were derivatives of cercosporin **7** (**a**: R=R' = $CH_2CH(OH)CH_3$; **b**: R = $CH_2CH(OCOCH_3)CH_3$, R' = $CH_2CH(OCOPh)CH_3$) [38] [39] and the third was an *o,o'*-bridged biphenyl derivative **8** (R = OCH_3, R' = *t*-Bu) [40][2]). Unfortunately, the molecular framework in **7** as well as **8** determines the conformation of the 1,3-dioxepine

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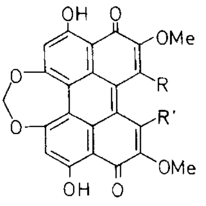
[1]) The 'olefinic strain' for bicyclo[4.4.1]undec-1-ene is in fact negative (−1.5 kcal/mol), which means that it is a so-called 'hyperstable' olefin, *i.e.* an olefin which is less strained than the parent hydrocarbon [35].

[2]) The reference codes for the retrieved structures are: **7a** BERPUJ, **7b** BOBFUT, and **8** TBSHDX [37].



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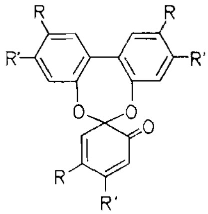

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ring. The perylenequinone part of **7** prefers planarity and heavily restricts the flexibility of the seven-membered ring. Accordingly, the observed conformation of the 1,3-dioxepine ring in **7** is boat-shaped with only the CH$_2$ group placed out of the main plane of the molecule [39]. In case of **8**, the three-atom bridge between the *o,o'*-positions of the biphenyl moiety twists the molecule and forces the seven-membered ring to assume a C_2 conformation [40]. The quality of the data for **7** and **8** does not allow a detailed comparison of bond lenghts and bond angles with our low-temperature structure of the keto-acetal **2**.

The saturated ring of **2** is a relatively flexible seven-membered ring in a distorted boat conformation [41] with the C=O bond and the C=C bond (C(5)–C(6)) arranged nearly parallel. The crystal packing exhibits no intermolecular distances shorter than the sum of the *van der Waals* radii.

Electronic Structure of 2 and 3. – The PE spectrum of **2** *(Fig. 1)* contains four peaks below 12 eV, the latter peak being accompanied by a shoulder on the low-energy side (estimated to 11.2 eV). The ratio between the corrected areas of the four peaks indicates the first two peaks to correspond to a single ionization each and the third and fourth to correspond to two and three ionizations, respectively.

The PE spectrum of **3** *(Fig. 1)* is similar in appearance to the PE spectrum of **2**, as expected for compounds having nearly identical structures, and exhibits four low-energy peaks with a ratio close to 1:1:2:4. In this case a distinct shoulder can be located on the low-energy side of the fourth peak. The PE-spectroscopically-determined ionization energies and the corresponding relative areas for **2** and **3** are collected in *Table 1.*

For acetone, the ionization corresponding to the C=O lone pair ($n_{C=O}$) is found at 9.71 eV [42]. Increasing the molecular framework lowers the lone-pair ionization energy to 9.14 eV in cyclohexanone [43], and for more heavily substituted ketones values of 8.6–8.9 eV have been reported [44] [45]. Contrary to this, introduction of electronegative atoms near the C=O group increases the $n_{C=O}$ ionization energy by inductive stabilization of the lone-pair orbital [19]. Considering **2** as a heavily substituted ketone and associating an inductive shift of 0.2–0.4 eV for each O-atom introduced in a β (allylic) position to the C=O group [46] [47], the ionization at 9.35 eV can be assigned to the C=O lone pair ($n_{C=O}$).

Similar arguments can be applied to exocyclic CH$_2$ compounds, here the $\pi_{C=CH_2}$ ionization is found at 9.13 eV in methylenecyclohexane [48] and as low as 8.86 eV in heavily substituted derivatives [45] [47] [48]. This enables us to assign the 9.27 eV ionization of **3** to the $\pi_{C=CH_2}$ orbital.

Having assigned the $n_{C=O}$ and $\pi_{C=CH_2}$ ionizations in **2** and **3**, respectively, we can correlate the remaining ionizations of **2** and **3** as shown in *Fig. 5*.

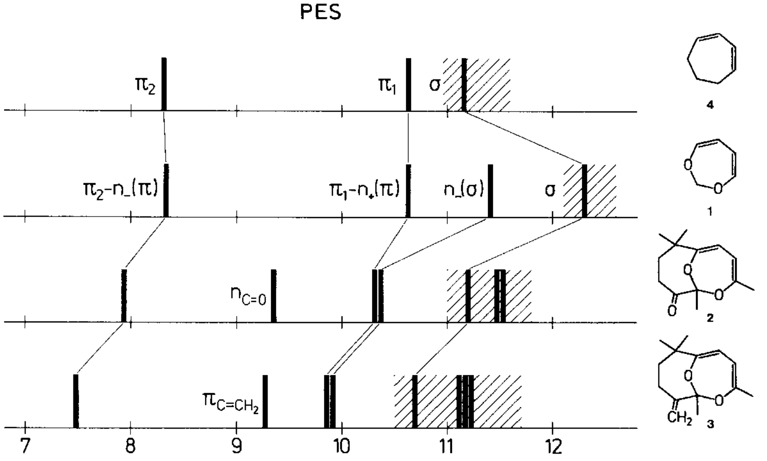

Fig. 5. *Correlation diagram for 1,3-cycloheptadiene* (**4**) [50], *1,3-dioxepine* (**1**) *and the bicyclic acetals* **2** *and* **3** *based on observed ionization energies*

From *Fig. 5* it can be concluded that for both **2** and **3**, the lowest ionization energy corresponds to ionization from the out-of-phase combination of the 'antisymmetric' diene π orbital and the 'antisymmetric' acetal lone pair combination[3]), *i.e.* the π_2–$n_-(\pi)$ orbital in **1**.

The second ionization energy has already been assigned to $n_{C=O}$ orbital in **2** and the $\pi_{C=CH_2}$ orbital in **3**, respectively, and the third ionization energy corresponds to the two degenerate orbitals, the out-of-phase combination of the 'symmetric' basis orbitals (π_1 and $n_+(\pi)$) and a combination of the σ-type O lone pairs resembling the $n_-(\sigma)$ orbital of **1**.

Fig. 5 also shows that the extension of the molecular framework (**1**→**2**) effects the σ-type orbitals three times as much as the π-type orbitals ($\Delta\sigma \approx 1.1$ eV and $\Delta\pi \approx 0.35$ eV) suggesting the destabilization to be caused by a hyperconjugative mechanism. On the contrary the shifts for the transformation **3**→**2** are nearly identical for both types of orbitals ($\Delta\sigma \approx \Delta\pi \approx -0.5$ eV) suggesting a purely inductive mechanism.

In conclusion, the electronic structure of the bicyclic acetals **2** and **3** resembles that of 1,3-dioxepine (**1**) superimposed with the characteristics of the C=O and C=C groups, respectively, although the dioxepine parts of **2** and **3** are somewhat distorted relative to the C_s boat conformation found for **1**.

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Experimental. – The compounds were prepared as described in [14] [15]. Purities were checked by ^{1}H- and ^{13}C-NMR spectroscopy (**1**, **2**, and **3**) and GC (**1**) before recording the PE spectra. The PE spectra were recorded on a *PS-18* spectrometer *(Perkin-Elmer)* at Department of General and Organic Chemistry, University of Copenhagen with a He(I) source and calibrated with a mixture of Ar and Xe introduced into the target chamber simultaneously with the sample. The recording temp. for **1**–**3** were r.t. (gas inlet), 40–42° and 28° (heated inlet), resp. The exper. resolution was 30 meV and the reported ionization energies are averages of four determinations.

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[3]) The classifications 'symmetric' and 'antisymmetric' have been maintained to illustrate the resemblance of the orbitals of **2** and **3** with the orbitals of the parent compound **1**.

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