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CONFORMATIONAL ANALYSIS OF α-METHOXYKETONES. A PHOTOELECTRON SPECTROSCOPIC INVESTIGATION OF 3-METHOXYBICYCLO[2.2.1]HEPTAN-2-ONES.

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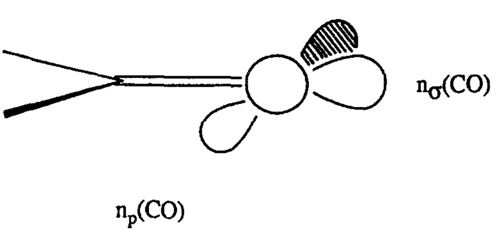
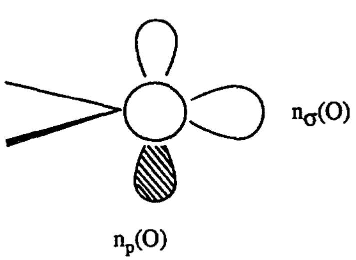
Summary: *The photoelectron spectra of 3-*endo*-(2), of 3-*exo*-methoxybicyclo[2.2.1]heptan-2-one (3) and of 2-*endo*,3-*endo*-dimethoxybicyclo[2.2.1]heptane (4) are analyzed in comparison with data reported for other analogous systems and with predictions based on quantum mechanical calculations. In 2, the "homo-gauche" conformer (2G) is more stable than the "homo-anti" conformer (2A) whereas in 3, the "homo-anti" conformer (3A) is slightly more stable than the corresponding "homo-gauche" rotamer (3G).*

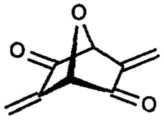
The spectroscopic and chemical properties of a polyfunctional molecule are more than the juxtaposition of the properties of each individual function because of the possibility of through-space and through-bond interactions.[1] Significant through-bond interactions involving the non-bonding electron pairs $n_p(CO)$ and $n_\sigma(CO)$ have been evidenced in the photoelectron (PE) spectra of 1,2-,[2] 1,3-,[3] 1,4-[4] and 1,5-diketones.[5,6] Through-bond interactions between n(O), n(N), and n(S) electron pairs in 1,4-dioxane[7] and crown-ethers,[8] in piperazine, and in 1,4-dithiane, respectively, have also been discussed.[9] Through-bond interactions of type n(N:), σ ↔ p(CO) and n(N:), σ → p(CO) have been evidenced in 3-ketopiperidines[10]





[#] Present address: Ecole Supérieure de Physique et de Chimie Industrielles, 10, rue Vauquelin, Paris 5, France and of type n(O), $\sigma \leftrightarrow$ p have been discussed in relation with the PE spectra of allylic ethers.[11] Recently, Röser et al.[12] have demonstrated the existence of sizeable interactions between the lone-pair orbitals of 3,6-dimethylidene-7-oxabicyclo[2.2.1]heptane-2,5-dione (**1**) by PE spectroscopy. Ab initio quantum calculations indicated that "through-bond" interaction dominate the picture.

We report here the PE spectra of 3-*endo*- (**2**) and of 3-*exo*-methoxybicyclo[2.2.1]heptan-2-ones (**3**) together with that of 2-*endo*,3-*exo*-dimethoxybicyclo[2.2.1]heptane (**4**) (Fig. 1). Evidences for the existence of through-bond interactions involving the n_p(CO) and n_p(O) electron pairs will be presented. The extent of these interactions depends on the conformation of the methoxy group.



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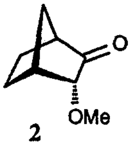

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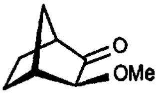

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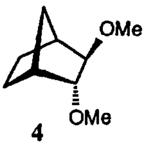

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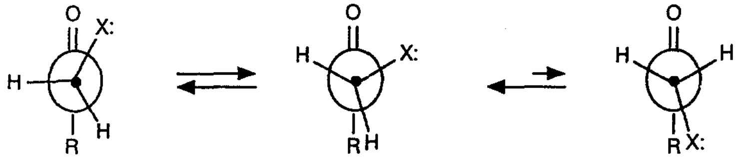
RESULTS AND SPECTRAL INTERPRETATION

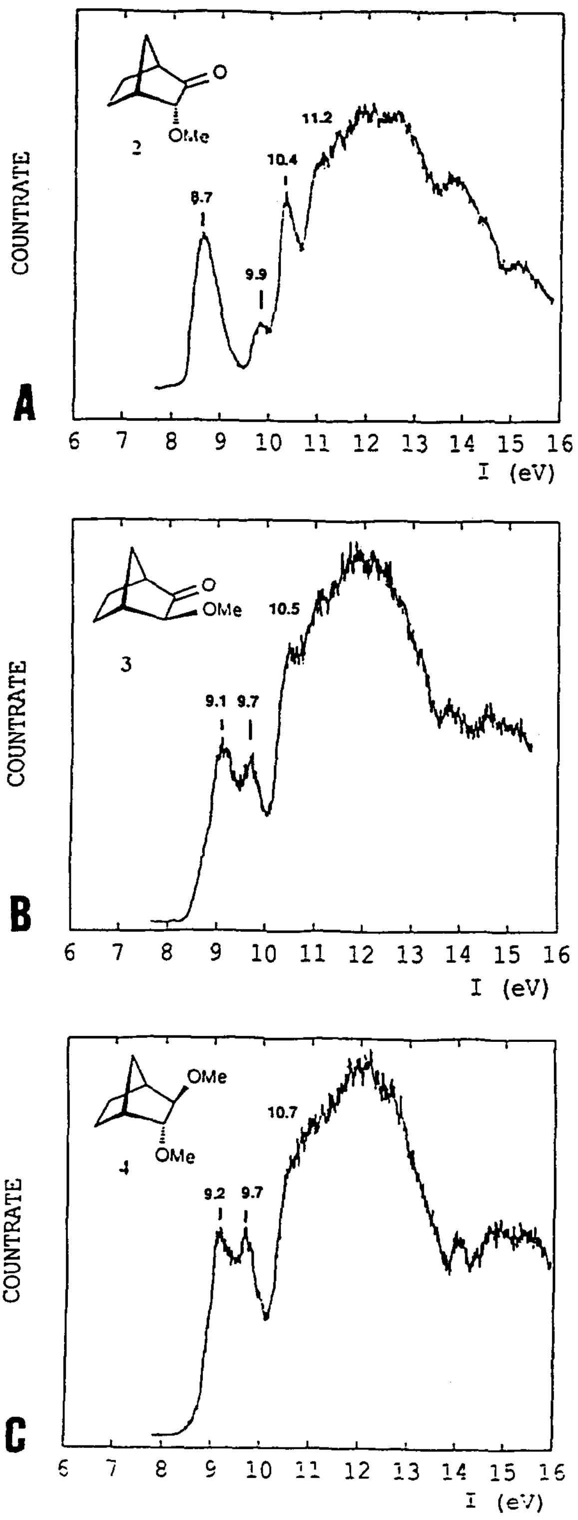
The PE spectra of the α-methoxyketones **2** and **3**, and of the diether **4** are reproduced in Figure 1. In the absence of ancillary experimental information such as vibrational fine structure, we rely on comparison of the observed band positions I^m_j (= position of band maximum) with those reported for analogous compounds (see Table 1) and by correlation with the computed AM1 and ab initio STO-3G orbital energies ϵ_j (cf. Table 2), assuming that $I^m_j \approx I^v_j$ (= vertical ionization energy) and validity of the Koopmans' theorem[13]($I^v_j = a + b(-\epsilon_j)$).

Because of the rotation about the C-OMe bond, the population of the possible conformers needs to be evaluated. Effect of conformation on the spectral properties of molecules, including on the PE spectra, has been widely documented.[14,15] In the case of α-substituted carbonyl compounds of type $RCOCH_2X$ (X=Cl, Br, I, O, S), several studies attest of the importance of through-bond and through-space interactions between the n(X:) and n(CO) electron pairs, the latter mode being more important in the *syn* (**5**) than in the corresponding *gauche* (**6**) or *anti* conformers (**7**).[16]



5 (*syn*) **6** (*gauche*) **7** (*anti*)

The first ionization energies of bicyclo[2.2.1]heptan-2-one (**8**)[17] and of 2-*endo*-methoxybicyclo-[2.2.1]heptane (**13**)[20] are nearly the same. To a first approximation they can be attributed to the n_p(CO) and n_p(O) non bonding electrons, respectively. The juxtaposition of both the methoxy and carbonyl groups as in


A
COUNTRATE
O
OMe
2
8.7
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10.4
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6 7 8 9 10 11 12 13 14 15 16
I (eV)
B
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O
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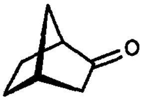
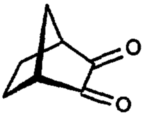
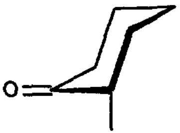
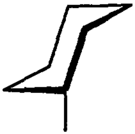
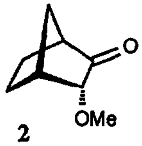
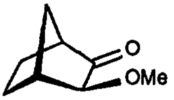
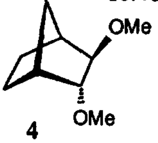
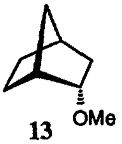
3
9.1
9.7
10.5
6 7 8 9 10 11 12 13 14 15 16
I (eV)
C
COUNTRATE
OMe
OMe
4
9.2
9.7
10.7
6 7 8 9 10 11 12 13 14 15 16
I (eV)

Figure 1.

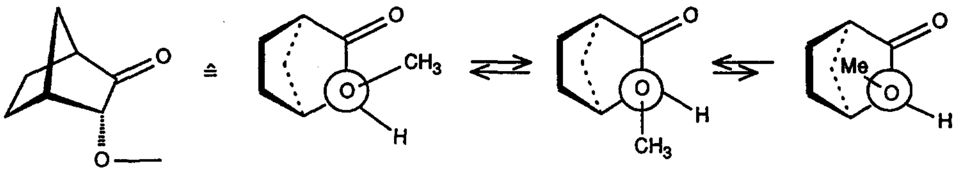
Table 1. Comparison of experimental ionization energies (I_j^m, eV) of α-methoxyketones **2**, **3** and **11**, of monoketones **8** and **10**, of diketone **9** and of methyl ethers **4**, **12** and **13**.

				
8 I_j^m: 9.15[17]	**9** 9.0[18] 10.5	**10** 9.4[18]	**11** 9.06[19] 10.46	**12** 9.22[20]
				
2 I_j^m: 8.7[a)] [9.9][b)] 10.4 11.2	**3** 9.1[a)] [8.8][b)] 9.7 10.4	**4** 9.2 9.7 10.7		**13** 9.17[20]

a) major conformer; b) minor conformer

2 and **3** leads to an inductive effect[21] on the average ionization energy which amounts to ca. 0.5 eV as evaluated by comparing the PE data of α-methoxycyclohexanone (**11**) with those of cyclohexanone (**10**) and methoxycyclohexane (**12**) ($[I_1^m(11) + I_2^m(11)]/2 - [I_1^m(10) + I_1^m(12)]/2$; see Table 1). This inductive effect is nearly the same as that introduced by the juxtaposition of two carbonyl groups, in a system like the bicyclo-[2.2.1]hepta-2,3-dione (**9**; $[I_1^m(9) + I_2^m(9)]/2 - [I_1^m(8)] = 0.6$ eV). One thus expects for the α-methoxyketones **2** and **3** an average ionization energy of ca. 9.65 eV due to the ejection of one electron from the MeO-C-C=O moiety. The PE spectrum of **2** (Fig. 1A) displays a first band centered at 8.7 eV whose area is more or less the sum of the area of the two following bands centered at 9.9 and 10.4 eV. This suggests that the PE spectrum of **2** is in fact the superposition of two PE spectra of two different conformers, the major one with $I^m_1 = 8.7$ eV and $I^m_2 = 10.4$ eV, and an average $(I^m_1 + I^m_2)/2 = 9.55$ eV that fits with our expectation, and the minor one with $I_2^m = 9.0 \pm 0.2$ eV and $I_2^m = 9.9$ eV (average $(I_1^m + I_2^m)/2 = 9.45 \pm 0.1$ eV) in a ratio of ca. 4:1.

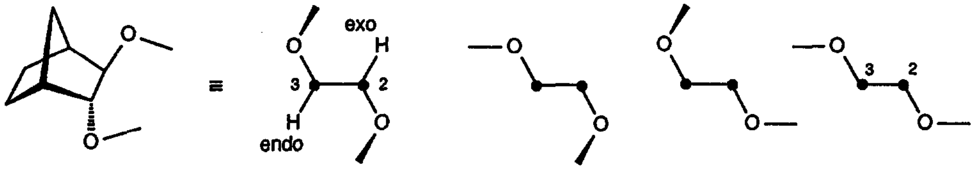
The relatively large energy difference $I_1^m - I_2^m = 1.7$ eV and the comparatively small difference of 0.9 ± 0.2 eV observed for the major and minor conformers, respectively, suggest a larger through-bond interaction between the $n_p(O)$ and $n_p(CO)$ non-bonding electron pairs in the former than in the latter conformer. The lower energy bands (I^m_1) correspond to $[n_p(CO) - n_p(O)]\sigma$ combination whereas the higher energy bands (I_2^m) are associated with $[n_p(CO) + n_p(O)]\sigma$ combinations of localized orbitals. In the major conformer the energy split of 1.7 eV is quite analogous to that found in the PE spectra of methoxyketone **11** (1.4 eV) and α-diketone **9** (1.5 eV). On that basis one can propose that the "homo-gauche" conformer **2G** is favoured over the "homo-anti" conformer **2A** (the designations "homo-gauche" and "homo-anti" are used here to distinguish this type of relationship with the *gauche* and *anti* designations used for conformers of type **6** and **7**, see also the conformers of **4**; the oxygen atom of the MeO group in **2** and **3** are *gauche* with respect to the carbonyl oxygen atoms). For an efficient through-bond interaction, the $n_p(O)$ orbital must overlap with the σC(2),C(3) bond; this overlap is expected to be better for **2G** than for **2A**. Conformer **2G'** in which the methyl group points toward the ethano bridge of the bicyclic skeleton is not envisioned here for reasons of steric hindrance (see our calculations here-below).



2G **2A** **2G'**

The PE spectrum of **3** (Fig. 1B) can be analyzed in a similar fashion as that of **2**. In that case, the major conformer is associated with the two bands centered at I_1^m = 9.1 and I_2^m = 9.7 eV, with an averaged ionization energy of 9.4 eV which is not too far apart from our expected value of 9.65 eV (see above). The intensity of the first band (I_1^m = 9.1 eV) is greater than that of the second band (I_2^m = 9.7 eV), indicating the superposition of two bands (between 8.2 and 9.3 eV) arising from two conformers of **3**. To the band centered at I_2^m = 10.5 eV might correspond a band between 8.5 and 9.0 eV, giving an averaged ionization energy of 9.5 - 9.7 eV, in perfect agreement with our expectations. Applying the same arguments as for the conformers **2A** and **2G**, we propose for **3** that the major conformer **3A** ("homo-anti") is slightly more stable than **3G** ("homo-gauche") in the gas phase. This situation is reverse to that observed for **2**! The reasons for that difference are not obvious and are not explained by our semi-empiral AM1 calculations (see below).[22]

Since two conformers exist in comparable amounts at equilibrium for **2** and **3**, at least four conformers[23] of similar stabilities are thus expected for 2-*endo*,3-*exo*-dimethoxybicyclo[2.2.1]heptane (**4**). This renders the interpretation of the PE spectrum of **4** (Fig. 1C) difficult. The maxima I_1^m = 9.2 and I_2^m = 9.7 eV might correspond to the superposition of several bands due to different rotamers. Nevertheless, if one considers an inductive effect of ca. 0.5 eV associated with the juxtaposition of two MeO groups, an average ionization energy of 9.7 eV (I_1^m (**13**) = 9.17, Table 1) is expected for I_1^m and I_2^m associated with each conformers **4gg**, **4ga**, **4ag** and **4aa** (Fig. 2). Therefore, the band at 9.2 eV (Fig. 1C) must be associated with a second band near 10.2 eV which may correspond to the shoulder visible at 10.1 eV. In that conformer, an energy difference I_2^m -I_1^m = 0.9 eV implies a significant through-bond interaction between the $n_p(O)$ electron pairs of the diether. Indeed, for 1,4-dioxane in which two σ(C,C) bond can interact favourably with the two $n_p(O)$ orbitals, a difference I_2^m -I_1^m = 1.2 eV was found.[21] One can thus propose that the gauche,gauche conformer **4gg** for which relatively good overlap can exist between the $n_p(O)_+$ combination and the σC(2),C(3) band is present in the equilibrium. Smaller through-bond interactions are expected for the other conformers of **4** whose ionization energies must be found between 9.2 and 10.0 eV (see Fig. 1C). These



4gg **4ga** **4ag** **4aa**

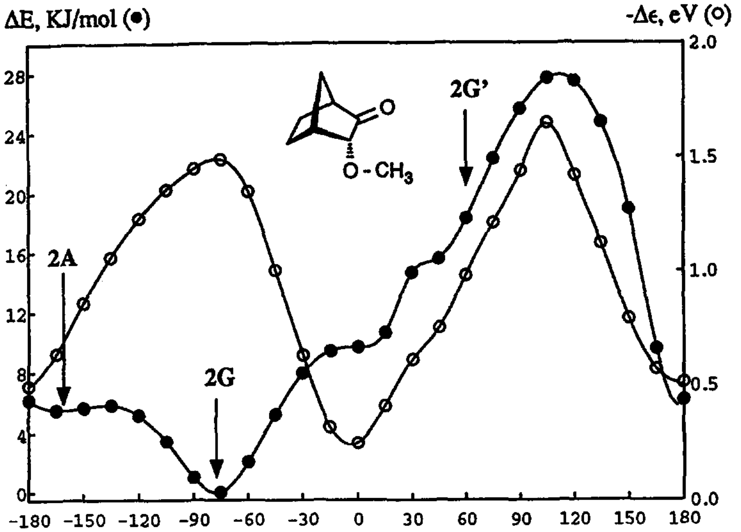
Fig. 2. Representation of four possible conformers of diether **4** (a refers to anti, g to gauche; e.g. **4ag** corresponds to 2-*endo*-MeO group is gauche and 3-*exo*-MeO group is anti).

interpretations are supported by our AM1 calculations, see Table 2.

Quantum mechanical calculations

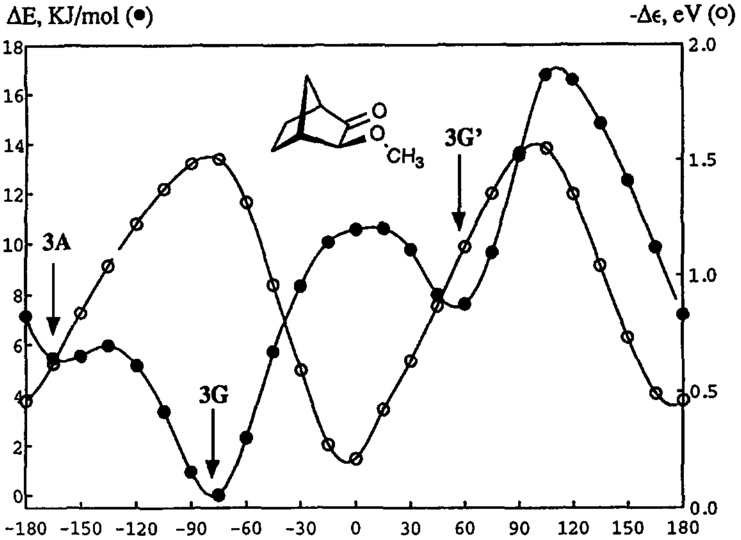
Because of the size of the molecules involved, only semi-empiral methods could be used to explore the rotation around the C-OMe bond of the conformers of **2**, **3** and **4**. We have thus applied the AM1 technique[24] to these systems. The new parametrization PM3[25] proposed by Stewart is better than AM1 for the calculation of heat of formation of organic compounds but we have found that for the calculation of rotation barrier, AM1 remains better.[26] Our results, reported in Fig. 3 and Table 2, predict for **2** that the "homo-gauche" conformer **2G** is more stable than the "homo-anti" conformer **2A** ($\Delta H_f \cong 5$ KJ/mol, in agreement with a conformer ratio of 4:1 as deduced from the PE data). In the case of **3** (Fig. 4), the "homo-gauche" conformer **3G** is also predicted to be more stable than **3A**, in contradiction to our PE data. The calculations show that the energy difference between the HOMO and subHOMO orbitals of the α-methoxyketones **2** and **3** reaches a maximum (ca. 1.5 eV) for **2G** and **3G** and a much smaller value (0.6 - 0.7 eV) for **2A** and **3A**, thus confirming our PE data interpretations. All minima were characterized by no negative eigenvalue for the Hessian matrix. It should be noted that the methyl part of the methoxy remains in the same orientation relative to the C-OMe bond during the rotation. Complete ab initio geometry optimization with the STO-3G[27] and 3-21G[28] basis sets have been performed on the AM1 optimized geometries of the minima **2A**, **2G**, **3A**, **3G** and **3G'**. The HOMO-subHOMO energy differences so-obtained (Table 3) show the same trend as for the AM1 results.

For reasons of comparison, we have also carried out AM1 calculations on α-methoxycyclohexanone (**11**). We find (Fig. 5,6) that the most stable conformers **11G** ($\Delta H_f = -416.7$ kJ/mol) and **11G'** ($\Delta H_f = -416.0$ kJ/mol) adopt the equatorial position for the ethereal oxygen atom and "homo-gauche" conformation for the methyl group. Relatively large energy differences ϵ(HOMO) - ϵ(subHOMO) = 1.17 and 1.47 eV are calculated (Fig. 5) for **11G** and **11G'**, respectively in agreement with the PE data[19] (Table 1).



Torsion Angle C(2)-C(3)-O-C

Fig. 3. ΔE=relative energie and $-\Delta\epsilon = \epsilon_{HOMO}-\epsilon_{subHOMO}$ of 3-*endo*-methoxybicyclo-[2.2.1]heptane-2-one (2) as functions of the rotation of the MeO group as given by AM1 calculations (with complete geometry optimization).



Torsion Angle C(2)-C(3)-O-C

Fig. 4. ΔE=relative energie and $-\Delta\epsilon = \epsilon_{HOMO}-\epsilon_{subHOMO}$ of 3-*exo*-methoxybicyclo-[2.2.1]heptane-2-one (3) as functions of the rotation of the MeO group as given by AM1 calculations (with complete geometry optimization).

Table 2. HOMO and subHOMO energies (ϵ, eV) of the most stable conformers of the α-methoxyketones **2**, **3** and **11**, of the diether **4**.

	AM1[a]				STO 3G//AM1[b]		
	ΔH_f(KJ/mol)	ϵ_{HOMO}	$\epsilon_{subHOMO}$	$\Delta\epsilon$	ϵ_{HOMO}	$\epsilon_{subHOMO}$	$\Delta\epsilon$
2G	-314.6	-9.83	-11.31	1.48	-7.72	-9.84	2.12
2A	-309.1	-10.10	-10.77	0.67	-8.11	-9.06	0.95
3G	-316.9	-9.87	-11.39	1.52	-7.77	-9.87	2.10
3A	-315.7	-10.11	-10.80	0.69	-8.11	-9.11	1.00
4gg[c]	-382.1	-10.03	-10.98	0.95	-8.14	-9.53	1.39
4ga	-384.1	-10.16	-10.58	0.42	-8.26	-9.03	0.77
4ag	-384.1	-10.26	-10.49	0.23	-8.37	-8.97	0.60
4aa	-382.5	-10.24	-10.39	0.15	-8.37	-9.78	0.41
11G	-416.6	-9.94	-11.11	1.17	-7.94	-9.32	1.38
11G'	-416.0	-9.91	-11.37	1.46	-7.95	-9.76	1.81
11A	-409.6	-10.16	-10.80	0.74	-8.31	-9.01	0.70

a) With complete geometry optimization

b) Single point calculation on AM1 optimized geometry

c) g refers to gauche comformation and a to anti, see Fig. 5

Table 3. Ab initio calculations of the most stable conformers of α-methoxy ketones **2** and **3**. Orbitals energies are given in eV.

	STO-3G				3-21 G			
	E_{tot} [hartrees]	ϵ_{HOMO}	$\epsilon_{Sub\text{-}HOMO}$	$\Delta\epsilon$	E_{tot} [hartrees]	ϵ_{HOMO}	$\epsilon_{Sub\text{-}HOMO}$	$\Delta\epsilon$
2G	-453.95804	-7.78	-9.98	2.20	-457.09131	-9.89	-12.02	2.13
2G'	-453.95050	-7.87	-9.53	1.66	-457.08683	-10.02	-11.33	1.31
2A	-453.95626	-8.11	-9.21	1.10	-457.08702	-10.13	-11.25	1.13
3G	-453.95826	-7.72	-9.97	2.25	-457.09233	-9.82	-11.86	2.04
3A	-453.95712	-8.11	-9.17	1.06	-457.08814	-10.12	-11.19	1.07

Recent high-level ab initio calculations on methoxyacetic acid[29,30a] and methoxyacetate anion[30a] suggested that the most stable conformers SG of the system (XCH_2OMe, X = COOH, COO^-) have a torsion angle O-C(1)-C(2)-O near 0° (*syn* conformation) and a torsion angle C(1)-C(2)-O-C near 60° (homo-gauche conformation). They equilibrate with slightly less stable conformers SA that have a torsion angle C(1)-C(2)-O-C near 180°. The greater stability of the SG vs. SA conformers for X = COOH and COO^- were attributed[30a] to an anomeric effect of these functions with the methoxy group (eq. (1) and (2)). We prefer to call it "homo-gauche" effect, by analogy with the well-documented "gauche effect" in 1,2-dimethoxyethane and related systems.[31] Altona and co-workers[30a] calculated for the methoxymethylammonium ion a reversed anomeric effect of about 6 KJ/mol (eq. (3)). These calculations indicate to us that the "homo-gauche" effect of the methoxy group in **2**, **11**, in methoxyacetic acid and its conjugate anion (eq. (1),

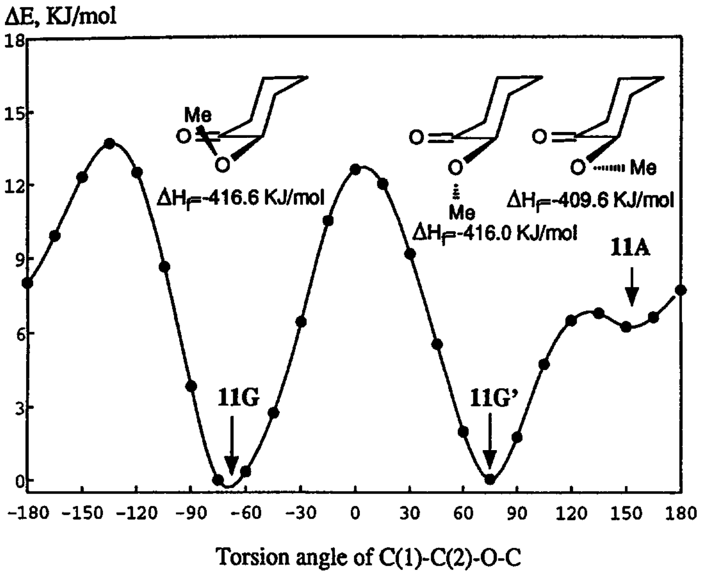


Fig. 5. ΔE = relative energie of equatorial 2-methoxycyclohexanone as function of the methoxy group rotation as given by AM1 calculations (with complete geometry minimization).

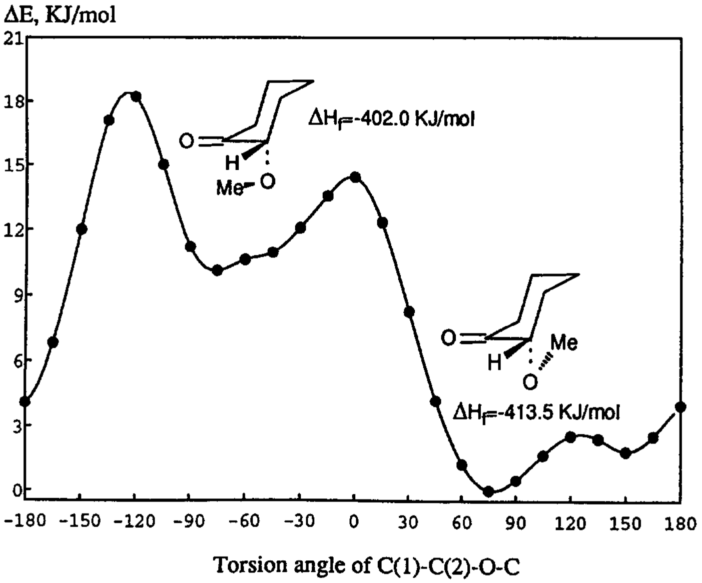
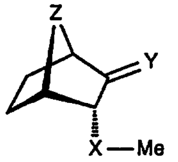
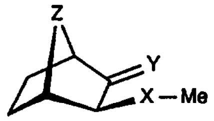


Fig. 6. ΔE = relative energie of axial-2-methoxycyclohexanone as function of the methoxy group rotation as given by AM1 calculations (with complete geometry minimization).

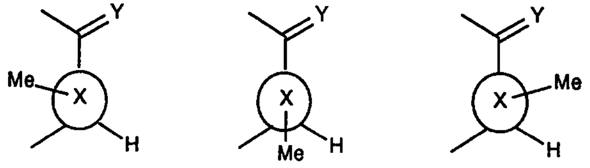
Table 4. AM1 calculated enthalpies (ΔH_f, KJ/mol) of the rotamers of bicyclo[2.2.1]heptane derivatives **13** - **26** (completely optimized geometries).



14 X=O; Y=O; Z=O
16 X=CH_2; Y=O; Z=O
18 X=O; Y=H,H; Z=O
20 X=CH_2; Y=H,H; Z=O
22 X=CH_2; Y=O; Z=CH_2
13 X=O; Y=H,H; Z=CH_2
25 X=CH_2; Y=H,H; Z=CH_2



15 X=O; Y=O; Z=O
17 X=CH_2; Y=O; Z=O
19 X=O; Y=H,H; Z=O
21 X=CH_2; Y=H,H; Z=O
23 X=CH_2; Y=O; Z=CH_2
24 X=O; Y=H,H; Z=CH_2
26 X=CH_2; Y=H,H; Z=CH_2

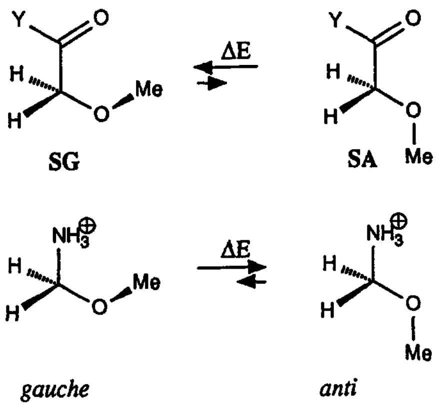


endo-MeX	*exo*-MeX	G'	A	G
14		-	-414.1	-420.4[b]
	15	$\boxed{-421.2}$[a]	-412.8	-418.7[b]
16		-	-309.0	-310.2
	17	-308.1	-314.4	-313.6
18		-	-332.9	-332.9
	19	$\boxed{-337.9}$[a]	-333.3	-333.7
20		-	-216.9	-216.9
	21	-214.8	-221.9	-221.5
22		-	-203.1	-204.7
	23	-199.7	-208.5	-208.1
13		-	-220.6	-219.4
	24	-	-224.0	-223.6
25		-	-101.7	-103.4
	26	-98.8	-107.2	-107.2

[a] most stable conformer G' showing the electrostatic stabilization between *exo*-MeO and O(7)

[b] values confirming the existence of a stabilizing electrostatic interaction between the MeO and carbonyl groups in these "homo-gauche"conformers.

(2)) might be due to electrostatic interactions between the carbonyl group oxygen center and the C-H moieties of the MeO group.[32] This hypothesis is supported by the finding of the reversed anomeric effect for eq. (3) and by our AM1 calculations on the conformation of 3-*endo*-methoxy-7-oxabicyclo[2.2.1]-heptan-2-one (**14**) and its 3-*exo* isomer **15** (Table 4). Contrary to the bicyclo[2.2.1]heptanones **2** and **3**,



eq. (1) Y=OH $\Delta E \cong$ -6 KJ/mol[30a]
eq. (2) $Y=O^{\ominus}$ $\Delta E \cong$ -13 KJ/mol

eq. (3) $\Delta E \cong$ +6 KJ/mol[30a]

whose "homo-gauche" conformers **2G'** and **3G'** were the least stable rotamers (MeO group oriented toward the ethano and methano bridge, respectively), the "homo-gauche" conformer **15G'** in which the MeO group is close to the ethereal bridge is the most stable rotamer. In the case of the *endo* isomer **14**, the conformer **14G** remains the most stable species. As a control for the importance of our electrostatic interaction hypothesis, we have examined the relative stabilities of rotamers of 3-*endo*- (**16**) and 3-*exo*-ethyl-7-oxabicyclo[2.2.1]heptane (**17**) and have found for these systems that the "homo-anti" (A) and "homo-gauche" rotamers (G) in which the methyl group points away from the ethano or methano bridges have the same stability (Table 4). The calculated enthalpies for the conformers of **19** also confirmed the possible electrostatic stabilization between the *exo*-MeO group and the O(7) ethereal bridge in the **19G'** conformer. In the case of 3-*exo*-ethyl-7-oxabicyclo[2.2.1]heptane (**21**), 3-*exo*-ethylbicyclo[2.2.1]heptan-2-one (**23**), 3-*exo*-methoxybicyclo[2.2.1]heptane (**24**) and 3-*exo*-ethylbicyclo[2.2.1]heptane (**26**) the corresponding "homo-gauche" conformers **21G'**, **23G'**, **24G'** and **26G'**, respectively, were calculated to be definitively less stable than the other possible conformers. Contrary to 3-*endo*- (**2**) and 3-*exo*-methoxybicyclo[2.2.1]-heptan-2-one (**3**) for which the "homo-gauche" conformers were calculated to be more stable than the corresponding "homo-anti" conformers, the AM1 calculated enthalpies for the 3-*endo* substituted derivatives **13**, **16**, **18**, **20**, **22** and **25** (Table 4) suggested no stability preference for the corresponding "homo-gauche" and "homo-anti" conformers in these systems, again confirming the existence of a stabilizing electrostatic interaction between the MeO and the carbonyl groups in the "homo-gauche" conformers of **2**, **3**, **11** and **14**. Our calculations also suggest that the gauche, gauche conformer **4gg** of 2-*endo*, 3-*exo*-dimethoxybicyclo-[2.2.1]heptane (**4**) benefits from a possible stabilizing interaction between the methyl moiety of one methoxy group and the oxygen atom of the other.

CONCLUSION

In agreement with AM1 calculations, the PE spectrum of 3-*endo*-methoxybicyclo[2.2.1]heptan-2-one (**2**) shows that the "homo-gauche" conformer **2G** is more stable than the "homo-anti" rotamer **2A**. This "homo-gauche" effect of the α-methoxyketone moiety (or anomeric effect[30a]) might be associated with an electrostatic attraction between the carbonyl and methoxy groups as suggested by model calculations. However, the PE spectrum of 3-*exo*-methoxybicyclo[2.2.1]heptan-2-one (**3**) is consistent with an equilibrium in which the "homo-anti" conformer **3A** is slightly more stable than the corresponding "homo-gauche" rotamer **3G**, in contradictions to predictions based on AM1 and ab initio calculations.

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Experimental Part.

Compounds **2** and **3** have been derived from 2-*exo*-3-*exo*-epoxybicyclo[2.2.1]heptane[33] applying the techniques described earlier.[34] Analytical samples of **2** and **3** were obtained by preparative thin layer chromatography and distillation in vacuo.

Characteristics of **2**: IR (Philips SP-3-300, $CHCl_3$) ν 1755, 1450, 1300, 1130, 1110, 1080, 1030, 990 cm^{-1}. ^{1}H-NMR (Bruker AC, 300 MHz) δ 3.60-3.55 (d, J = 4.5 Hz, 1 H), 3.50 (s, 3 H); 2.90-2.80 (m, 1 H); 2.70-2.60 (m, 1 H); 2.5-1.5 (m, 6 H). ^{13}C-NMR (Bruker, 90.55 MHz, CD_2Cl_2, 243 K): δ 214.4 (s, CO), 85.0 (C(3)), 57.9 (MeO), 49.5 (C(1)), 37.8 (C(4)), 31.3 (C(7)), 26.5 (C(6)), 18.8 (C(5)). MS (JEOL D 300, 70 eV): m/z 140 (15), 112 (13), 71 (100).

Characteristics of **3**: IR ($CHCl_3$) ν 1755, 1190, 1115, 1100, 1080 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 3-45 (s, 3 H); 3.05 (d, J = 2.7 Hz, 1 H); 2.65-2.0 (m, 2 H); 2.2-2.1 (m, 1 H); 1.95-1.45 (m, 2H), 1.65-1.30 (m, 3 H). ^{13}C-NMR (Bruker, 90.55 MHz, CD_2Cl_2, 243 K): δ 215.2 (s, CO), 83.5 (C(3)), 57.9 (MeO), 47.9 (C(1)), 39.4 (C(4)), 34.2 (C(7)), 24.1 (C(6)), 23.4 (C(5)). MS (70 eV) m/z 140 (5), 112 (5), 71 (100).

Synthesis of 2-*endo*,3-*exo*-dimethoxybicyclo[2.2.1]heptane (**4**). An anh. THF (2 mL) solution of 3-*endo*-methoxy-2-*exo*-bicyclo[2.2.1]heptanol obtained by methanolysis of 2-*exo*,3-*exo*-epoxybicyclo-[2.2.1]heptane[14] (1.13 g, 8 mmol) was added dropwise (30 min) to a stirred slurry of NaH (0.24 g, 10 mmol), MeI (1.7 g, 12 mmol) in anh. THF (6 mL) heated to 45-50°C under Ar atmosphere. After stirring at 45°C for 30 min, the mixture was cooled to 0°C and hydrolyzed by dropwise addition of H_2O. The mixture was extracted with Et_2O (30 mL, twice). The combined organic extracts were washed with brine (20 mL) and dried ($MgSO_4$) and the solvent distilled off. The residue was purified by preparative thin layer chromatography (SiO_2, Merck Kieselgel 60, PF 254-266, elution with hexane/AcOEt 4:1; R_f (**4**) = 0.8), yielding 0.985 g (79%), colourless oil. IR ($CHCl_3$) ν 1450, 1190, 1100 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 3.45-3.4 (m, 1 H); 3.35, 3.27 (2s, 2 MeO); 2.95-2.85 (m, 1 H); 2.5-2.4 (m, 1 H); 2.3-2.2 (m, 1 H); 1.7-1.1 (m, 6 H). ^{13}C-NMR ($CDCl_3$) δ 89.2 (2 C), 56.8, 56.0, 40.1, 38.0, 33.8, 25.4, 19.6. MS (70 eV) m/z 156 (20), 125 (30), 87 (70), 81 (98), 71 (95), 67 (100).

The PE spectra were recorded on a PS18 photoelectron spectrometer (Perkin Elmer Ltd., Beaconsfield) at room temperature. The spectra were calibrated with Ar (15.76 eV, 15.94 eV) and Xe (12.13 eV, 13.44 eV). A resolution of ca. 20 meV on the Ar line $^{2}P_{3/2}$ was obtained.

Computational methods. Semi-empirical calculations were carried out using the Mopac 5.0 program[35] on a Sun Sparc Station 1. Ab initio calculations were carried out using the Gaussian 90[36] on a Cray 2, with the Gamess program[37] on a Cray XMP and with the Gaussian 86[38] program on a NAS XL 60 computer.

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