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Dynamics of Eight-Membered Rings. 1,3-Dioxocane and Its *gem*-Dimethyl Derivatives

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Abstract: The ^1H and the natural-abundance ^{13}C NMR spectra of 1,3-dioxocane and its 6,6-dimethyl, 2,2-dimethyl, and 2,2,6,6-tetramethyl derivatives (I to IV, respectively) have been measured over the temperature range of -10 to -170 °C. All four compounds exist as boat-chairs. Two conformational processes are found in each compound and the free-energy barriers are as follows: I, 5.7 and 7.3; II, 4.9 and 6.4; III, 6.4 and 11.0; IV, 5.8 and 10.8 kcal/mol. The lower energy processes in I and II are pseudorotations in which twist-boat-chairs are intermediates, whereas the corresponding processes in III and IV are pseudorotations in which boat-boats are intermediates. The reasons for these differences are discussed.

Eight-membered rings that have relatively low ring-torsional barriers can be grouped together from the conformational point of view.¹ This class of compounds includes cyclooctane, cyclooctanone, and a number of heterocyclic eight-membered rings. Heteroatoms can be regarded as generalized substituents and can be used to introduce conformational perturbations that are more or less predictable. For example, the replacement of a methylene group by an oxygen atom is expected to reduce transannular nonbonded repulsions and to have significant effects on torsional barriers and internal angle strains. A really satisfactory understanding of the conformations of such rings therefore should be based on a unified conformational scheme that includes both carbocyclic and heterocyclic eight-membered compounds.¹

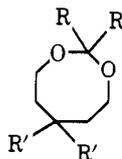
We report here a conformational study of 1,3-dioxocane (1,3-dioxacyclooctane) (I) and its three *gem*-dimethyl derivatives (II, III, and IV). In preliminary communications,^{2,3} it was deduced that I^{2,3} and III³ exist in boat-chair conformations. On the basis of 100 MHz ^1H NMR data obtained over the range of room temperature to -130 °C, it was suggested³ that II and IV adopted boat-boat conforma-

tions and that the reason for this preference was that the alternative boat-chair conformations were impossibly strained, as judged from Hendrickson's strain-energy calculations on methylcyclooctane.⁴ However, the most serious nonbonded repulsion in II or IV involves an oxygen atom and a methyl group rather than a methylene and a methyl group as in the appropriate conformations of methylcyclooctane. The previous NMR data on II and IV actually are not inconsistent with boat-chair forms provided that suitable conformational processes are rapid on the NMR time scale under the conditions used. We have therefore reinvestigated the ^1H NMR spectra II, III, and IV at both lower temperatures and at a higher magnetic field than those previously employed, and have also measured the ^{13}C NMR spectra of compounds I to IV as a function of temperature.

Experimental Section

Compounds I, II, III, and IV were prepared from the appropriate diols and carbonyl compounds by known procedures.⁵ NMR spectra were obtained on a superconducting solenoid spectrometer operating at 59 kG.⁶ The proton spectra were obtained with standard 5-mm tubes in a frequency-sweep mode. The ^{13}C spectra are Fourier transforms of accumulated free-induction decays and were obtained with 10-mm tubes. All ^{13}C NMR spectra, with the exception of a few spectra obtained for assignment purposes, were taken with protons noise decoupled. The solvent for all NMR spectra was an approximately 2:1 mixture of CHCl_2F and CHClF_2 . Tetramethylsilane was used as an internal reference for both the ^1H and ^{13}C spectra. All temperatures were measured with a copper-constantan thermocouple situated in the probe a few centimeters below the sample and connected to a Newport Laboratories digital thermometer reading to 0.1 °C and accurate to 0.2 °C.

Free energies of activation were calculated from rate constants by the absolute rate theory with a transmission coefficient of 1.



- I, R = R' = H
 II, R = H; R' = Me
 III, R = Me; R' = H
 IV, R = R' = Me

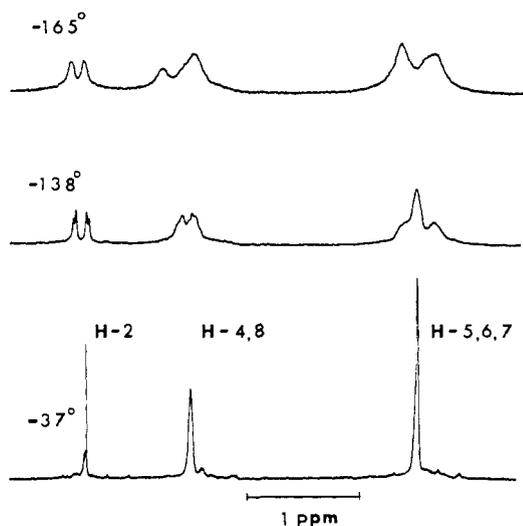


Figure 1. ^1H NMR spectra (251 MHz) of 1,3-dioxocane (I) at various temperatures.

The rate constants were obtained at the coalescence temperatures of the most widely separated peaks in the ^1H NMR spectra by the expression $k = \pi\Delta\nu/\sqrt{2}$.⁷ The errors given in the text are our best estimates of 90% confidence limits and include possible systematic errors and the effects of couplings and natural line widths. Only rough rate constants were obtained in the ^{13}C NMR spectra because of the limited signal-to-noise ratio. Furthermore, as a result of the high power (ca. 10 W) used for decoupling protons, the temperature measurements associated with these spectra are of lower accuracy ($\pm 3^\circ\text{C}$) than those of the ^1H spectra ($\pm 1^\circ\text{C}$). The accuracy (± 0.3 kcal/mol) of the free-energy barriers obtained from the ^{13}C spectra was entirely adequate for determining a correspondence with one of the two barriers obtained in the ^1H spectra.

Results and Discussion

For convenience we will present the experimental results in terms of the framework described below. It will be shown that two distinct dynamic NMR effects are observed for each dioxocane, and therefore at least two conformational processes must exist in each case. The process that is responsible for the higher-temperature dynamic NMR effect has the higher free-energy barrier and operationally will be referred to as the higher energy process. The lower temperature dynamic NMR effect is then associated with the lower energy process.

Aside from conformational considerations, all four dioxocanes have C_{2v} symmetry, and the NMR parameters obtained at room temperature are consistent with this (time-averaged) symmetry. At the lowest temperature investigated, however, the four dioxocanes give spectra consistent with unsymmetrical conformations, and each compound is found to exist as a mixture of two mirror-image chiral conformations. At intermediate temperatures the time-averaged symmetry observed is either C_2 or C_s and it is not the same for all four dioxocanes. The temperature ranges where the observed time-averaged symmetries are C_{2v} , C_2 , or C_1 will be termed the high-, intermediate-, and low-temperature regions, respectively. In the two temperature ranges between these three regions the spectra show at least some resonances that are broadened by dynamic NMR effects. Since the C_{2v} point group has two symmetry planes (as well as a C_2 axis), the C_s symmetry could arise in two ways. However, it is virtually impossible from conformational considerations to introduce a time-averaged symmetry plane that passes through all the ring members, without at the same time introducing the full C_{2v} symmetry. Thus, the C_s symmetry will refer only to a symmetry plane passing through C-2, C-6, and the exocyclic bonds to these two

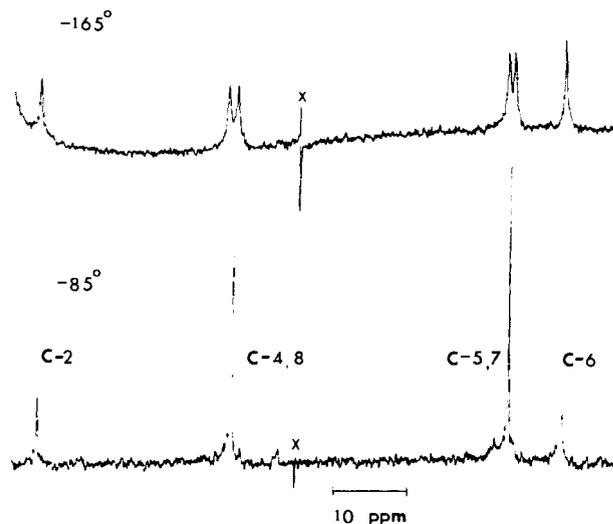


Figure 2. ^{13}C NMR spectra (63.1 MHz) of 1,3-dioxocane (I). The lines marked with X's are beats.

atoms. The presence of a time-averaged C_2 axis makes the two protons on C-2 in I be isochronous, whereas the C_s time-averaged symmetry mentioned above does not require this. Similar effects hold for the protons on C-2 and for the protons and carbons of the methyl groups on C-2 and C-6 in II, III, and IV. Thus, a distinction between the two symmetries can readily be made by examining the NMR bands of atoms or groups attached to C-2 or C-6. On the other hand, C-4 and C-8 are isochronous in I, II, III, or IV as long as either C_2 or C_s time-averaged symmetry is present, and these carbon atoms, as well as C-5 and C-6, are useless in distinguishing between C_2 and C_s symmetries. Protons on C-4,5,6,8 are not useful for these symmetry determinations either, because of the lack of observable long-range coupling.

1,3-Dioxocane (I). The ^1H NMR spectra of this compound at various temperatures are shown in Figure 1. In the high-temperature region, the sharp low-field singlet at δ 4.65 is assigned to protons on C-2 and the band at δ 3.72 is assigned to protons on C-4 and C-8. The remaining protons, which should exhibit two different chemical shifts, coincidentally give rise to a single line at δ 1.70. All three signals broaden below -100°C and a new sharp spectrum is obtained at about -140°C (intermediate temperature region). The protons on C-2 give a resolved AB quartet ($\nu_{AB} = 29$, $J_{AB} = 5.7$ Hz) at -138°C , while the protons on C-4 and C-8 now exhibit two chemical shifts (δ 3.72 and 3.82). The high-field line is too complex for analysis. The coalescence temperatures for the three sets of bands are virtually the same, viz., $-122 \pm 2^\circ\text{C}$. The dynamic NMR effect that takes place in the temperature range -100 to -140°C arises from the higher energy conformational process and this is calculated to have a ΔG^\ddagger of 7.3 ± 0.2 kcal/mol. Since the protons on C-1 are anisochronous in the intermediate-temperature region, the time-averaged symmetry must be C_s , and C_2 symmetry is rigorously excluded.

The protons on C-4 and C-8 in I give rise to a broadened band in the range of -150 to -160°C and in the low-temperature region (e.g., -165°C) there are two resolved bands in the intensity ratio of 3:1 at δ 3.72 and 4.0, respectively. The most reasonable interpretation is that there are four chemical shifts for these protons, and that there is a near coincidence of three resonances. The protons on C-2 still give only two chemical shifts in this region, although the splitting due to spin-spin coupling in the AB quartet cannot be resolved at these low temperatures. The ^1H

Table I. ^{13}C NMR Chemical Shifts in 1,3-Dioxocanes I, II, III, and IV

Temp. $^{\circ}\text{C}$	Chemical shifts ^a					
	C-2	C-4,8	C-5,7	C-6	Me-2	Me-6
I	-85	95.7	69.0	30.4	23.2	
	-165	95.8	68.6	30.1	23.1	
II	-85	95.1	65.7	42.7	32.9	29.3
	-165	94.9	63.5	40.8	33.0	23.9
			68.5	44.3		35.6
III	-120	100.6	63.6	30.3	25.1	25.1
	-160	100.7	62.8	28.8	25.2	23.9
IV	-115	100.6	60.3	42.7	32.1	25.3
	-165	100.5	58.3	39.7	32.3	23.3
			61.9	44.6	26.4	35.0

^a In ppm downfield from internal tetramethylsilane- ^{13}C .

NMR data are thus consistent with a mixture of an unsymmetrical form and its mirror image. The lower energy process is calculated to have a ΔG^{\ddagger} of 5.7 ± 0.2 kcal/mol at -150°C .

The conclusions derived from the ^1H NMR data are supported by the ^{13}C NMR spectra shown in Figure 2. As expected, only the lower energy process is now observed, and dynamic NMR effects are restricted to the C-4,8 and C-5,7 resonances (Table I). It is interesting that the chemical shift splittings which occur at low temperature for these carbon atoms are relatively small (ca. 1 ppm).

6,6-Dimethyl-1,3-dioxocane (II). The ^1H NMR spectra of this compound are shown in Figure 3. In the high-temperature region the C-2 protons give rise to a singlet at δ 4.61, and the two triplets at δ 1.56 and 3.70 can be assigned to the C-5,7 and the C-4,8 protons, respectively. The intense singlet at δ 1.01 belongs to the methyl groups. Broadening takes place below -120°C and a new relatively sharp spectrum is found at about -140 to -150°C . The C-2 proton band splits into an AB quartet ($\nu_{\text{AB}} = 35.5$, $J_{\text{AB}} = 5.4$ Hz), which is best resolved at about -154°C . The C-5,7 proton band splits into two well separated bands (δ 1.30 and 1.83), with the low-field resonance never becoming sharp. Three resonances at δ 1.27, 1.52, and 2.11 in the ratio of 2:1:1 are found for these protons at -166°C . The doublet at δ 1.27 probably results from coincidences in chemical shifts of two protons with the splitting coming from geminal coupling to the protons at δ 1.52 and 2.11. The relatively large frequency difference between the bands at δ 1.52 and 2.11 is the reason for the broadness of the resonance at δ 1.83 at -145°C , as the latter resonance arises from the coalescence of these two bands. The methyl peak of II splits into two resonances below -142°C , while the C-4,7 protons also split into two at intermediate temperatures, but become more complex at very low temperatures. The presence of two resonances each for the methyl groups and the C-2 protons at intermediate temperatures indicates that the time-averaged symmetry under these conditions is C_s and not C_2 , just as with I. The low-temperature spectrum of II is consistent with this compound existing as a 1:1 mixture of mirror-image unsymmetrical conformations. The free energies of activation for the two processes in II are 4.9 ± 0.2 and 6.4 ± 0.2 kcal/mol.

The ^{13}C NMR spectrum of II near ambient temperatures shows five resonances (Table I). At intermediate temperatures (ca. -140 to -150°C) only the methyl carbons show two resonances. At low temperatures (e.g., -165°C), all the high-temperature resonances are split, with the excep-

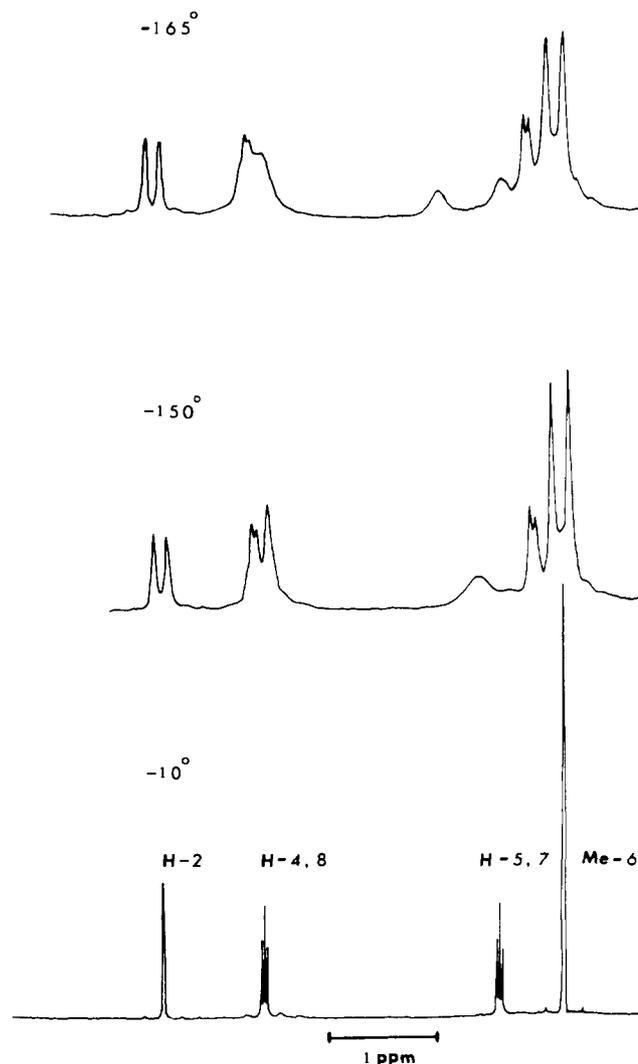


Figure 3. ^1H NMR spectra (251 MHz) of 6,6-dimethyl-1,3-dioxocane (II).

tion of the bands of C-2 and C-6 (Table I). These splittings are completely consistent with and strongly support the picture deduced from the proton spectra of II.

2,2-Dimethyl-1,3-dioxocane (III). The ^1H NMR spectra of this compound are shown in Figure 4. In the high-temperature region (e.g., -10°C), protons at C-4 and C-8 give rise to a band (δ 3.59) which is broad because of the complex spin system involving these protons and those on C-5, C-6, and C-7. The latter protons show a single unresolved broad band at δ 1.60. The methyl groups give a sharp single line at δ 1.34. Below -45°C the band of the C-4,8 protons splits into two and at -102°C two well resolved multiplets are found (δ 3.60 and 3.97) (Figure 4). The protons on C-5,6,7 also change, but not in an easily analyzable fashion, while the methyl band remains sharp. A second dynamic NMR change takes place below about -135°C and at -156°C a new sharp spectrum is observed. Protons on C-4,8 now give rise to four chemical shifts (δ 3.57, 3.72, 3.95, and 4.06), the methyl groups give two separate resonances (δ 1.36 and 1.48), and the remaining protons show complex bands between δ 1.50 and 2.00.

The presence of two methyl resonances and four α -proton resonances in the ratio of 1:1:1:1 at -156°C is consistent with a 1:1 mixture of an unsymmetrical conformation and its mirror image. The presence of only one methyl resonance at -102°C shows that the time-averaged symmetry at this temperature cannot be merely C_s , as this would re-

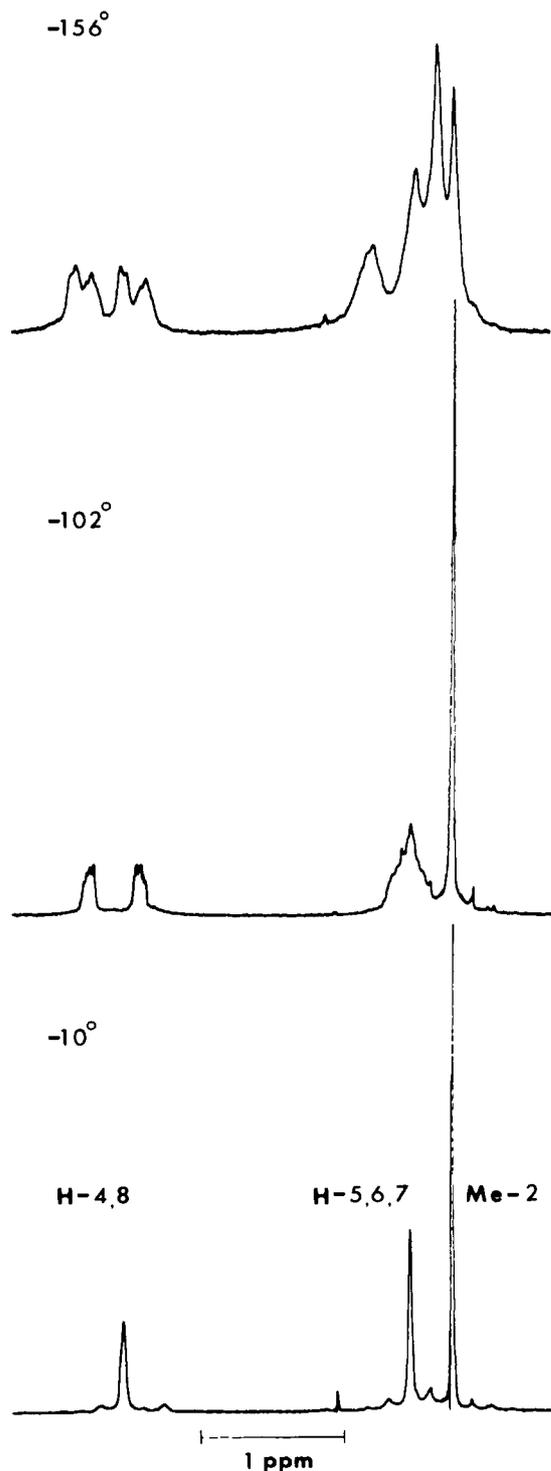


Figure 4. ^1H NMR spectra (251 MHz) of 2,2-dimethyl-1,3-dioxocane (III).

quire two methyl bands, as are found at -156°C . The spectrum at intermediate temperatures is completely consistent with a time-averaged C_2 symmetry as this requires a single methyl band and two chemical shifts for the α protons, just as observed. Thus III has a different time-averaged symmetry at intermediate temperatures from that shown by either I or II. The free energies of activation for the two processes in III are 6.4 ± 0.2 and 11.0 ± 0.2 kcal/mol.

The ^{13}C NMR spectrum of III in the high-temperature region shows the presence of four resonances (C-6 and the methyl carbons are superposed) (Table I). In the intermedi-

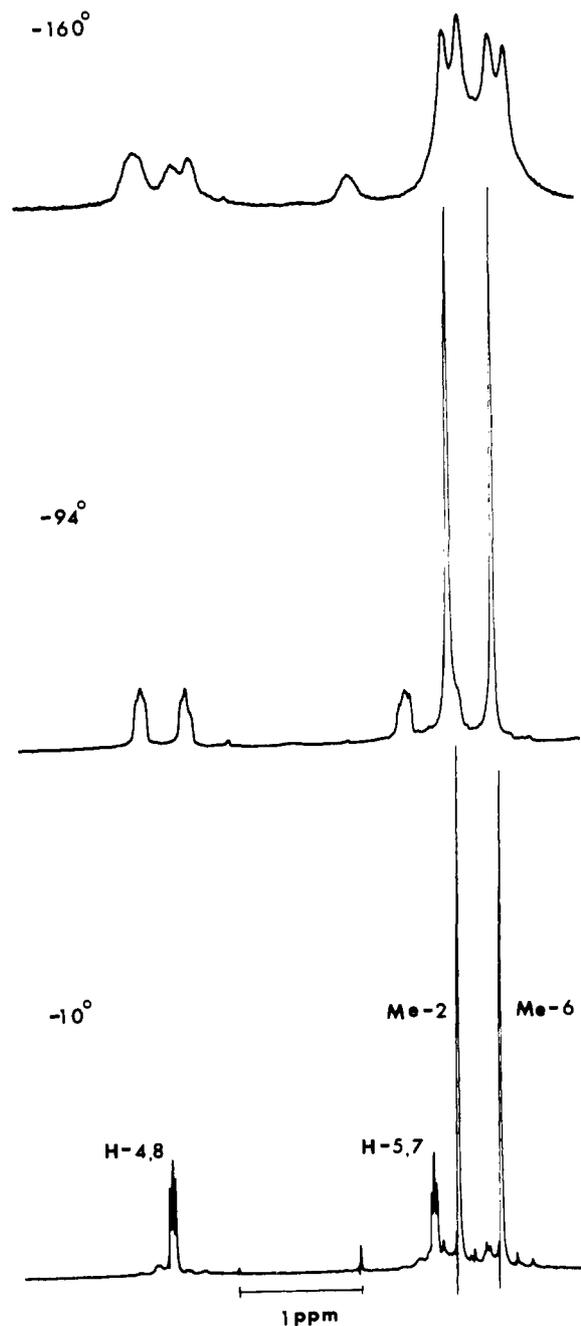


Figure 5. ^1H NMR spectra (251 MHz) of 2,2,6,6-tetramethyl-1,3-dioxocane (IV).

ate temperature region, where the proton spectrum has changed greatly from that at higher temperatures, the ^{13}C NMR spectrum still exhibits the same four sharp lines. At low temperatures (e.g., -160°C), however, all ^{13}C NMR lines change to 1:1 doublets with the exception of C-2 and C-6, which remain single lines. Only the lower energy process is visible in the ^{13}C NMR spectrum, and this process, when fast, introduces a time-averaged C_2 symmetry and leads to single resonances for the C-4,8, C-5,7, and methyl carbons. Thus the evidence from the ^{13}C NMR spectra of III strongly supports the interpretation given above to explain the features found in the ^1H NMR spectra.

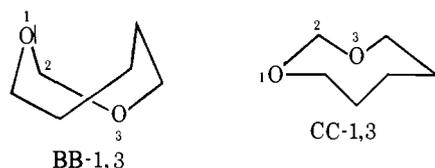
2,2,6,6-Tetramethyldioxocane (IV). The ^1H NMR spectra of IV are shown in Figure 5. In the high-temperature region the spectrum consists of an AA'XX' system given by protons (δ 3.64) on C-4,8 and protons (δ 1.47) on C-5,7, and two singlets at δ 1.01 and 1.35 given by methyl groups on C-6 and C-2, respectively. Below -45°C , the reso-

nances at δ 3.64 and 1.47 each split into two well-separated bands whereas the methyl signals remain unchanged. At -94 °C, the chemical shifts of the four methylene resonances are δ 1.61, 1.74, 3.55, and 3.92. A second dynamic NMR effect takes place below about -120 °C. All four methylene groups probably split into doublets but this change is clearly visible only for the resonance at δ 3.55, which gives bands at δ 3.56 and 5.70. The "doublet" centered at δ 4.01 is not resolved, but can be identified by the broadness of the band. Only one component, at δ 2.24, of the doublet arising from the resonance at δ 1.74 can be identified. The remaining component of this doublet and both components of the doublet arising from the resonance at δ 1.61 are hidden under the bands of the methyl groups. Finally, each methyl group in IV gives a separate resonance at -160 °C, so that four methyl chemical shifts (δ 0.96, 1.13, 1.33, and 1.46) are observed. The spectrum at -160 °C is consistent with a 1:1 mixture of an unsymmetrical conformation and its mirror image. The presence of a single line for each of the two *gem*-dimethyl systems at intermediate temperatures requires a time-averaged C_2 symmetry under these conditions. The free energies of activation for the two processes in IV are 5.8 ± 0.2 and 10.8 ± 0.2 kcal/mol.

The ^{13}C NMR spectrum of IV (Table I) shows the expected six resonances at intermediate and high temperatures. At -167 °C all resonances except those at C-2 and C-6, which remain extremely sharp, are split into doublets, as expected from the changes observed in the proton spectrum.

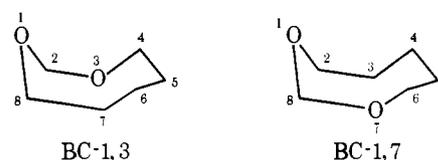
Conformations of 1,3-Dioxocanes. The NMR results presented above establish that each of the four dioxocanes, I, II, III, and IV, exists in a conformation devoid of symmetry. This excludes the boat-boat conformations previously suggested for III and IV, as these have symmetry, e.g., a C_2 axis in BB-1,3.

The conformations in the crown family are the crown itself, the chair-chair (CC), and the twist-chair-chair and these have D_4 , C_{2v} and D_2 symmetries in cyclooctane. Although the latter two conformations can be unsymmetrical for 1,3-dioxocane, e.g., CC-1,3, the extremely low barriers^{1,8} separating members of this family are expected to lead to a C_s time-averaged symmetry, even at extremely low temperatures. This conclusion holds for any one conformation, or any mixtures of conformations, in the crown family. Thus crown forms do not fit the experimental NMR data. Furthermore, the observed dipole moments of the 1,3-dioxocanes are in much better agreement with boat-chair than with crown conformations.³



The absence of symmetry and the presence of two conformational processes in each dioxocane are in perfect agreement with a boat-chair conformation where the oxygens are situated at either sites 1 and 3 or 1 and 7, i.e., BC-1,3 or its mirror image BC-1,7. Strong arguments can be made that these conformations should be energetically favored for the 1,3-dioxocanes. In the first place, the most stable conformation of cyclooctane is the boat-chair with the best crown-family conformation (the twist-chair-chair) about 1.8 kcal/mol higher in energy than the boat-chair.^{8,9} Second, the placement of oxygen atoms at sites 1 and 3 (or 1 and 7) gives rise to a favorable torsional angle arrangement about

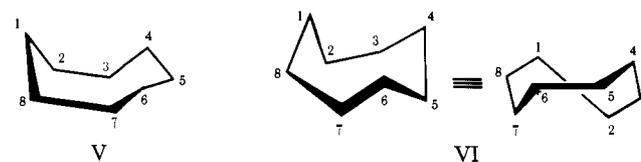
the O-CH₂-O unit that is virtually the same as the one found in dimethoxymethane (i.e. + gauche + gauche or - gauche - gauche).^{2,3} Third, an oxygen at site 3 or 7 should give rise to a considerable relief of the nonbonded repulsion that exists between the inward pointing hydrogen atoms at these sites in cyclooctane. Strain-energy calculations on oxocane (oxacyclooctane) indeed show that the best position of the oxygen atom in the boat-chair conformation of this compound is 3 or its mirror-image site, 7.¹⁰ The next best site for the oxygen atom in oxocane is at position 1, and in this case there is a relief of the steric repulsions present in cyclooctane between the inward pointing hydrogen at site 1 with hydrogens at sites 4 and 6. Thus the greatest relief of nonbonded strain in the cyclooctane boat-chair as a result of replacing two methylene groups by oxygen atom is expected to occur if the oxygen atoms are placed either in positions 1 and 3 or in positions 1 and 7.



From the experimental data and the theoretical arguments presented above, it is virtually certain that 1,3-dioxocane has the BC-1,3 type of conformation. The 2,2-dimethyl derivative of 1,3-dioxocane should also have this type of conformation since this places the bulky methyl groups in the favorable quasiisoclinal or corner positions where steric strain is quite small.^{3,4} We are ignoring here the decrease in the internal angle on going from a methylene group to a CMe₂ group, and small differences in nonbonded repulsions between *gem*-dimethyl groups and other atoms which occur even when the substituents are in favorable sites. In the case of the 6,6-dimethyl derivative (II), the methyl groups are not in the best possible positions in the BC-1,3 conformation, but the strongest nonbonded interaction is with an oxygen atom and this should be much lower than the repulsion present in the corresponding cyclooctane compound, which has been estimated to be 5.1 kcal/mol by Hendrickson.⁴ Our experimental data prove that the methyl-oxygen repulsion in II does not lead to a change of the ring conformation from a boat-chair to a boat-boat, despite the more favorable placement of the *gem*-dimethyl group in the latter conformation. This supports our previous conclusion that the boat-boat as well as the twist-boat-boat conformation are relatively high in energy in cyclooctane itself.^{1,8}

The introduction of a second *gem*-dimethyl group, which occurs on going from III to IV, should not introduce a serious conformational perturbation as the change is the same as occurs on going from I to II.

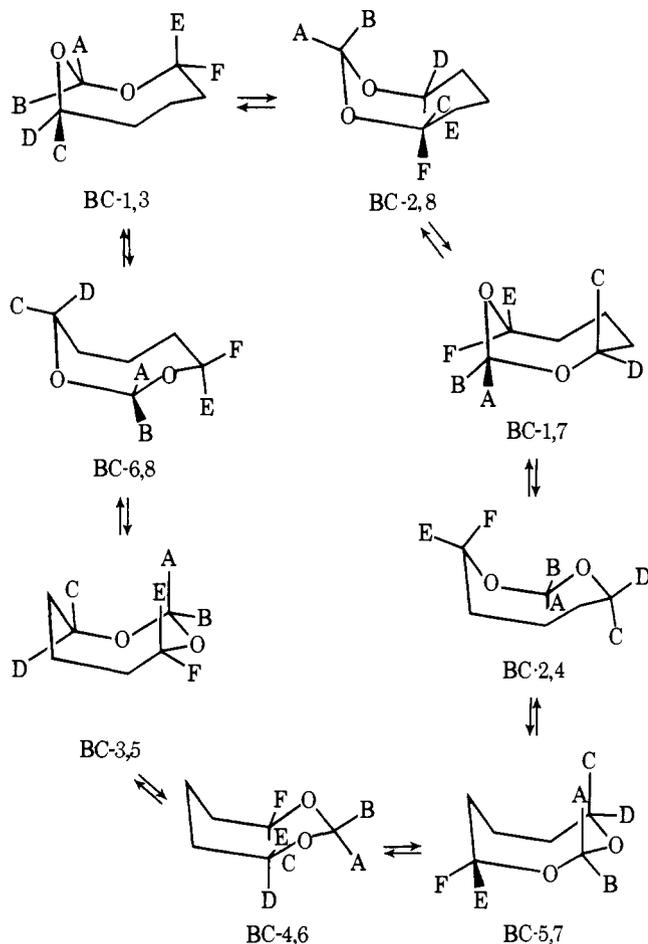
Conformational Processes and Barriers. The lowest energy conformational process in the cyclooctane boat-chair (V) is a pseudorotation in which the twist-boat-chair (VI)



is an intermediate.^{1,8} In this process, either the torsional angle ω_{1234} or the torsional angle ω_{1876} passes through zero, depending on which of the two possible mirror-image twist-boat-chair is desired. The twist-boat-chair obtained by changing ω_{1234} from a positive to a negative angle is shown in VI and this has a C_2 axis passing through the midpoints of bonds 1-2 and 5-6. Although the pseudorotation barrier

has not been measured directly, strain-energy calculations indicate that it is about 3.3 kcal/mol and that the twist-boat-chair lies about 1.7 kcal/mol in energy above the boat-chair.⁸ The analogous pseudorotation process in the 1,3-dioxocane boat-chair is also expected to be of relatively low energy, and sequences of pseudorotation steps result in the interconversion of the BC-1,3 form with its mirror-image BC-1,7, as shown in Scheme I. There are two paths

Scheme I



available for this conformational racemization. In one path, the plane-symmetrical BC-2,8 is the sole intermediate boat-chair; in the other, there are five intermediate boat-chairs, one of which, namely BC-4,6, is plane symmetrical (note that numbers in designations such as BC-2,8 refer to conformational labeling in the boat-chair, and in the present case implicitly refers to the positions of the oxygen atoms).

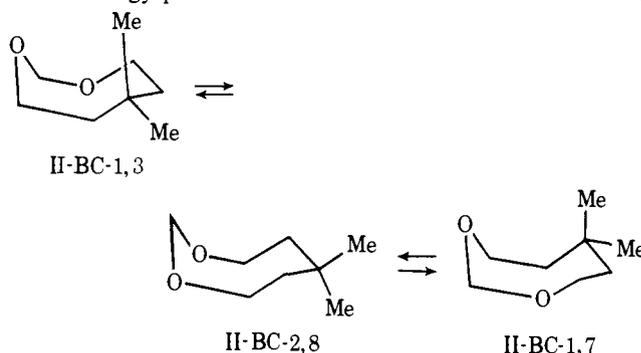
The exchange that takes place on going from the BC-1,3 to the BC-1,7 form can be visualized in the following way. Since the BC-2,8 (or the BC-4,6) form is a (high-energy) intermediate, and this conformation has a plane of symmetry, it follows that fast pseudorotation of the type described above will introduce a time-averaged C_s symmetry.¹¹ The A and B protons are unaffected when this process is fast, but protons C and E, which are configurationally cis, acquire the same chemical shift, at least in achiral solvents. Thus C and E become a pair of enantiotopic protons, as do D and F, but A and B remain diastereotopic as do C and D, etc. It is also clear that fast pseudorotation causes the α and α' carbons (C-4 and C-8) in 1,3-dioxocane to become enantiotopic and thus to have the same chemical shift in an achiral solvent.

The pseudorotation of BC-1,3 to BC-2,8 via a twist-boat-chair probably reaches an energy maximum when the fragment $-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$ has a torsional angle close to

zero degrees. The strain energy, and particularly the non-bonded component of the energy at this geometry, should be comparable or even higher than in the BC-TBC transition state in cyclooctane since the C-O bond length is shorter than the C-C bond length and the C-O-C angle is smaller than the C-C-C angle. On the other hand, the strain energy in the ground state conformation, BC-1,3, should be considerably lower than in the cyclooctane boat-chair for reasons stated in the last section. Therefore, the barrier to pseudorotation of the boat-chair in 1,3-dioxocane by this path can be expected to be significantly higher than the corresponding barrier in cyclooctane and very likely should be high enough to observe by dynamic NMR at low temperatures. Similar arguments apply to the alternate pseudorotation path that proceeds via the BC-4,6 form.

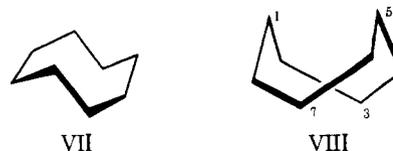
The experimental evidence shows that 1,3-dioxocane exhibits a time-averaged C_s symmetry at intermediate temperatures and therefore the lower energy process in this compound is consistent with pseudorotation sequences which interconvert the BC-1,3 and BC-1,7 conformations as shown in Scheme I.

The *gem*-dimethyl group in 6,6-dimethyl-1,3-dioxocane (II) should lead to an increase of the strain energy in the ground state boat-chair conformation (II-BC-1,3) as compared to the parent compound for reasons given in the last section. Pseudorotation of II-BC-1,3 to II-BC-1,7 by the sequence involving II-BC-2,8 (cf. Scheme I) leads, according to molecular models, to a partial relief of the excess strain energy and this is consistent with the observation that the lower energy process in II has a barrier which is 0.8 kcal/



mol less than in I. The alternate pseudorotation pathway, which proceeds through II-BC-4,6, is undoubtedly very unfavorable, since it forces one or other of the two methyl groups into the highly hindered 1, 3, and 7 positions during the pseudorotation itinerary.

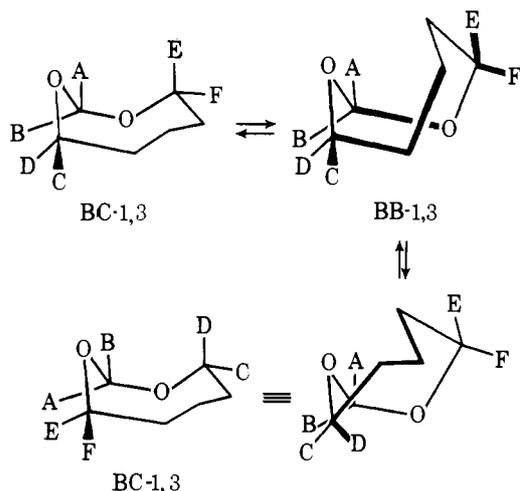
The higher energy process in 1,3-dioxocane can be called a ring inversion,^{1,12} although the mechanism is probably different from the ring-inversion process in cyclooctane. In the latter compound the transition state for ring inversion is probably the chair (VII) or, less likely, the twist-chair



form.^{1,8} Interconversion of the boat-chair with the boat-boat (VIII) in cyclooctane is also a possible mechanism for ring inversion but appears to be a distinctly higher energy path than that through the chair form, mainly because it is necessary to bring the methylene groups at 1 and 5 or 3 and 7 in the boat-chair close together to avoid very large internal angle distortions.⁸ In 1,3-dioxocane, however, the groups which are brought close together are an oxygen atom and a methylene group and nonbonded repulsions

should be much less than in the cyclooctane case (Scheme II). Although we have not carried out strain-energy calcula-

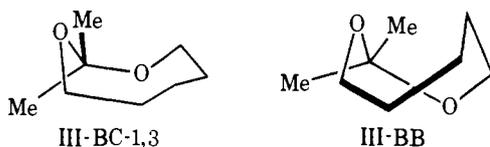
Scheme II



tions on 1,3-dioxocane to test this supposition, quantitative strain-energy calculations on the BC-3 to boat-boat change in the closely related compound, oxocane, reveal a barrier for this process of 7.2 kcal/mol,¹⁰ compared to one of 10.7 kcal/mol in cyclooctane.⁸ Additional evidence for a comparatively low barrier for this process in 1,3-dioxocane can be adduced from the experimental data on the *gem*-dimethyl compounds, to be discussed below.

The higher temperature process in II has a lower barrier than the corresponding process in I. This fact also points to a boat-boat pathway for this process as the methyl groups move to less sterically hindered positions in the boat-chair to boat-boat interconversion (Scheme II), whereas the reverse is true for the boat-chair to chair interconversion.

The lower temperature process in the 2,2-dimethyl derivative (III) introduces a time-averaged C_2 symmetry, and therefore the change involved cannot be a pseudorotation via a twist-boat-chair as an intermediate. The process can, however, be a pseudorotation of III-BC-1,3 via the axial symmetric boat-boat conformation, III-BB, exactly as described previously in Scheme II (A = B = Me, C = D = E = F = H). This is not a ring inversion, because pseudorotation via the twist-boat-chair is taking place much more slowly than is the pseudorotation via the boat-boat and therefore the ring torsional angles do not all change their signs.^{12,13} The free-energy barrier for this process in III is



close to that for the higher temperature processes in I and II, as it should be, since the mechanisms in the three cases are postulated to be the same, and nonbonded repulsions in the transition states should be similar.

The higher temperature process in III has a barrier which is strikingly higher than either of the two processes seen in I and II. Nevertheless, the higher temperature process in III probably has the same mechanism as the lower temperature process in I and II. The difference in barrier heights is a result of the unfavorable positions that the geminal methyl groups in III are required to take up in the pseudorotation of the boat-chair, III-BC-1,3, in the manner shown in Scheme I. Either III-BC-2,8 or III-BC-6,8 is an intermediate and the transition states leading to either of these boat-chairs should retain some of the unfavorable

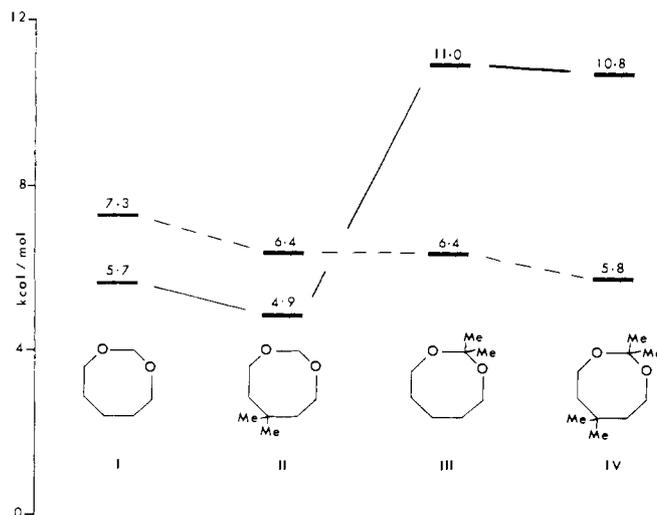


Figure 6. Relationships of the conformational free-energy barriers in the 1,3-dioxocanes, I, II, III, and IV. The full lines link barriers for boat-chair to twist-boat-chair processes and the dotted lines link barriers for boat-chair to boat-boat processes.

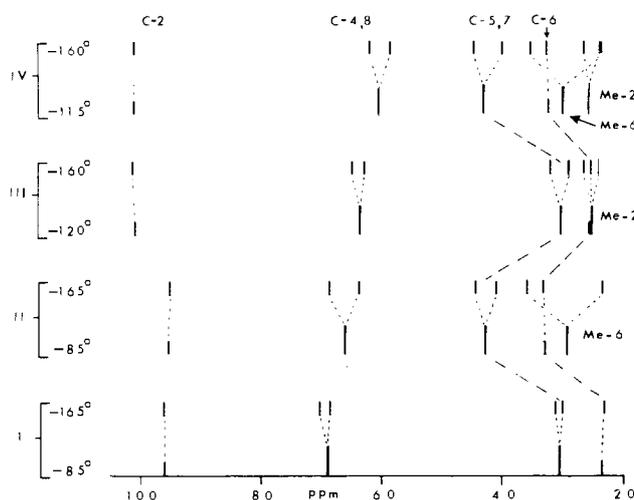
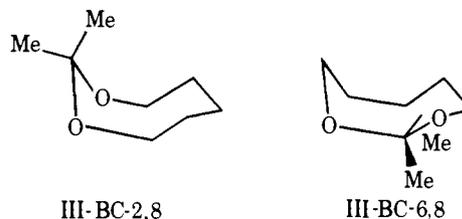


Figure 7. Diagrammatic representation of the ^{13}C chemical shifts in the 1,3-dioxocanes, I, II, III, and IV.



nonbonded interactions that are present in III-BC-2,8 and III-BC-6,8.

The tetramethyl compound IV behaves much the same as does III, the main effect of the extra geminal groups in IV being to raise the ground state energy more than the energies of the two transition states, exactly as is the case on passing from I to II. The relationships of the various barriers in the four dioxocanes are shown diagrammatically in Figure 6.

^{13}C Chemical Shifts. The averaged ^{13}C chemical shifts of C-2, C-3,8, and C-4,7 in 1,3-dioxocane are similar to those of structurally related carbons in cyclic six- and seven-membered acetals.¹⁴ Certain regularities can be observed in the ^{13}C chemical shifts of the dioxocanes (Table I and Figure 7). The chemical shift differences between the two

methyl groups at C-6 in II and IV at low temperatures are much greater than those between the two methyl groups at C-2 in III and IV, in agreement with the presence of an approximate *local* C_2 axis passing through C-2 in the preferred boat-chair conformations of these compounds. Methyl groups at C-6, by contrast, are in very different environments, the axial methyl group having gauche γ shielding interactions¹⁵ with the methylene groups at positions 4 and 8 in the boat-chair, whereas the equatorial methyl group lacks any γ interaction.

The chemical shifts of C-4 and C-8 in III are at higher field than in I as a result of gauche γ shielding effects¹⁵ of the geminal methyl groups in III. Since one methyl group shields C-4 while the other shields C-8, the shielding effects should be similar, as observed, viz., 5.6 and 6.2 ppm. The resonances of C-5, C-6, and C-7 in III should not be strongly influenced by the methyl groups, and indeed the chemical shifts of these nuclei are similar to those found in I. The α and β effects resulting from the introduction of geminal methyl groups in I to give II, III, and IV are fairly large and deshielding, as expected.¹⁵

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- (7) This expression is strictly valid for an exchange process between two equally populated sites and where exchange is the only broadening effect; errors resulting from coupling and natural line-width effects are least when the chemical shift difference is greatest. The experimental data available are not suitable for obtaining meaningful values of ΔH^\ddagger or ΔS^\ddagger , even through the errors in ΔG^\ddagger are not large [F. A. L. Anet and R. Anet, "Dynamic Nuclear Magnetic Resonance Spectroscopy", F. A. Cotton and L. M. Jackman, Ed., Academic Press, New York, N.Y., 1975, p 543].
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- (10) F. A. L. Anet, J. Krane, and I. Yavari, unpublished work. We have not carried out strain-energy calculations on 1,3-dioxocane itself because of the difficulty of taking into account the dipole-dipole energy of the cyclic acetal system.
- (11) It may seem paradoxical that the twist-boat-chair, which has C_2 symmetry in cyclooctane, gives rise to a time-averaged C_s symmetry when that conformation is an intermediate in the pseudorotation of the BC-1,3 form of 1,3-dioxocane (I). The TBC conformation in cyclooctane has only a C_2 axis, and this axis bisects *bonds* on opposite sides of the molecule, whereas I, because of its substitution pattern, can only have a C_2 axis passing through opposite ring atoms. Thus all twist-boat-chairs of I are unsymmetrical. The C_2 time-averaged symmetry must occur if either the BC-1,8 or the BC-4,6 conformations are intermediates, although it is not necessary that any intermediate have C_s symmetry for a C_s time-averaged symmetry to occur.
- (12) Ring inversion can be (strictly) defined as a process that results in all the ring torsional angles changing their signs but without any change in their absolute magnitudes.¹ We shall use a generalized definition in which small changes in the magnitudes of ring torsional angles are allowed, and where time-averaged torsional angles can be used when another process is much faster than ring inversion.¹
- (13) The overall change described in Scheme II is a ring inversion only if an appropriate second process (e.g., pseudorotation via the twist-boat-chair) is already fast.¹²
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The Electronic Structure of Molecules by a Many-Body Approach. IV. Ionization Potentials and One-Electron Properties of Pyrrole and Phosphole

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Abstract: The valence ionization potentials (IP's) of pyrrole and (the presently still unknown) phosphole molecule are studied by an ab initio many-body approach which includes the effect of electron correlation and reorganization beyond the Hartree-Fock approximation. Whereas for pyrrole the first IP is due to the $1a_2(\pi)$ molecular orbital, the first IP of phosphole is due to the $2b_1(\pi)$ orbital. For the valence IP's at higher energy there is also little agreement in the ordering. For pyrrole the Hartree-Fock approximation appears to supply the correct ordering, but it does not give the correct ordering in the case of phosphole. For pyrrole there are two IP's due to σ -type orbitals between the IP's due to the π orbitals and for phosphole none. A number of one-electron properties are calculated in the one-particle approximation and compared with available experimental and theoretical data. The localized molecular orbitals are discussed as well.

I. Introduction

The five-membered heterocyclic molecules furan, thiophene, pyrrole, and phosphole have very similar structures and are isoelectronic in the valence electrons. A great similarity in the photoelectron spectra (PES) is thus expected and can be found when the gross features of the PES of these molecules are examined.^{2,3} Starting with the low

binding energy region the spectra consist of two well-resolved bands which correspond to the IP's due to the first two π orbitals and which frequently exhibit vibrational structure. A more detailed look at the assignment of the various peaks reveals, however, considerable differences among the molecules in particular concerning the position of the third π orbital.

Only a small number of experimental investigations of