The photochemistry of **1** provides an interesting contrast to the photochemistry of monocyclic cycloheptadienones. Direct irradiation of cyclohepta-3,5-dienone (**4**) leads to decarbonylation, while triplet-sensitized photolysis gives the cyclobutene.[16] A dibenzo-3,5-cycloheptadienone also decarbonylates upon direct photolysis.[17] 2,2,7,7-Tetramethylcyclohepta-3,5-dienone (**5**) undergoes a $[_\pi 2_a + {}_\sigma 2_a]$ rearrangement on either direct or sensitized photolysis.[18]

In polar solvents, the behavior of **1** is similar to that of **5**. Intersystem crossing is more efficient than singlet decarbonylation, and the ^{3}n–π^* state (or the "^{3}CT" state[13]) is lowest in energy, leading to $[_\pi 2_a + {}_\sigma 2_a]$ rearrangement. In nonpolar solvents, the behavior of **1** is similar to that of **4**. In the latter, the lowest energy diene $^3\pi$–π^* state undergoes cyclobutene formation, probably *via* the cis,trans diene,[16] while in the more strained **1**, the twisted $^3\pi$–π^* state attacks ground-state **1** to form dimer. In solvents of intermediate polarity, both reactive triplet states of **1** are populated.

The inefficiency of intersystem crossing and the π–π^* nature of the lowest triplet state of **4**, the efficiency of intersystem crossing and the n–π^* (or CT) nature of the lowest triplet of **5**, and the efficiency of intersystem crossing and closeness of the π–π^* and n–π^* (or CT) triplet states of **1** suggest that the relative energies of the various states of 3,5-cycloheptadienones are exceedingly sensitive to both symmetry and substituents. Furthermore, the differences in intersystem crossing efficiency in these closely related systems are most likely related to the energy split between ^{1}n–π^* and $^3\pi$–π^* states.[15]

Kinetic and emission experiments designed to extract rate constants and state energies as a function of solvent polarity are now in progress.

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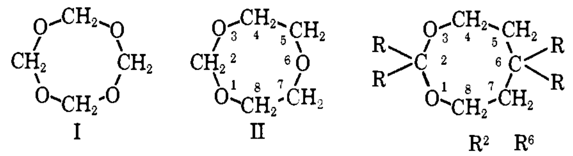
Conformational Studies of Oxygen-Heterocyclic Eight-Membered Rings

Sir:

The primary reason why cyclooctane and several substituted derivatives, including those having one exocyclic double bond (>C=O and >C=CH$_2$), prefer the boat–chair to the diamond-lattice type boat–boat conformation[1] is clearly the transannular repulsion that would exist between two pairs of 1,5-hydrogen atoms in the latter. This repulsion might be reduced if opposing CH groups are replaced by opposing oxygen lone pairs, or even turned into attraction if a CH interacts transannularly with an oxygen lone pair. We have therefore studied the cyclic tetramer of formaldehyde[2] (I) as an example of the first situation and cyclic formals of pentane-1,5-diol[3] (IIIa) and diethylene glycol[4] (II) as examples of the second situation. Derivatives having *gem*-dimethyl groups in one or two positions (IIIb–d), so as to further favor the boat–boat conformation, have also been examined.

Scheme I



	R^2	R^6
IIIa	H	H
b	Me	H
c	H	Me
d	Me	Me

The nmr spectrum at 100 MHz of tetrameric formaldehyde (I) in CDCl$_3$ (or CHFCl$_2$) is a single line above +10°, but on cooling it broadens and splits into an AB quartet ($\Delta\nu_{AB}$ = 61 Hz, J = 9 Hz) plus a single line which becomes sharp below −40°. On further cooling, the relative intensity of the single line decreases rapidly. A plot of ln K against $1/T$ from −130 to −40° is linear and gives for the equilibrium ΔH = 2.3 kcal/mol and ΔS = 8.5 eu, meaning that the "quartet" conformer (or conformational family) preponderant at low temperature has both the lowest enthalpy and the lowest entropy. Extrapolation shows that the "single-line" conformer (or conformational family) must constitute over 60% at room temperature. The infrared spectrum in CS$_2$ solution also shows two sets of lines whose relative intensity varies with temperature. The same set which gains intensity on cooling becomes more dominant in acetonitrile solution than in CCl$_4$, hence belongs to the more polar conformer. This line set also resembles most nearly the spectrum of the crystal, where we assume a symmetrical crown to be present as in the known crystal structure[5] of tetrameric acetaldehyde (all-cis isomer). The correlation of the crystal conformer to the "nmr quartet" conformer is supported by the observation that the strongest Raman line, presumably the ring pulsation mode, is sharp at 910 cm^{-1} in the solid, but broad at 925 cm^{-1} with a shoulder at 910 cm^{-1} in solution. These lines are also seen in the ir spectra. The strongest Raman line of the related but conformationally homogeneous 1,3,5-trioxane is single at 960 cm^{-1} both in the solid and in solution.[6] The magnitude of the observed dipole

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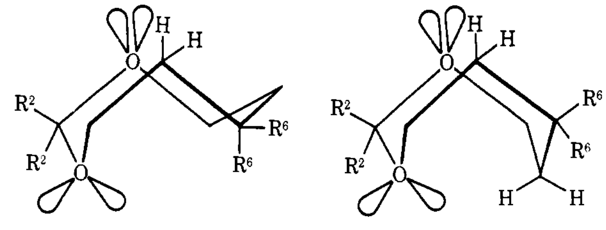

Figure 1.

moment (2.58 D) at a temperature (25°) where the less polar conformer is dominant suggests that this also has a sizable dipole moment. We conclude that the quartet represents a crown conformation; its low entropy suggests that it is rigid and symmetric as in the crystal. The single nmr line of the second conformer and its high entropy might have indicated a twist–boat of S_4 symmetry averaged to a boat–boat of D_{2d} symmetry. However, the ring pulsation should then be infrared inactive and the dipole moment zero. It therefore seems more likely that we have to do with a "pseudorotating" boat–chair family, which should have produced an nmr quartet at sufficiently high resolution. Apparently, transannular lone-pair interaction is still repulsive enough to disfavor the boat–boat.

The cyclic formal II having an extra ether oxygen in the 6 position gives at 100 MHz a single high-temperature nmr line for the 2-protons, which on cooling is observed to broaden and split into a quartet ($\Delta\nu_{AB} = 89$ Hz, $J = 8$ Hz) and a single line, the other protons giving a complex pattern. The coalescence temperature (−50°) is lower than for tetraoxacyclooctane, and the intensity ratio is about 1:1 and does not change on further cooling down to −100° in CS_2 and $CHFCl_2$ solution. The same mixture must be present also in the liquid, since the infrared spectrum shows the same sharp bands as do CS_2 solutions from +40 to −100°. The dipole moment (1.31 D) gives no further information, but clearly 1,3,6-trioxacyclooctane has two equienthalpic and equientropic conformers. Again, a crown is suggested for the "quartet" conformer and a boat–chair for the "singlet" conformer, the essential difference from the previous ring system being that the constitutional symmetry does not fit a symmetrical crown conformation so that "pseudorotation" may occur through all members of the crown family. Its entropy is thereby increased, while the entropy of the boat–chair on the other hand may be decreased by transannular CH–O interactions.

Of the four 1,3-dioxacyclooctanes III, those with *gem*-dimethyl substitution at carbon 2 or 6 or both (IIIb–d) have observable coalescence phenomena but at still lower temperatures (−80, −120, and −70°). The low-temperature nmr spectra all indicate a single conformer, as do the sharp and temperature invariant ir bands. The low observed dipole moments ($\lesssim$ 1.0 D) strongly suggest that only conformations having +gauche,+gauche orientation of the two CO bonds around the 2-carbon, such as the boat–chair and boat–boat (Figure 1), should be considered, since we find a dipole moment of 0.99 D for dimethoxymethane, which is known[7] to have exclusively this conformation. For 1,3-dioxane with +gauche,−gauche orientation the dipole moment is as large as 1.9 D, while the conformationally intermediate 1,3-dioxolanes have intermediate values.[8] The lower values observed when the 2-carbon is *gem*-dimethyl substituted (0.58 and 0.61 D for IIIb and d, as compared with 0.73 and 1.00 D for IIIa and c) is presumably a consequence of a more perfect bond staggering and a more nearly tetrahedral OCO angle, and in accord with the observed moment of 0.61 D for 2,2-dimethoxypropane. When the 6 position is *gem*-dimethyl substituted (IIIc,d), the boat–chair conformation becomes impossible[9] if the oxygen atoms are to occupy the positions indicated by the dipole moments (Figure 1). The boat–boat conformation is in these cases further supported by the single nmr line for the 2-hydrogens or 2-methyls and by the stronger splitting of the 5- (and 7-) CH_2 than the 4- (and 8-) CH_2 protons. One of the 5-hydrogens is internal, the other external, while the 4-hydrogens occupy corner positions. For the 2-*gem*-dimethyl-substituted compound IIIb the two arguments above apparently contradict each other; although there is only one methyl signal, the 4- (and 8-) CH_2 protons now split more than the 5- (and 7-) CH_2 protons. It seems most likely that the single conformation of this dioxacyclooctane, as well as of the unsubstituted one (IIIa), with also no observable splitting of the 2-CH_2 protons, is a boat–chair with accidental degeneracy of the 2-methyls or 2-hydrogens, since the local symmetry is here nearly that of a twofold axis as in the boat–boat (Figure 1).

To favor the boat–boat over the boat–chair it thus seems insufficient to build into the eight-membered ring the 1,3-dioxa grouping with its favorable dipole orientation across a +gauche,+gauche corner and the possibility of two transannular CH–O interactions. It seems also necessary to have geminal substitution in the 6 position, while such substitution is not needed in the 2 position.

The synthesis of the 1,3-dioxacyclooctanes III and of the corresponding doubling products, the 1,3,9,11-tetraoxacyclohexadecanes, will be reported elsewhere.

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The Conformation of Eight-Membered Oxygen Heterocycles (Oxocanes). Evidence from 251-MHz ^{1}H Nuclear Magnetic Resonance

Sir:

The successive replacement of methylene groups in cycloctane by oxygen atoms is expected to have unusual conformational effects, because of the small size and