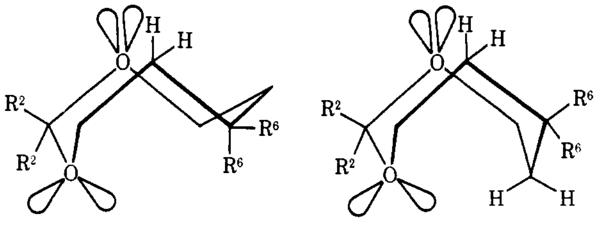

Figure 1.

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.

Acknowledgment. We are grateful to Professor F. A. L. Anet and Mr. P. J. Degen for having communicated to us their results on some of these compounds.[10] We also thank Professor J. M. Lehn for the use of his Varian XL-100 instrument and Dr. T. Drakenberg for technical advice.

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* Address correspondence to this author at: Department of Chemistry, Brandeis University, Waltham, Mass. 02154.

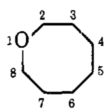
Johannes Dale,* Terje Ekeland, Jostein Krane
Kjemisk Institutt, Universitetet i Oslo
Oslo 3, Norway

Received November 8, 1971

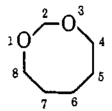
The Conformation of Eight-Membered Oxygen Heterocycles (Oxocanes). Evidence from 251-MHz ^{1}H Nuclear Magnetic Resonance

Sir:

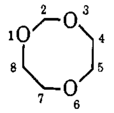
The successive replacement of methylene groups in cycloctane by oxygen atoms is expected to have unusual conformational effects, because of the small size and polar nature of the ether function.[1] We have, therefore, investigated by nmr spectroscopy the conformations of the following compounds: oxocane (I);



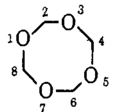
I



II



III



IV

1,3-dioxocane (II); 1,3,6-trioxocane (III); and 1,3,5,7-tetroxocane (formaldehyde tetramer) (IV).

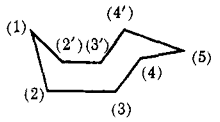
It has been reported[2] that the 60-MHz ^1H nmr spectrum of oxocane does not show evidence for slow ring inversion down to −160° and that the barrier to ring inversion in oxocane therefore appears to be much lower than in cyclooctane. We have now reinvestigated the nmr spectrum of oxocane at a higher spectrometer frequency, namely 251 MHz.[3] At 25°, the protons on C-2 and C-8 of oxocane[4] give a rough 1:2:1 triplet (spacing $\simeq$ 6 Hz) at τ 6.37 while all the other protons give rise to a broad band at 8.38. The triplet broadens at low temperature, and at −147° it is replaced by two well-separated broad singlets, while the high-field portion of the spectrum is transformed into three broad bands at τ 8.16, 8.27, and 8.52. Thus, ring inversion in oxocane is slow on the nmr time scale at −147°, and the free-energy barrier ($\Delta G^{\ddagger}$) for this process at the coalescence temperature (see Table I) is 7.4 kcal/mol, only slightly lower than the 8.1 kcal/mol barrier[5] in cyclooctane. The failure to obtain evidence for slow ring inversion at 60 MHz is not surprising in view of the small chemical-shift difference ($\simeq$10 Hz) of the strongly coupled C-2 and C-8 methylene protons at this lower spectrometer frequency.

Table I. Nmr (251 MHz) and Kinetic Parameters for Oxocanes

Compd	Solvent	$\Delta\nu^a$ (temp, °C)	Coalescence (temp, °C)	$\Delta G^{\ddagger\,b}$
I	2:1 $CHCl_2F$–$CHClF_2$	44^c (−147)	−122	7.4
II	2:1 $CHCl_2F$–$CHClF_2$	33^d (−143)	−125	7.3
		70^c (−168)	−155	5.7
III	$CHCl_2F$	220^d (−100)	−81	8.7
		17^d (−150)	−135	6.8
IV	$CHCl_2F$	160^d (−38)	−15	12.0

[a] Chemical-shift differences in hertz at the temperatures indicated in parentheses. [b] In kcal/mol; calculated from absolute rate theory from rough rate constants obtained at the coalescence temperatures; estimated error ±0.3 kcal/mol. [c] $\Delta\nu$ for protons on C-2 and C-8 in I and C-4 and C-8 in II. [d] $\Delta\nu$ for protons on C-2.

Present evidence strongly supports the boat–chair conformation for cyclooctane and its simple derivatives, including cyclooctanone and methylenecyclooctane.[5–11] In the following discussion, we use a double labeling system with numbers in parentheses to indicate positions in the boat–chair (BC) conformation (see below), and ordinary numbers to indicate carbon atoms and their attached hydrogen atoms (see structures I–IV).

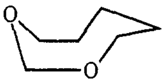


boat-chair

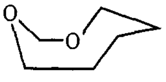
The replacement of a CH_2 group by an oxygen atom in the BC conformation of cyclooctane should lead to a large decrease in nonbonded (transannular) repulsion for positions (1), (3), and (3′), and, to a lesser extent, for positions (4) and (4′). The present nmr results on oxocane can be rationalized on the basis of the BC(1) form (*i.e.*, oxygen at the (1) position) since this form has a plane of symmetry and can give rise to but a single degenerate conformational process, namely ring inversion. The BC(3) and BC(3′) forms are mirror images and should give rise to two conformational processes, as are observed in cyclooctanone.[5] Since only one process is observed in oxocane, the BC(3)–BC(3′) forms would have to interconvert very rapidly even at −150° and this appears rather unlikely, although not impossible. Additionally, arguments based on the rotational barrier in the fragment OCH_2 can be made to support the BC(1) form. Oxocane therefore most likely exists in the BC(1) form, and in this respect is similar to methylenecyclooctane.[5]

The 251-MHz spectrum of 1,3-dioxocane[12] (II) consists of a sharp singlet at τ 5.35 and somewhat broadened singlets at 6.28 and 8.30. Upon lowering the temperature, the low-field signal transforms into a narrow AB quartet and the signals at τ 6.28 and 8.30 become broad two- and three-line patterns, respectively. At still lower temperatures, the low-field AB quartet remains unchanged but a second transformation takes place in the high-field portion with the signal at τ 6.28 (C-4 and C-8 methylenes) appearing as two broad lines with approximate relative intensities of 1:3. Thus, two conformational processes can be identified in II, and relevant coalescence temperatures and barriers are given in Table I.

The boat–chairs with oxygens at the (1) and (3) or (1) and (3′) positions [BC(1)(3) and BC(1)(3′), respectively] account nicely for the nmr results on 1,3-



BC(1)(3)



BC(1)(3′)

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[1] For example, *cis*-2-methyl-5-*tert*-butyl-1,3-dioxane exists almost exclusively in a chair conformation with the *tert*-butyl group axial, whereas the corresponding hydrocarbon would undoubtedly have that group equatorial: E. L. Eliel and M. C. Knoeber, *J. Amer. Chem. Soc.*, **88**, 5347 (1966).

[2] L. A. Paquette and R. W. Begland, *J. Org. Chem.*, **32**, 2723 (1967).

[3] The spectra were obtained on a superconducting solenoid nmr spectrometer: F. A. L. Anet, G. W. Buchanan, and C. H. Bradley, Eleventh Experimental NMR Conference, Pittsburgh, Pa., April 1970.

[4] F. Nerdel, J. Buddrus, W. Brodowski, and P. Weyerstahl, *Tetrahedron Lett.*, 5385 (1966).

[5] F. A. L. Anet and M. St. Jacques, *J. Amer. Chem. Soc.*, **88**, 2585, 2586 (1966); F. A. L. Anet in "Conformational Analysis," G. Chiurdoglu, Ed., Academic Press, New York, N. Y., 1971, p 15; F. A. L Anet, M. St. Jacques, and P. M. Henrichs, *Intra-Sci. Chem. Rep.*, **4**, 251 (1970).

[6] J. E. Anderson, E. S. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 1386 (1969).

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dioxocane. Interconversion of these forms, a process analogous to pseudorotation in cyclooctane, does not lead to mutual exchange of the two protons on C-2, but does lead to exchange of C-4 with C-8, and C-5 with C-7. As expected, the barrier (5.7 kcal/mol) for this process is lower than that (7.3 kcal/mol) for ring inversion. The conformational picture here is analogous to that of cyclooctanone, which shows corresponding barriers of 6.3 and 7.5 kcal/mol. Interestingly, the dihedral angles in the conformations given above for the fragment $CH_2OCH_2OCH_2$ correspond to those found in dimethoxymethane[13] and thus represent a low-energy geometry.

The two remaining compounds, 1,3,6-trioxocane (III)[14] and 1,3,5,7-tetroxocane (IV),[15] show rather similar behavior in that each exists as a mixture of two conformations in solution. The proton spectrum of III at 25° consists of two sharp singlets at τ 5.25 and 6.45 with relative intensities of 1:4. Upon cooling, the signals broaden and by −100° the low-field line has changed into a widely spaced AB quartet which contains within it a sharp singlet. The AB quartet represents one conformer (A), where ring inversion is slow, and the singlet a second conformer (B), where ring inversion is rapid. At the same temperature (−100°), the high-field pattern consists of an intense singlet superposed on a multiplet. At still lower temperatures (−150°), the low-field singlet of conformer B becomes a narrowly spaced AB quartet, while changes in the high-field line are obscured by extensive overlap with signals from conformer A. The ratio ($\simeq$1:1) of these two conformations shows essentially no temperature dependence from −100 to −150°.

At 25°, the proton spectrum of 1,3,5,7-tetroxocane (IV) consists of a broad line at τ 4.96 which sharpens markedly on heating to 40°. As the temperature is lowered to −40° the spectrum of IV changes to a widely spaced AB quartet (conformation A) and a singlet (conformation B) near the center of the quartet. Although the singlet broadens somewhat near −160° it does not become a resolved AB quartet as does the rather similar singlet of III under the same conditions. Also, in contrast to III, the relative intensities of the forms A and B are strongly temperature dependent, indicating an entropy difference of 6 ± 2 eu, with the A form favored at low temperatures. At −86°, $K(\mathrm{A} \rightleftharpoons \mathrm{B})$ is 0.17.

With III and IV, boat-chairs should become less favorable, because of repulsions between transannular oxygen atoms. The widely spaced AB quartets in the A forms of III and IV are in striking contrast to the narrowly spaced AB quartets of II and the B forms of III and IV. Tentatively, more or less twisted boat-chairs are assigned to the B conformations. The A forms of III and IV likely are twist chair–chair and symmetrical crown forms, respectively.[16,17] Further experiments, including the determination of ^{13}C spectra, are in progress.

Acknowledgments. We thank Professor J. Dale and Drs. T. Ekeland and J. Krane for informing us of their results[18] on some of the compounds discussed in the present paper. We also thank the National Science Foundation and the United States Public Health Service for support of this research.

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(15) Y. Miyake, S. Adachi, N. Yamauchi, T. Hayashi, and M. Akimoto, U. S. Patent 3,426,041 (1969); *Chem. Abstr.*, 70, 87867 (1969).

(16) These assignments are consistent with the large entropy difference between the A and B forms of IV, since the crown form of IV has a C_4 axis, whereas the twisted boat–chair has no symmetry axes and furthermore exists in *d* and *l* forms. The entropy difference resulting from these symmetry affects is 3R ln 2 or 4.2 eu, with the A form of lower entropy, as found experimentally.

(17) X-Ray diffraction studies on three different saturated eight-membered rings with heteroatoms in the 1, 3, 5, 7 positions show that these compounds possess crown conformations: L. Pauling and D. C. Carpenter, *J. Amer. Chem. Soc.*, **58**, 1274 (1936); D. Grandjean and A. Leclaine, *C. R. Acad. Sci.*, **265**, 795 (1967); H. Schenck, *Acta Crystallogr., Sect. B*, 27, 185 (1971). A tetrabromocyclooctane, on the other hand, has been found to have a twist chair–chair conformation: G. Ferguson, D. D. MacNicol, W. Oberhanshi, R. A. Raphael, and J. A. Zabkiewicz, *Chem. Commun.*, 103 (1968).

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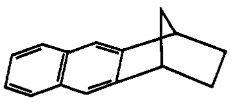
F. A. L. Anet,* P. J. Degen
Contribution No. 2883
Department of Chemistry, University of California
Los Angeles, California 90024

Received November 22, 1971

A Spectroscopic Study of Some Dibromonaphthonorbornenes. A Possible Case of "Inverse" External Heavy Atom Induced Spin Orbital Coupling[1]

Sir:

We report a study at 77°K in EPA of the fluorescence and phosphorescence of the dibromonaphthonorbornenes **2–5**. A comparison of these new data with those formerly reported[2] for **6**, **7**, and **8** reveals interesting and unexpected effects on spin orbital coupling when two external heavy atoms perturb the naphthalene chromophore.



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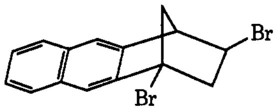

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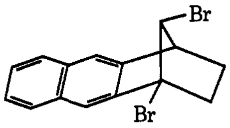

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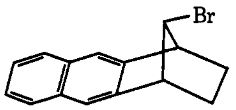

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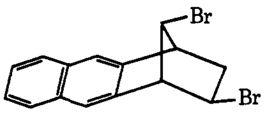

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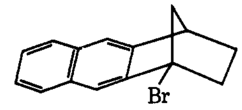

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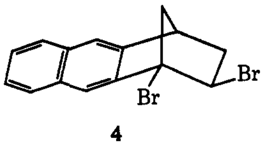

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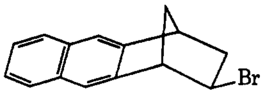

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(1) (a) Molecular Photochemistry. LI. Paper L: A. Yekta and N. J. Turro, *Mol. Photochem.*, 3, 307 (1972). (b) The authors wish to thank the Air Force Office of Scientific Research for its generous support of this work (Grant No. AFOSR-70-1848).

(2) G. Kavarnos, T. Cole, Jr., P. Scribe, J. C. Dalton, and N. J. Turro, *J. Amer. Chem. Soc.*, 93, 1032 (1971).