NMR Studies on Cyclic Arsenites. Geometric Isomerism in Methyl-substituted 2-Chloro- and 2-Methoxy-1,3,2-dioxarsenanes

DAGFINN W. AKSNES and SVEIN TØGERSEN
Department of Chemistry, University of Bergen, Allegaten 70, 5014 Bergen-The University, Norway

In two recent papers, the NMR spectra of several arsenanes have been studied. As a continuation of previous work we have prepared the following eight methyl-substituted 1,3,2-dioxarsenanes and investigated their NMR spectra:

\[ \text{X} = \text{Ar}_2 \]

- I: \( X = \text{Cl}, \quad R_1 = R_4 = \text{H} \)
- II: \( X = \text{Cl}, \quad R_1 = \text{H}, \quad R_4 = \text{CH}_3 \) (cis methyl)
- III: \( X = \text{Cl}, \quad R_1 = \text{CH}_3, \quad R_4 = \text{H} \) (trans methyl)
- IV: \( X = \text{Cl}, \quad R_1 = R_2 = \text{CH}_3 \)
- V: \( X = \text{OCH}_3, \quad R_1 = R_4 = \text{H} \)
- VI: \( X = \text{OCH}_3, \quad R_1 = \text{H}, \quad R_4 = \text{CH}_3 \) (cis methyl)
- VII: \( X = \text{OCH}_3, \quad R_1 = \text{CH}_3, \quad R_4 = \text{H} \) (trans methyl)
- VIII: \( X = \text{OCH}_3, \quad R_1 = R_2 = \text{CH}_3 \)

The conformational preferences of external substituents on six-membered arsenites have received little attention. The related methyl-substituted arsenanes are, however, configurationally stable about the arsenic atom in the sense that geometrical isomers have been observed. Pairs of geometrical isomers have also been found for 2-methoxy- and 2-ethoxy-4-methyl-1,3,2-dioxaphosphorinane and cis-2-methoxy-4,5-dimethyl-1,3,2-dioxaphosphorinane. It seems, therefore, likely that the prepared arsenanes might exist as a mixture of two geometrical isomers.

Compounds I – IV were prepared according to a procedure of Kamai and Chadaeva, from trichloroarsine and 1,3-butadienol, 2,4-pentanediol, and 2-methyl-2,4-pentanediol as appropriate, in ether solution using triethyl amine as base. The crystalline cis-2-chloro-4,6-dimethyl-1,3,2-dioxarsenane (II) was separated from the liquid trans-dimethyl form (III) in the racemic mixture by fractional distillation at 5.5 mmHg pressure.

Treatment of compounds I – IV with methanol in ether solution in the presence of excess triethylamine yielded the corresponding methoxy derivatives. All compounds were purified by vacuum distillation. The boiling points and melting points of the prepared compounds are listed in Table 1 together with the chemical shifts of the C – CH\(_3\) protons.

A broadening and partial collapse of the NMR spectrum for a neat sample of III was observed. Dilution of the sample in benzene reduced the broadening considerably. We therefore believe in accord with previous conclusions, that the broadening is due to intermolecular exchange of chlorine.

<table>
<thead>
<tr>
<th>Compound</th>
<th>B.p. °C</th>
<th>M.p. °C</th>
<th>( n_D )</th>
<th>Chemical shifts δ°</th>
<th>Me4c</th>
<th>Me4e</th>
<th>Me4a</th>
</tr>
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<tr>
<td>I</td>
<td>34 – 38(^a)</td>
<td>20 – 21</td>
<td>1.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>II</td>
<td>60</td>
<td>38 – 39</td>
<td>1.21</td>
<td>1.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>66</td>
<td></td>
<td>1.5095</td>
<td>1.20</td>
<td>1.42</td>
<td></td>
<td></td>
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<tr>
<td>IV</td>
<td>45 – 47(^b)</td>
<td></td>
<td>1.4958</td>
<td>1.33</td>
<td>1.38</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>43 – 44</td>
<td></td>
<td>1.4674</td>
<td>1.55</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>VI</td>
<td>49 – 50</td>
<td></td>
<td>1.4613</td>
<td>1.05</td>
<td>1.05</td>
<td></td>
<td></td>
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<tr>
<td>VII</td>
<td>52 – 53</td>
<td></td>
<td>1.4701</td>
<td>1.18</td>
<td></td>
<td>1.39</td>
<td></td>
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<tr>
<td>VIII</td>
<td>39 – 40(^a)</td>
<td></td>
<td>1.4627</td>
<td>1.15</td>
<td>1.20</td>
<td>1.46</td>
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\(^a\) 0.3 mmHg. \(^b\) 0.05 mmHg. \(^c\) From first-order analysis.
Fig. 1. The 60 MHz NMR spectrum of compound V in benzene solution (ca. 50% v/v). Upper trace: a freshly prepared sample; lower trace: the same sample after about one month.

infra) we believe that the investigated molecules are a mixture of two principal chair forms A and B differing essentially in the orientation of the substituent on arsenic. On basis of 1,3-steric interactions the B structure would seem more probable than A; however, in the related phosphites and sulfites a strong preference for axial 2-substituents has been reported (anomeric effect). Hence, a possible contribution from the C conformer must also be considered.

When $R_1 = \text{CH}_3$ and $R_2 = \text{H}$ the A and C conformers are identical. In general, however, conformer A is certainly more stable than C which makes a negligible contribution when $R_4 = \text{CH}_3$ owing to severe diaxial methyl-interactions. The 1,3-non-bonded interactions are probably greatly reduced in A compared to the analogous phosphorinane ring as previously explained. The above evidence thus indicates that A is the thermodynamically more stable form.

The NMR spectra of compounds I–IV showed the presence of only one isomer. A large vicinal coupling constant (10–12 Hz) observed in compounds I, II, and IV is typical for an axial-axial coupling in a chair conformation. We therefore believe that these compounds are formed mainly in one preferred configuration which corresponds to the thermodynamically more stable form A. The low-field doublets at 1.42 ppm and 1.59 ppm have been assigned to the axial methyl hydrogens at the 6 position in III and IV, respectively. The remaining doublets at higher field are due to the equatorial methyl groups at the 4 and 6 positions. In particular, the high-field methyl signal at 1.25 ppm in I indicates a preference for an equatorial methyl group in accord with previous results for the corresponding chlorophosphate. The observation that the NMR signals of axial methyl protons appear at lower field than equatorial methyl signals agrees with previous results for related systems.

The NMR spectra of freshly prepared samples of the methoxy derivatives showed that these molecules existed almost entirely in one form (Fig. 1). These compounds appeared to be unstable, however, since the presence of a new species was observed after some time. About 30% of this new species was found for V (Fig. 1) whereas smaller amounts were observed for the other methoxy compounds. The rate of conversion into the new material also seemed to be acid catalyzed. These results are most readily explained by assuming that the methoxy compounds are a mixture of geometrical isomers A and B (possibly in equilibrium with C).

The preparation of V–VIII via the cyclic chloro-compounds is thus expected to give the unstable isomer B in nearly pure form. We believe, in accord with previous results for the related phosphites that this process involves an inversion about the arsenic atom as a result of an $S_{N2}$ reaction.

The large axial-axial coupling constants (10.4–12.3 Hz) observed in the unstable forms of V, VI, and VIII again indicate measurable

amounts of only one chair conformation. In VII, however, the vicinal coupling constants spanning from 3.1 to 8.4 Hz, appear to be time-averaged values resulting from an equilibrium between B and C in which C predominate.

Again the axial methyl proton signals appear at lower field than the corresponding equatorial methyl signals. The methyl signal of V (Fig. 1) clearly demonstrates that axial and equatorial methoxy substituents at arsenic give rise to different stereo-specific substituent effects.

Experimental. The 60 MHz NMR spectra of the eight compounds were examined in benzene solutions (ca. 50 % v/v for the liquid compounds). A small amount of TMS was added and used as internal standard and look signal source. The spectra were run at ambient probe temperature (ca. 30 °C) on a JEOL-C-60H spectrometer.


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Conformational Energies and Conversion Barriers for Cyclononane

STEINAR RUSTAD and HANS M. SEIP

Department of Chemistry, University of Oslo, Oslo 3, Norway

A novel approach to semiquantitative calculations of conformational energies of C_9-C_{14} cycloalkanes has been suggested by Dale. The method is based on the reasonable assumptions that the bonding energies are of minor importance and that and the main part of the non-bonded interactions can be included in the torsional potentials. According to Dale, cyclononane has three conformations which he denoted [333] (D_3 symmetry), [234] (C_1) and [12222] (C_2) of Fig. 1). He found [333] to be the most stable form, [234] and [12222] were found to be 1.4 and 2.8 kcal mol^{-1} less stable, respectively. We used these results as a starting point for the present, more accurate calculation. Results for an additional conformation with C_3 symmetry considered by Bixon and Lifson, are also included.

The conformational energies were calculated according to the method first applied by Westheimer, and later used by many others in various versions. A combination of the steepest-descent and the Newton-Raphson method was used to obtain the energy minima. The computer program was written by one of us (S.R.) in FORTRAN EXTENDED for CYBER 74. A subroutine for calculating the dependent structural parameters for the molecule must be provided.

For cyclononane we used the cartesian coordinates for the carbon atoms as independent parameters. The van der Waals energy was calculated as described by Eliel et al., with the necessary constants from their book (p. 452). The intrinsic barrier to torsion about a CC bond was given the value 2.65 kcal mol^{-1}. The CCC angle was assigned the normal value 112° and the bending force constant 1.086 mdyn Å rad^{-1}. The normal value and the stretching force constant for a CC bond were taken as 1.535 Å and 4.534 mdyn Å^{-1}. The CH bond lengths and the HCH angles were kept at the fixed values 1.113 Å and 112°. The planes through HCH were assumed perpendicular to the planes through CCC, bisecting the CCC angles. No symmetry restrictions were imposed on the models during the minimalization. The iteration procedure was terminated when the absolute value of the shifts in the independent parameters were less than 10^{-2} Å.

Table 1 gives the calculated conformational energies and the corresponding torsional angles and bond angles. Results obtained by Dale and by Bixon and Lifson are also included. The agreement is quite good. As in previous calcula-