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PMR LINE-BROADENING OBSERVATION OF A SWINGING AND OF A PSEUDOROTATORY CONFORMATIONAL INTERCHANGE IN AN OCTANO-BRIDGED OXA-QUADRICYCLANE.

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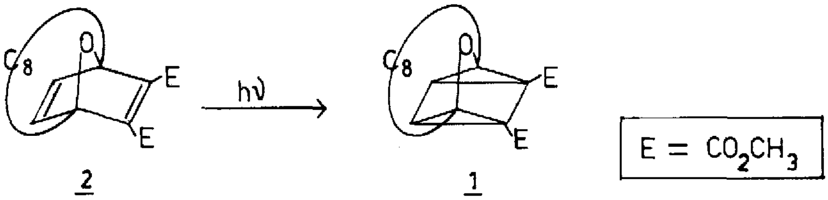
Our interest in the mechanism of metal- and acid catalyzed reactions of oxa-quadricyclanes has brought us to a 3-oxa-quadricyclane in which the oxygen atom is shielded by a methylene chain of 8 C-atoms. For this purpose we synthesized[1] 2,4-octano-1,5-dicarbomethoxy-3-oxa-quadricyclane (1) by intramolecular photocyclization of the corresponding oxa-norbornadiene (2).[2] In the present communication we report the results of a PMR spectroscopic investigation of compound 1, which shows the existence of two conformational interchanges of the octano-bridge.



At +35°C the PMR spectrum of 1 consists of two singlets at δ 3.66 (6H) and δ 2.55 (2H) - arising from the ester hydrogens and the tertiary hydrogens respectively - and three multiplets at δ 1.95-2.10 (4H), δ 1.45-1.84 (8H) and δ 1.19-1.45 (4H) - due to the octano-chain hydrogens. The signal at δ 2.55 has

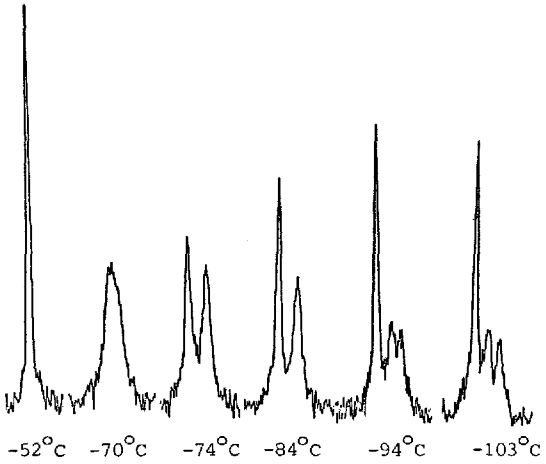


Figure 1. 100 MHz PMR recordings of the two-hydrogen signal at δ 2.55 of 1 in CS_2 at various temperatures (Sweep width 500 cps)

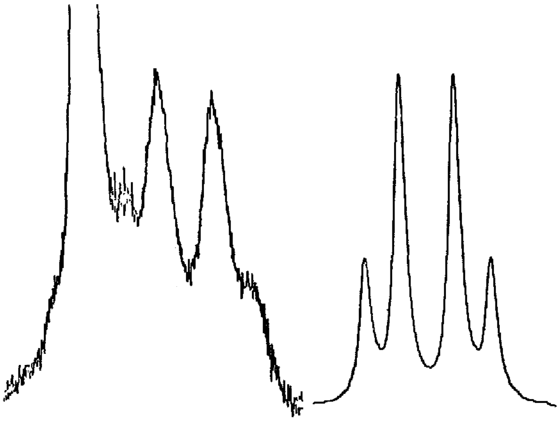
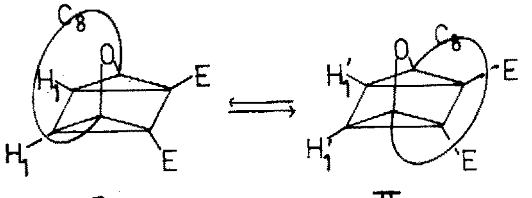


Figure 2. 100 MHz PMR signal of 1 centered around δ 2.55 at -103°C and the simulated AB pattern (Sweep width 100 cps)

been recorded at various temperatures as shown in Figure 1.[3] As one observes, at -52°C there is still one sharp signal, which at lower temperatures starts to broaden. Coalescence occurs at -70°C and at -74°C two singlets are observed at δ 2.59 and δ 2.52. The free-enthalpy of activation at the coalescence temperature is estimated[4] to be $G^{\ddagger}_{203}$ = 10.6 kcal/mole. Upon further lowering of the temperature the low-field singlet at δ 2.59 remains sharp, whereas the high-field singlet at δ 2.52 becomes broader, (see Figure 1, -84°C) which indicates, that another line-broadening process is starting to operate. At -94°C the signal is split up. Expansion of the spectrum at -103°C shows that an AB pattern is present (see Figure 2). The chemical shift difference between A and B is 6.6 Hz and the coupling constant J_{AB} is 2.6 Hz.[5] At the coalescence temperature (-90°C) the free-enthalpy of activation is estimated[4] to be $G^{\ddagger}_{183}$ = 9.4 kcal/mole.

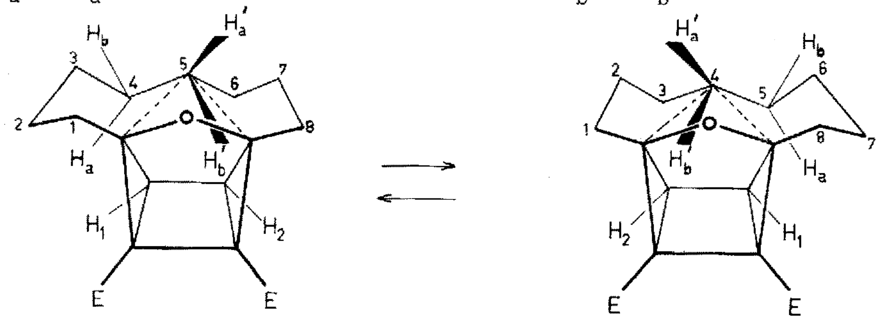
The first line-broadening process is ascribed to a swinging of the polymethylene chain over the oxygen atom as depicted in Figure 3. In the literature, examples of such processes have been reported previously for a furanophane,[6a] for [n](1,3)-cyclophanes[6b,c] and for the oxa-norbornadiene 2 (E=CN).[2a] At temperatures below -70°C the two conformers I and II interchange so slowly, that they are observed separately in the PMR spectrum of compound 1, since the two equivalent hydrogens H_1 in I are different from the two equivalent hydrogens H_1' in II. The fact that the observed signals at δ 2.52 and δ 2.59 are of almost equal intensity indicates that there is hardly any steric interaction between the octano-ring hydrogens and the ester-substituents.



I II

Figure 3. Interconversion of conformers I and II by a swinging mode of the octano-chain.

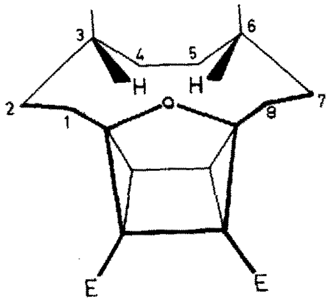
The second line-broadening process, which leads to the AB pattern centered around δ 2.52, is ascribed to a conformational change by a pseudorotatory process in I, which is shown in Figure 4.[7] The conformational change is believed to proceed as follows: starting from III, H_a' moves downwards along the oxygen atom, whereas H_a moves in the opposite direction, to reach IV, in which the original positions of H_a and H_a' (and, of course, also the positions of H_b and H_b') have been interchanged. This



III IV

Figure 4. Degenerate interconversion of conformers III and IV by pseudorotation in the octano-bridge. (The dotted lines complete six- and five-membered rings)

pseudorotation involves the eight carbon atoms of the octano-bridge and is likely to interconvert a cyclohexane ring fragment (chair form) and a cyclopentane ring fragment (puckered) in the way depicted in Figure 4.[8] At sufficiently low temperatures ($< -90^{\circ}C$) this pseudorotation is slow enough, to allow conformers III and IV to be observed separately, as evidenced by H_1 being no longer equivalent to H_2. There are a number of factors which are likely to contribute to the energy barrier of the pseudorotation. Firstly there is a transannular effect in the 11-membered ring between the C-O-C fragment and the hydrogens at C_3, C_4, C_5 and C_6. In the pseudorotation process the hydrogens H_a and H_a' interfere with the C-O bonds. In addition, in the transition state there is an appreciable steric repulsion between the hydrogens of carbon atoms 3 and 6 and the oxygen atom (see Figure 5). Secondly, during the pseudorotation C-C and C-H eclipsing occurs in the octano-bridge (see Figure 5).[9] The observation, that in the oxa-norbornadiene 2 (E=CN) the energy-barrier of pseudorotation is smaller than that in 1 (even at $-100^{\circ}C$ there is no line-broadening due to pseudorotation[2a]), can be explained by the fact that the octano-bridge in compound 2 is less strained than that in compound 1 as shown by Dreiding molecular models.



V

Figure 5. Transition state of the pseudorotation, showing the steric interaction between oxygen and two hydrogens at C_3 and C_6, and the eclipsing C_3-C_4 and C_5-C_6 bonds.

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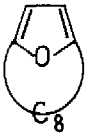
References and Notes.

1. The reactivity of 1 towards acid and metal complexes will be described elsewhere; manuscript in preparation.
2. a. R. Helder and H. Wynberg, Tetrahedron Lett., 1973, 4321; b. H. Hogeveen and T.B. Middelkoop, ibid., 1973, 4325.
3. No definite conclusions from the signals due to the octano-bridge hydrogens can be drawn about the described processes.
4. Values for $k_{coal.}$ of the two processes were estimated by applying the following simplified formules: $k_{coal.} = \pi\delta\nu/\sqrt{2}$ (process I ⇄ II) and $k_{coal.} = \pi\sqrt{(\nu_A-\nu_B)^2 + 6J_{AB}^2}/\sqrt{2}$ (process III ⇄ IV) From these values the $\Delta G^{\ddagger}$ parameters were calculated using the formula: $\Delta G^{\ddagger} = 4.57\,T_{coal.} \times [10.32 - \log k_{coal.}/T_{coal.}]$. H. Günther, "NMR-Spektroskopie", Georg Thieme Verlag, Stuttgart, 1973, p. 240.

5. A similar coupling constant ($J = 2.8$ Hz) is found for 2-methyl-1,5-dicarbomethoxy-3-oxa-quadricyclane. H. Prinzbach, P. Vogel and W. Auge, Chimia 21, 469 (1967).
6. a. H. Nozaki, T. Koyama and T. Mori, Tetrahedron 25, 5357 (1969); b. S. Hirano, H. Hara, T. Hiyama, S. Fujita and H. Nozaki, ibid., 31, 2219 (1975), Tetrahedron Lett., 1972, 403 and Chem. Lett., 1972, 707; c. F. Vögtle, Tetrahedron 25, 3231 (1969).
7. An analogously degenerate conformational interchange will supposedly occur in conformer II, but this change cannot be detected by the PMR signal at δ 2.59. This process can possibly be observed by CMR-spectroscopy.
8. A pseudorotation process has been used by Nozaki et al. to explain the temperature-dependent PMR-spectrum of [6](1,3)-cyclophane.[6b]
9. We feel that these factors can also explain the difference between the temperature-dependent PMR-spectra of the furanophane 3 and thiophenophane 4, as reported by Nozaki et al.[6a] They observed a one-hydrogen signal at δ -1.5 at -100°C in the case of compound 4, whereas, at the same temperature, in the case of compound 3, a two hydrogen signal at δ 0.0 was observed. This indicates that the energy-barrier of pseudorotation in compound 4 is much higher than that in compound 3. In this case the larger Van der Waals radius of sulphur compared to that of oxygen (1.85 and 1.40 Å respectively)[10] and the combined effects of different bond-lengths and bond-angles ($\mathrm{C}^{\diagup\mathrm{S}\diagdown}\mathrm{C}$ 92°; $\mathrm{C}^{\diagup\mathrm{O}\diagdown}\mathrm{C}$ 106°; C-S 1.71 Å; C-O 1.36 Å)[11] may contribute to the factors mentioned in the pseudorotation III $\rightleftarrows$ IV.



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10. Handbook of Chemistry and Physics, 45th edition, 1964-1965. D-90.
11. a. B.Bak, D. Christensen, L. Hansen-Nygaard and I. Rastrup-Anderson, J. Mol. Spectry., 7 58 (1961) (thiophene) b. ibid., 9, 124 (1962) (furan).