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THE BARRIER TO TERT-BUTYL ROTATION IN THE 1,3-DIOXANE SERIES. INFLUENCE OF A SPIRO RING.

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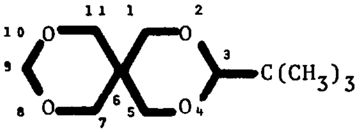
The recent paper[2] by Bushweller's group which reports measured *tert*-butyl rotational barriers in various 1,3-diheteroatomic ring compounds prompt us to disclose our observations on 3-*tert*-butyl-2,4,8,10-tetraoxaspiro(5,5)-undecane (1).



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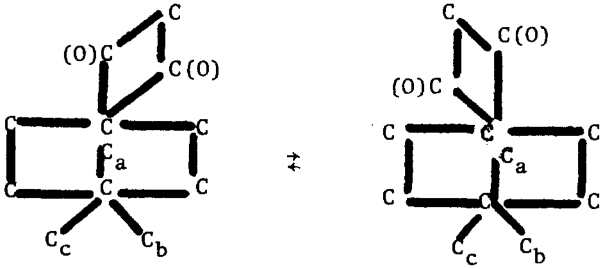
At low temperatures (*ca*. -100°C), in methylene chloride-benzaldehyde (3 : 1 V/V) solution (10%), compound 1 exhibits a pronounced broadening of the *tert*-butyl resonance in the 100 MHz pmr spectrum. We could not achieve low-enough temperatures for resolution of individual methyl resonances in the slow exchange limit[3]. The marked departure from a Lorentzian lineshape[4], taken together with the large difference in linewidth at half-height between the peak in question (29 Hz at -109°C) and that of tetramethylsilane (3.8 Hz at the same temperature) rules out an effect of solvent viscosity. Degassing of the solution to remove dissolved oxygen does not reduce the observed broadening. This very large broadening seen in the *tert*-butyl line of 1 at low temperatures is not reciprocated in the resonance of the 3-methine proton in the same molecule. We checked that the *tert*-butyl resonances of pivalonitrile, 3,3-dimethyl-1-butyne, and 2-*tert*-butyl-5,5-dimethyl-1,3-dioxane all remain sharp at *ca*. -100°C. Slow rotation of the tert-butyl group must then be responsible for the broadening observed.

Computer simulation of the spectrum was performed[5] in order to define simultaneously the limiting chemical shifts in the absence of exchange[3] and the rate of internal rotation. The match between the calculated and observed lineshape was monitored from the linewidths both at one-half and one-eighth the total height. The *tert*-butyl resonance remained symmetric at all temperatures : we could thus assume that one of the methyl groups resonates approximately (± 5 Hz) midway between the other two. Inversion of the second ring in 1 also exchanges methyl groups :



However, the inversion barrier[6] is about 1.3 kcal./mole higher than the rotational barrier (vide infra) and at -105°C tert-butyl rotation is about twenty times as rapid as ring inversion. Ring inversion has a negligible effect on the tert-butyl lineshape. At -105°C[7], a limiting chemical shift difference of 19 Hz is obtained for the outermost methyl protons. The rotational barrier $\Delta G^{\neq} = 8.5 \pm 0.2$ kcal./mole.

This value agrees within experimental error with the result for 2-methyl-2-tert-butyl-1,3-dioxane[2]. Yet, the geminal interaction between the tert-butyl group and a methyl group is absent from molecule 1. Our observation that the tert-butyl group of 2-tert-butyl-5,5-dimethyl-1,3-dioxane does not exhibit line broadening at low temperature supports the idea that the geminal methyl group plays a crucial conformational role in the mono-ring system[2]. In molecule 1, the spiro-junction may pinch the C_1-C_6-C_5 angle somewhat, and this may be coupled to a slight opening and flattening of the O-C_3-O section.

In 2-tert-butyl-5,5-dimethyl-1,3-dioxane, a similar interaction may be reduced by rotation of the axial 5-methyl group. Thus, a flattening of the O-C_3-O section in 1 accompanied by increased steric repulsion in the transition state for tert-butyl rotation appears to be due to conformational transmission of the slight constraint from the spiro-junction.

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(5) We thank Professor Martin Saunders, Chemistry Department, Yale University, for making his multi-site exchange program available to us.

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(7) All temperatures were measured with a coaxial methanol-dimethyl ether probe constructed and calibrated by W.E. Frankle. A complete description can be found in his doctoral dissertation, Princeton University, 1970.