Ring Inversion in Spiro-systems

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Summary Attaching rings of various sizes to a six-membered ring in a spiro-fashion affects the barrier to inversion of the six-membered ring, smaller rings increasing this barrier.

INCREASED bond-angle strain in the transition state makes a substantial contribution to the barrier to inversion of six-membered rings. Hendrickson[1] has calculated this contribution to be 4·1 kcal./mole in the case of cyclohexane, while Allinger and his co-workers[2] suggest 2·0 kcal./mole. Placing a constraint on bond-angle distortion should thus have a marked effect on ring-inversion barriers.

Ring inversion of the compounds (Ia—e) *and* (II)

Compound[a]	*n*	$\delta\nu$[b]	*Tc*[c]	$\Delta G^\ddagger$ [d]
(Ia)	4	47·8	− 77	9·2
(Ib)	5	62·3	− 84	8·8
(Ic)	6	43·1	−100	8·1
(Id)	7	40·4	−106	7·9
(Ie)	8	37·8	−104	8·0[e]
(II)[f]	—	21·5	−100	8·4

[a] (Ia) is 7,7-dimethyl-5,9-dioxaspiro[3,5]nonane. (Ib—e) are similarly named. The solvent was dichlorodifluoromethane except for (II) when it was acetone.[4]

[b] Relative chemical shift in Hz. of the two methyl group signals below the coalescence temperature. Operating frequency 100 MHz.

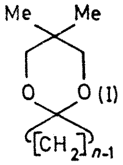
[c] Coalescence temperature of the two methyl group signals, degrees.

[d] Free energy of activation for ring inversion at the coalescence temperature, kcal./mole (±0·1 kcal./mole).

[e] ±0·2 kcal./mole.

[f] Operating frequency 60 MHz.

In the series of compounds (Ia—e), the bond angle at the 2-position of the 1,3-dioxan ring is affected by the size of the second ring. The Table shows barriers to inversion of the dioxan ring (based on coalescence of n.m.r. signals from the geminal dimethyl group as the temperature is raised[3]).



(I)

	n
a	4
b	5
c	6
d	7
e	8

The barriers found are spread around that for 2,2,5,5-tetramethyl-1,3-dioxan (II)[4] in a consistent way. The more strained the ring attached to the dioxan, the more that ring opposes changes from the stable chair conformation of the dioxan ring, *i.e.*, the higher the barrier to inversion of the dioxan ring.

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