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CONFORMATIONAL MOBILITY OF THE 1,3,2-DIOXAPHOSPHORINAN RING SYSTEM

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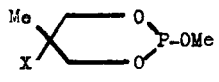
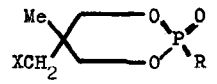
The temperature - independence of the ^1H n.m.r. spectra of 5,5-dimethyl-2-methoxy-1,3,2-dioxaphosphorinan (I; X = Me) and related cyclic esters of trivalent phosphorus is regarded as indicative of the conformational immobility of the ring and the lack of inversion at phosphorus (1 - 5). The view has also been expressed elsewhere (6 - 9) that the 1,3,2-dioxaphosph(V)orinan ring is similarly rigid, e.g. the ^1H spectrum of 5,5-dimethyl-2-oxo-2-piperidino-1,3,2-dioxaphosphorinan (II; X = H, R = $C_5H_{10}N$) is essentially unchanged between $-35^\circ C$ and $+100^\circ C$.



(I)



(II)

Evidence is now presented to indicate that the 1,3,2-dioxaphosph(V)orinan system can be conformationally mobile. The ring methylene region of the ^1H n.m.r. spectrum of trans-5-bromomethyl-2,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan (II; X = Br, R = Me) in deuteriochloroform (δ CMe 1.13, δ PMe 1.60, δ CH_2Br 3.53 p.p.m.) and in deuterio-acetone (δ CMe 1.02, δ PMe 1.57, δ CH_2Br 3.78 p.p.m.) shows pronounced changes with variation in temperature (Figs. 1 and 2). The cis isomer (δ CMe 0.98, δ PMe 1.60, δ CH_2Br 3.63 p.p.m. in $CDCl_3$)behaves similarly spectroscopically. For both stereoisomers, and also for other compounds described, the chemical shifts of groups attached at C-5 and at phosphorus show a movement to lower fields with lowering of temperature.

By contrast, the proton spectra of cis- and trans-2-benzyl-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan (II, X = Cl, R = CH_2Ph) and the stereoisomeric tosyl derivatives (II; X = $MeC_6H_4SO_3$, R = CH_2Ph) show no changes for $CDCl_3$ solutions between $-30^\circ C$ and $+30^\circ C$ other than a slight broadening of bands. Calculations such as those performed elsewhere (6) would indicate that pronounced changes in the spectra of the ring

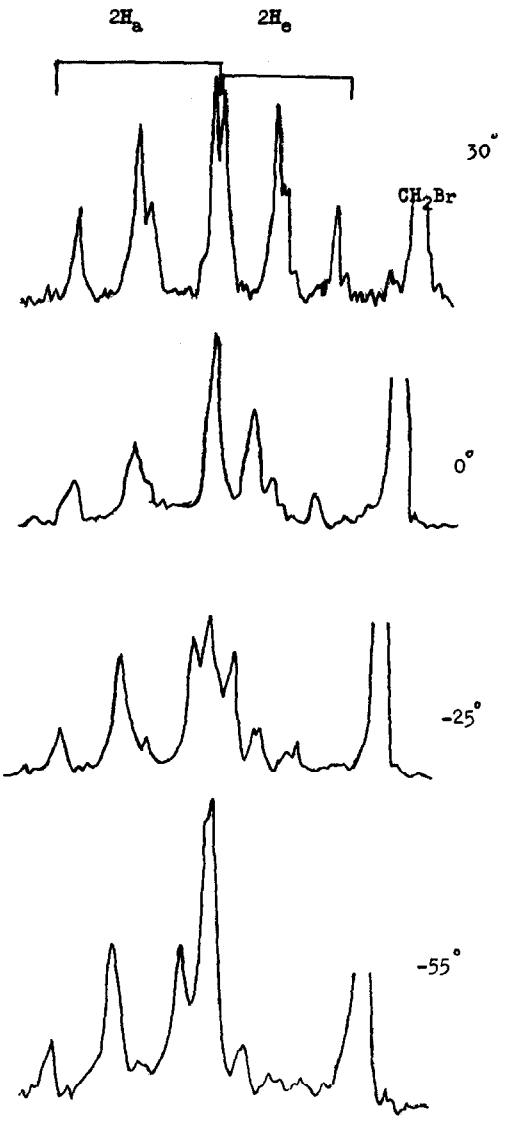


Fig. 1 (in $CDCl_3$)

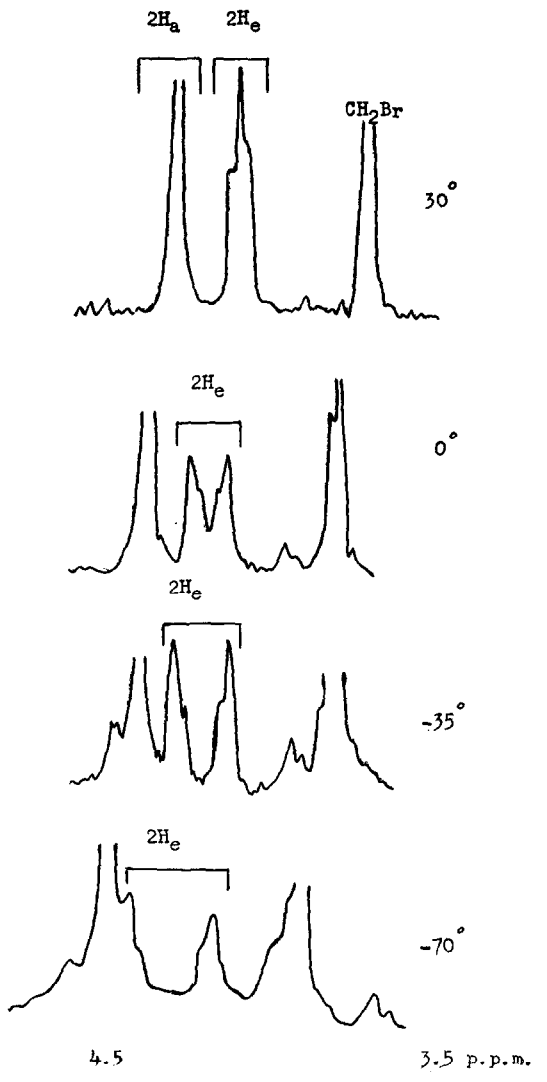


Fig. 2 (in CD_3COCD_3)

Spectra of trans-5-bromomethyl-2,5-dimethyl-2-oxo-1 3.2-dioxaphosphorinan.

methylene groups might be expected with the retardation of conformational flipping involving movement of a benzyl group from axial to equatorial position (or vice versa) with concomitant changes in the shielding of methylene protons by the benzene ring.

It could be argued that for the phosphite (I; X = Me) with only two possible differing conformations (methoxyl group axial or equatorial), changes in $|J_{POCH_{eq.}}|$

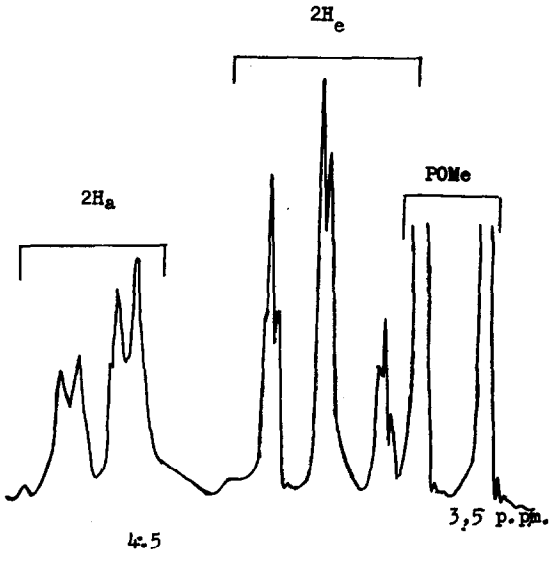


Fig. 3 (Isomer 1)

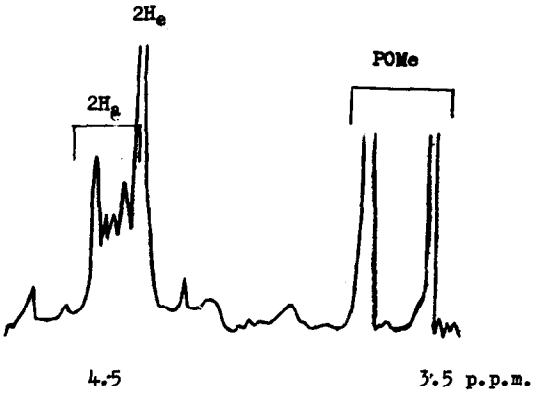


Fig. 4 (Isomer 2)

Spectra of 2-methoxy-5-methyl-5-nitro-1,3,2-dioxaphosphorinan

and $|J_{POCH_{ax.}}|$ might be insufficient to produce observable changes in the spectra of the ring methylene region, and hence that the conformational stability was apparent rather than real. The two stereoisomers of 2-methoxy-5-methyl-5-nitro-1,3,2-dioxaphosphorinan (prepared from partially separated stereisomeric phosphorochloridites and purified by chromatography) exhibit totally different ^{1}H n.m.r. spectra (Figs. 3 and 4). Structurally, they must differ in conformation at C-5. From the known shielding behaviour of the nitro group (10, 11) we suggest that isomer 1 possesses equatorial NO_2, and isomer 2 an axial NO_2 group. Slowing down of the process of ring inversion should thus be readily observable in the spectra of the ring methylene groups. However for example, the spectrum of isomer 2 in $CDCl_3$ remains unchanged within the temperature range $+30^\circ$C to -50°C. This we take as confirmation that the dioxaphosphorinan ring in (I; X = NO_2) is rigid, and hence probably also that in (I; X = Me).

These results raise the interesting speculation that, as in other heterocyclic systems capable of conformational flipping (12), a lone electron pair has an effective 'volume' at least as large as a methyl group in controlling conformational equilibria for the 1,3,2-dioxaphosphorinan ring.

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