The ^{31}P Nuclear Magnetic Resonance Spectrum of Menthyl Methylphosphinate

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Summary The large difference (4·3 p.p.m.) in the ^{31}P n.m.r. chemical shifts of the epimers of menthyl methylphosphinate is explained by assuming unequal π-interactions between the bridge-oxygen atom and the phosphorus atom in the *down*-conformations.

IN a previous publication, the ^1H n.m.r. spectra and some stereospecific reactions of the title compound (I) have been communicated.[1] We now report an interpretation of the ^{31}P n.m.r. spectra of (I). The spectrum of a mixture enriched with one epimer (*b*) is shown in the Figure, together with the upfield half of the spectrum of the isolated pure epimer *a*. Apparently, each epimer corresponds with a pair of multiplets, widely spaced due to strong coupling between the phosphorus atom and the directly bound hydrogen atom (^1J *ca.* 535 Hz). The multiplets are octets due to coupling to the methyl protons (^2J 14·8 Hz) and to the methine proton (^3J *ca.* 9 Hz).

The complete separation of the signals of the epimers ($\Delta\delta^{31}P$ 4·3 p.p.m.), permits an accurate determination of the ratio of the epimers. Obviously, this large value of 4·3 p.p.m. for $\Delta\delta^{31}P$ cannot be explained by the differences in magnetic- and electric-field effects in the epimers. It is also unlikely that a difference in association of the two epimers would be responsible for the effect.† We suggest that unequal electron densities in the 3*d*-orbitals at the phosphorus atom are responsible. A change in electron distribution around phosphorus is also indicated by the small but significant inequality of the ^1J coupling constant in the two epimers, as derived from the ^1H n.m.r. spectra,[1] ($^1J_{Ia}$ 536·2 Hz; $^1J_{Ib}$ 534·6 Hz).

Due to steric effects, the weighted average over the various conformer populations, of the dihedral angle between the C(1)OP plane and the OP(O) plane will differ in the two epimers. Although in related compounds the *up*-conformation‡ was suggested,[2,3] a molecular model of (I) shows that here the *down*-conformation is the more stable one, due to the small dimensions of the substituents H and Me. The model further shows the absence of steric interference by the freely rotating isopropyl group§ with the substituents at the chiral phosphorus atom in the *up*-conformation, whereas unequal steric interactions are evident in the *down*-conformation. From the disappearance of the difference in the ^{31}P n.m.r. chemical shifts ($\Delta\delta^{31}P$ $< 0·06$ p.p.m.) of the two epimers of *eq,eq*-3-methylcyclohexyl methylphosphinate (II) ($\delta^{31}P$ −28·5 p.p.m.) it is reasoned that this difference is present in the *down*-conformation only. This is further substantiated by the observed larger value of $\Delta\delta^{31}P$ (5·6 p.p.m.) in the thiono-analogue (III) of (I), which has a larger population of the *down*-conformation due to the larger size of sulphur. ($\delta^{31}P$ −60·1 p.p.m. and −65·7 p.p.m.).

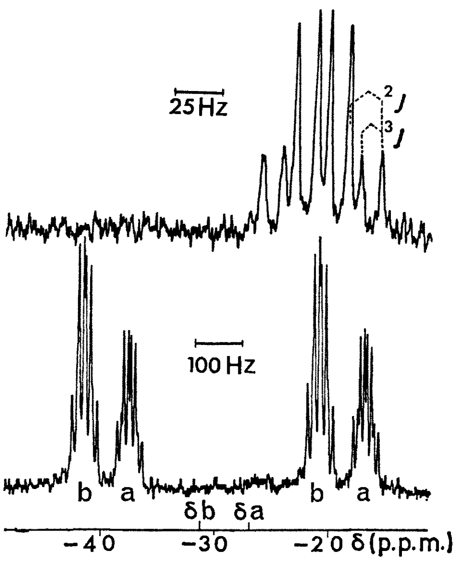
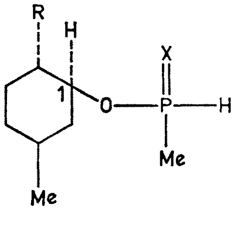


FIGURE. ^{31}P *n.m.r. spectrum* (*at* 24·3 *MHz*) *of an epimeric mixture of menthyl methylphosphinate* (I) *enriched with one of the epimers* (b), *obtained with a JEOL JNM-C-60H spectrometer at* 60° (*neat*) *to reduce viscosity. The wide scan is the resultant of time-averaging* 14 *scans with a "Digiac" spectrum computer of Digico Ltd., England. The expanded segment is a direct scan of the high-field octet in the spectrum of the isolated pure epimer* a. *The values of the* ^{31}P *n.m.r. chemical shifts given in Figure and text are relative to external* 85% H_3PO_4. ($\delta^{31}P_{Ia}$ − 26·9 p.p.m., $\delta^{31}P_{Ib}$ − 31·2 p.p.m.).

The molecular model of the least hindered *down*-conformer of (I) with the absolute configuration (*S*) at phosphorus shows a planar C(1)OP(O) structure, whereas steric hindrance prevents such coplanarity in (*R*)P-(I). Consequently, we expect slightly unequal π-interactions between the 2*p*-orbitals of the oxygen atom and the 3*d*-orbitals of the phosphorus atom, resulting in a differering degree of π-electron feed-back¶ from the bridge-oxygen to



(I) X = O, R = Pr^i
(II) X = O, R = H
(III) X = S, R = Pr^i

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† Phosphinates are known to give weak hydrogen-bonded complexes (see R. Wolf, D. Houalla, and F. Mathis, *Spectrochim. Acta*, 1967, **23A**, 1641). Moreover we observed that a chemical shift difference persisted in a 10% (w/v) solution of (I) in methanol.

‡ For the definition of "*up*" and "*down*" conformation see ref. 2.

§ The diastereotopic methyl groups of the isopropyl give rise to separate ^1H n.m.r. signals in each epimer (ref. 1). This is due to intrinsic asymmetry and not to a hindered rotation, because these signals are invariant from −50 to 100°.

¶ The value of 4·3 p.p.m. for $\Delta\delta^{31}P$ leads to the calculation of a difference in the *d*-orbital occupation number of 0·08 (see M. M. Crutchfield, C. H. Dungan, and J. R. van Wazer, in "Topics in Phosphorus Chemistry," ed. M. Grayson and E. J. Griffith, Interscience, New York, 1967, vol. V, pp. 114 and 189).

the phosphorus. This feed-back is largest for epimer *a* (high-field signals).

Unequal dihedral angles of the planes through HC(1)O and C(1)OP in the two epimers of (I) are strongly indicated by the methine proton–phosphorus spin coupling constant ^3J, which has a value of 8·6 Hz in epimer *a* and 9·6 Hz in epimer *b*; [compare (II): ^3J 8·5 Hz for both epimers and (III): ^3J 9·8 Hz and 12·7 Hz for the 'upfield' and 'downfield' epimers, respectively]. The parallelism between $\Delta\delta^{31}$P and Δ^3J for the epimers of (I), (II), and (III) confirms the abovementioned views concerning the relative importances and the geometries of the *down*-conformation in these compounds. Since the vicinal proton–phosphorus spin coupling constant decreases as the dihedral angle between the PO and CH bonds increases from 0° to a small value,[4] we tentatively assign the absolute configuration $(R)_P$ to (Ia).

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