

CONFORMATIONAL PROPERTIES OF ORTHO-SUBSTITUTED N-ARALKYL-PYRIDINIUM IONS.

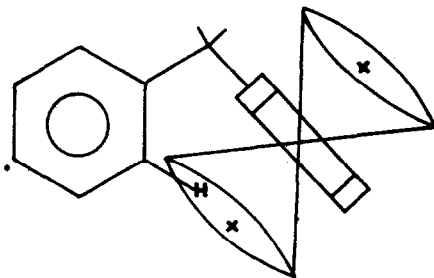
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(Received in UK 3 July 1972; accepted for publication 12 July 1972)

Intramolecular charge-transfer phenomena have been recently¹ observed for several substituted N-aralkyl-pyridinium ions of the type shown in Table 1. The conformational properties of these compounds are of interest because the relative orientation of the two aromatic moieties might be crucial for the through-space p-orbital interactions involved in the CT mechanism^{1,2}.

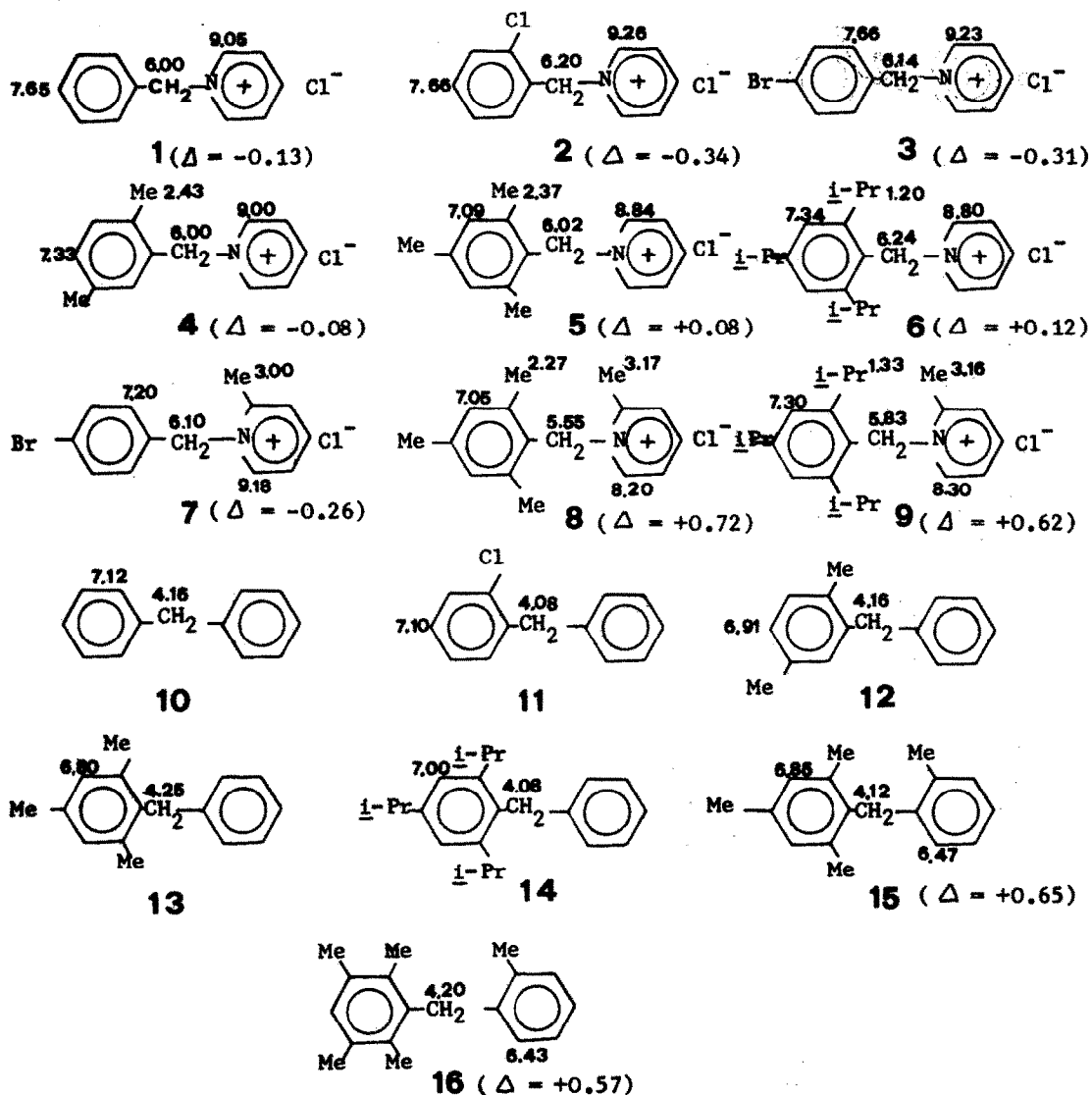
We have been interested in the study of the conformational properties of diphenylmethanes (DPM) and have proposed³ that a number of triply-ortho-substituted DPM exist predominantly in a conformation (I) where the ortho aromatic hydrogen lies below the adjacent ring, experiencing its diamagnetic shielding. Other types of ortho substitution lead to skew forms with non-perpendicular interplanar dihedral angles³.



I

Due to the close structural similarity of DPM and N-aralkyl-pyridinium (PPyM), one might expect the same kind of conformational preference also in the latter compounds. However, recently⁴ it has been claimed that mesityl-4-cyanopyridinium (an ortho-disubstituted compound) adopts predominantly the perpendicular form I.

Table 1 - Chemical shifts and diamagnetic shielding values^a of relevant groups in ortho-substituted N-*o*-alkyl-pyridinium ions^b and diphenylmethanes.



^a Differences in chemical shifts (in parentheses) were measured as the difference between the chemical shift of each PPyM derivative and that of ortho nuclear protons in the pyridinium hydrochloride (8.92 ppm). For the corresponding DPM figures see Reference 3.

^b Chemical shifts measured in ppm in D_2O downfield from DSS as internal standard at 60 MHz, 38°.

NMR data provide useful information on the conformation of these angular molecules. In fact, the shielding on the ortho positions, due to the ring current⁵ of the adjacent nucleus, is a function of the molecular conformation.

In Table 1 the NMR chemical shifts of the ortho pyridinium protons are reported for a number of variously substituted PPyM. Only in the tri-ortho-substituted compounds 8 and 9 does the ortho nuclear proton appear sensibly shielded.

The magnitude of the shielding observed (Table 1) compares pretty well with the corresponding shielding effects in DPM³. This evidence indicates that, contrary to all other substituted PPyM derivatives in Table 1, compounds 8 and 9 exist preferentially in form I.

Interestingly enough, the perpendicular conformation I causes a diamagnetic shift of about 0.5 ppm on the methylene protons in compounds 8 and 9, with respect to 5 and 6, probably due to the long-range shielding of the nitrogen p-orbital in this particular orientation. This effect is nearly absent in the corresponding DPM, included in Table 1 for comparison.

The positive charge distributed over the pyridinium ring exerts a noticeable electron-withdrawing effect on the adjacent phenyl ring whose protons appear deshielded with respect to the corresponding DPM derivatives (Table 1).

It is hoped that our findings may also prove helpful in the study of the dependence of the CT spectra of N-alkyl-pyridinium ions on the molecular conformation.

References

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