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EVIDENCE FOR π-POLARISATION FROM ^{13}C N.M.R. SPECTRA OF 4-PHENYL-1-SUBSTITUTED-BICYCLO[2.2.2]OCTANES

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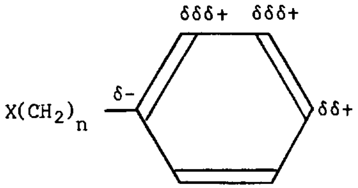
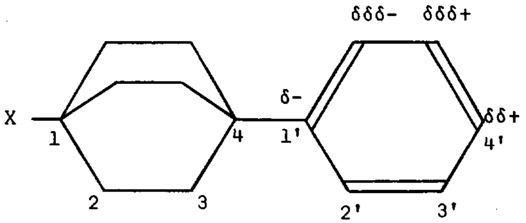
The effect of substituent X in $PhCH_2X$,[2,3] $Ph(CH_2)_2X$[2,4] and $Ph(CH_2)_3X$[2,4] on the ^{13}C chemical shifts for the carbon atoms of the phenyl group has been interpreted in terms of a π-polarisation mechanism represented as shown in 1.[2] This interpretation contradicts extensive evidence from ^{19}F chemical shift studies in a wide variety of systems including 1-substituted-4-(*p*-fluorophenyl) bicyclo[2.2.2]octanes.[5]



1



2

We present ^{13}C chemical shifts for thirteen 4-phenyl-1-substituted-bicyclo[2.2.2]octanes, 2. This system is ideal for the study of effects arising from a substituent dipole because the geometry of the bicyclic system ensures that (*a*) the distance between the substituent, X, and the phenyl group is constant (whereas conformational variations will exist for substituents in 1), (*b*) the orientation of the substituent dipole is fixed and directed along the major axis of the ring system, (*c*) resonance effects are absent, and (*d*) the steric effects at the carbon atoms in the phenyl group are constant for all substituents. The data listed in the Table provide unequivocal evidence for π-polarisation in the phenyl group of 2. The substituent chemical shifts (SCS) at each position have been examined by dual substituent parameter analysis using σ_I and σ_R^o and the resulting correlations are shown below; in none of the cases was the contribution of σ_R^o to the correlation statistically significant.

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