

CARBON-13 SUBSTITUENT CHEMICAL SHIFTS OF
4-SUBSTITUTED BICYCLO[2.2.2]OCT-1-YL CYANIDES

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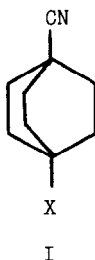
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Summary The carbon-13 substituent chemical shifts of 4-substituted bicyclo[2.2.2]oct-1-yl cyanides are a linear function of the substituent inductive parameters

The bicyclo[2.2.2]octane system is very useful in substituent studies since groups at the 1- and 4- positions are held rigidly with respect to each other with the substituent-bicyclo-octyl bonds coaxial. This geometry is furthermore close to that in 1,4-disubstituted benzenes and so acts as a model for such systems in the absence of π -electron effects. Studies¹ have mainly involved the acidities of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and the fluorine-19 substituent chemical shifts (SCS) of a series of 4-substituted bicyclo[2.2.2]oct-1-yl fluorides². In the latter study² it was concluded that substituent electronegativity effects were important as well as substituent electric field effects. This result is surprising as other evidence³ suggests that such electronegativity effects should be unimportant after the first or second carbon atoms next to the substituent.

We report here results for the carbon-13 SCS of a series of 4-substituted bicyclo[2.2.2]oct-1-yl cyanides, (I)



This work is part of an ongoing investigation of the spectral properties (nmr, ir) and proton transfer equilibria of bicyclo[2.2.2]octyl cyanides, amines, carboxylic acids and carboxylates. The syntheses and other properties will be reported in a full paper. The SCS relative to bicyclo[2.2.2]oct-1-yl cyanide in ppm downfield, measured in deuteriochloroform are: 4-CN, 2.04; 4-F, 1.76; 4-Br, 1.75, 4-Cl, 1.65, 4-OMe, 0.97, 4-CO₂Et, 0.94; 4-Me, 0.00. These SCS are correlated with σ_I values according to equation (1) with a correlation coefficient of 0.995.

$$\delta - \delta^0 = -3.60 \sigma_I \quad (1)$$

The excellent correlation including substituents such as methyl and cyanide suggests that electronegativity effects are negligible.

There is also no evidence for the presence of resonance contributions as indicated by the dual substituent parameter analysis⁴ which gives equation (2) with a normalized standard deviation of 0.07.

$$\delta - \delta^0 = -3.59 \sigma_I + 0.07 \sigma_R \quad (2)$$

These results may be compared to the only approximate relationship between SCS and σ_I values found⁵ for the cyano shifts in 2-substituted-1-cyanoethanes where the conformation is not fixed.

To our knowledge, equation (1) represents the first satisfactory correlation of carbon-13 SCS data solely with the inductive parameter σ_I .

References

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