Substituent Effects on $J(Me_2C{=}X)$: a Change of Sign

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THE sign of the long-range coupling in acetone has, until recently, remained unknown, although Holmes and Kivelson[1] suggested it to be negative. In the most successful theoretical treatment of long-range couplings to date, Barfield[2,3] concluded that couplings between geminal methyl groups across sp^2-hybridised carbon atoms in hydrocarbons (and indeed, *all* four-bond HH couplings across carbon) will be negative. Both the Barfield and Holmes–Kivelson predictions are at variance with a recent determination of the absolute sign of $^4J_{HH}$ in acetone, which indicates it to be positive.[4] No other sign determinations have been reported.

In the course of another investigation we prepared 2-methylpropenyl acetate and were able to resolve all three couplings (in C_6D_6), making possible a determination of the sign of the coupling between the methyl groups relative to the allylic couplings (assumed to be negative)[2,3]. All three couplings are of the same sign; hence $^4J_{HH} = 0{\cdot}49$ Hz, bearing out the prediction of the Barfield theory.

The opposite signs of the acetone ($+0{\cdot}53$ Hz) and 2-methylpropenyl acetate ($-0{\cdot}49$ Hz) couplings suggested that, in molecules of the type $Me_2C{=}X$, as the electronegativity of X is steadily increased the long-range coupling constant increases algebraically. Consideration of the Pauling electronegativities of carbon (2·5) and oxygen (3·5) suggested that the transition point ought to occur in the vicinity of nitrogen (3·0). Accordingly we synthesised acetone anil and recorded its n.m.r. spectrum. We were unable to resolve *any* long-range coupling between the nonequivalent methyl groups. The widths at half-height of the methyl resonances (0·41 and 0·33 Hz) were virtually indistinguishable from the acetone line-width (0·31 Hz, present in the sample). The slight broadening of the lower-field line may result from interaction of one methyl group with nitrogen.

These results can be accommodated by an extension of the Pople–Bothner-By theory of *geminal* HH couplings, which predicts mesomerically electron-withdrawing substituents to cause an algebraic increase in the coupling constant.[5] Other compounds are under investigation in order to obtain wider confirmation of this trend.

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