Bridgehead–Bridgehead ^{13}C–^{13}C Coupling Constant of a Bicyclobutane

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Summary The ^{13}C n.m.r. spectrum of diethyl 1-methyl-3-phenylbicyclo[1,1,0]butane-2,4-dicarboxylate containing three ^{13}C labels has provided a value of 5·4 Hz for the bridgehead–bridgehead ^{13}C–^{13}C coupling constant in agreement with theoretical predictions.

As a result of our interest in highly strained small ring systems we recently reported on the ^{13}C–^{13}C coupling constants in 1-cyanobicyclo[1,1,0]butane.[1,2] This involved observing the ^{13}C satellites of natural abundance ^{13}C resonances in a rather unstable molecule. We observed satellites corresponding to a bridgehead–bridgehead coupling constant of 16 Hz which was in disagreement with theoretical values. We have now synthesized diethyl 1-methyl-3-phenylbicyclo[1,1,0]butane-2,4-dicarboxylate[3] containing *ca.* 90% ^{13}C at the two bridgehead positions and *ca.* 65% ^{13}C in the methyl group. PhMgBr was treated with $^{13}CO_2$ (from $Ba^{13}CO_3$) to produce $Ph^{13}CO_2H$[4a] which was reduced with $LiAlH_4$ to $Ph^{13}CH_2OH$, which was converted into $Ph^{13}CH_2Cl$ with $SOCl_2$, treatment of which with Mg gave the Grignard reagent. Carbonation with ${}^{13}CO_2$ produced $Ph^{13}CH_2{}^{13}CO_2H$.[4a] ${}^{13}CH_3I$ was prepared from ${}^{13}CO_2$[4a] and converted into ${}^{13}CH_3Li$,[4b,c] reaction of which with the $Ph^{13}CH_2{}^{13}CO_2H$ gave $Ph^{13}CH_2{}^{13}CO^{13}CH_3$.[4d] Conversion into the hydrazone followed by treatment with CF_3CO_2Hg afforded $Ph^{13}C{\equiv}{}^{13}C^{13}CH_3$,[4e] reaction of which with ethyl diazoacetate afforded the desired labelled bicyclobutane.[3,4f]

The ${}^{13}C$ n.m.r. spectrum of this molecule provided the following ${}^{13}C$–${}^{13}C$ coupling constants: a bridgehead–bridgehead ${}^1J_{CC}$ 5·4 ± 0·5 Hz, methyl–bridgehead ${}^1J_{CC}$ 53·2 ± 0·5 Hz and methyl–bridgehead ${}^2J_{CCC} = 2{\cdot}4 \pm 0{\cdot}5$ Hz. The absolute value of ${}^1J[C(1)–C(3)]$, 5·4 Hz, is much closer to the value of −5·6 Hz predicted recently by INDO calculations[5] than the original value we reported.[1,2] This value of 5·4 Hz should be reliable since it was obtained using highly labelled material.

It is not apparent to us what the discrepancy is between the two determinations except to note that the original work showed the satellites around both bridgehead carbons but with poor signal to noise. In this determination, of course, there is no signal to noise problem.

The long range ${}^2J_{CCC}$ is, as expected,[6] small although somewhat larger than for simple aliphatic systems. In addition, ${}^1J_{CC}$ for the methyl group with the bridgehead carbon is quite large for a 'saturated' system,[7] and is compatible with a bridgehead carbon hybridized between *sp* and *sp*^{2}.[8] From the relationship between ${}^1J_{CH}$ and hybridization presented by Newton *et al.*[9] and the observation that ${}^1J_{CH} = 129$ Hz for the methyl group, and assuming that the orbital involved in bonding around carbon is 100% *s*, which does not necessarily hold,[10] we conclude that the methyl orbital bonding the bridgehead carbon has 22·6% *s*-character. From the relationship between ${}^1J_{CC}$ and hybridization[5] we conclude that the bridgehead carbon uses an orbital which has 45·2% *s*-character to bond the methyl group. This is in qualitative agreement with the hybridization obtained using ${}^1J_{CH}$ and the appropriate equations relating ${}^1J_{CH}$ to hybridization.[2,7,9,11]

The phenyl group probably does not affect the bridgehead–bridgehead coupling constant by more than, at most, 5%. This is demonstrated by the following series of ${}^{13}C$–${}^{13}C$ coupling constants.[7] Acetylene, ${}^1J_{CC}$ 170·6 Hz; phenylacetylene ${}^1J_{CC}$ 175·9 Hz; ethylene, ${}^1J_{CC}$ 67·2 Hz; styrene, ${}^1J_{CC}$ 70 Hz; ethane, ${}^1J_{CC}$ 34·6 Hz; and ethylbenzene, ${}^1J_{CC}$ 34 Hz.

The chemical shifts (rel. to Me_4Si) for the methyl carbon, the bridgehead carbon bonding to the methyl group, and the bridgehead carbon bonding to the phenyl group are 4·25, 24·02, and 29·02 p.p.m. respectively.

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