Two and Three Bond ^{13}C–^{13}C Spin Coupling Constants in Adamantane Derivatives

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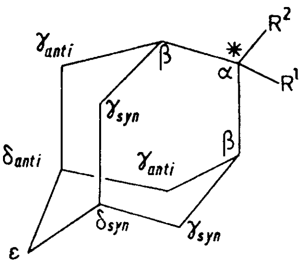
Summary The ^{13}C–^{13}C spin coupling constants in six adamantane derivatives labelled and substituted at C-2 have been measured and interpreted in terms of their conformational dependence.

Although the conformational dependence of ^{13}C–^{13}C geminal and vicinal coupling constants has been calculated recently,[1] the literature is lacking in experimental examples where these coupling constants were measured without the possibility of conformational[1] or rotational[2] averaging. In aromatic systems π interaction seems to be important for the coupling constant transmission;[3] the applicability of a Karplus type[4] equation is questionable[1] for aliphatic systems.



(1)

(a) $R^2, R^1 = O$
(b) $R^2 = H, R^1 = OH$
(c) $R^2 = H, R^1 = NH_2$
(d) $R^2 = H, R^1 = NH_2 \cdot HCl$
(e) $R^2 = H, R^1 = NHCOPh$
(f) $R^2 = H, R^1 = CO_2H$

$* = 80$ at % ^{13}C

Therefore we have synthesized a series of 2-adamantane derivatives (**1**) where a ^{13}C label was incorporated at the α-carbon atom and was thus directly a part of the rigid tricyclic system.[5] The chemical shifts of some of the compounds are already reported in the literature;[2,6] our assignments (Table) are in agreement with these findings. Although isochronism has been reported for the δ_{anti} and

TABLE

^{13}C–^{13}C Spin coupling constants[a] and chemical shifts[b] in (**1**)

		α	β	γ_{syn}	γ_{anti}	δ_{syn}	δ_{anti}	ε
(**1a**)	J	—	35·9	1·1		2·0		<0·5
	δ	218·2	47·0	39·3		27·5		36·4
(**1b**)	J	—	34·5	1·8	0·7	1·7	1·3	<0·5
	δ	74·5	34·6	31·0	36·6	27·6	27·1	37·6
(**1c**)	J	—	33·9	1·5	<0·5	1·6	1·3	<0·5
	δ	59·5	35·1	30·8	37·8	27·8	27·4	38·0
(**1d**)[c]	J	—	31·0	1·3	<0·5	1·6	1·5	<0·5
	δ	57·0	31·3	30·7	37·3	27·6	27·4	37·6
(**1e**)[d]	J	—	33·3	1·5	<0·5	1·4	<0·5	<0·5
	δ	53·0	32·0	32·2	37·2	27·2	27·1	37·6
(**1f**)[e]	J	—	32·1	1·2	<0·5	1·4f	<0·5f	<0·5
	δ	49·5	29·5	33·6	38·1	27·5	27·5	37·4

[a] Given in Hz, accuracy ±0·25 Hz, measured with a Varian XL-100-15 spectrometer. [b] δ p.p.m. relative to Me_4Si in $CDCl_3$ given for the unlabelled compounds. [c] Measured in D_2O relative to $Me_3SiCD_2CD_2CO_2Na$ (TSP) and calculated from the equation δ(TSP) − δ(Me_4Si) = 1·7 p.p.m. [d] δ_{Ph} 135·4, 131·3, 128·6, and 126·8; $\delta_{C=O}$ 166·7 p.p.m. [e] $\delta_{C=O}$ 180·9 p.p.m.; $^1J_{CC}$ 54·4 Hz. [f] Assignment for the coupled carbon atom tentative.

δ_{syn} carbon atoms,[6] we have been able to resolve these resonances. The assignments of these lines follow the result of a lanthanide shift experiment for (**1b**). The carbon atom with a larger bound shift is assigned to the δ_{syn} carbon atom. This assignment is in accordance with reported δ effects in cyclohexyl systems.[7]†

The results given in the Table show that there are significant conformational dependences for $^2J_{CC}$ and $^3J_{CC}$ whereas $^1J_{CC}$ does not vary substantially. An interesting effect is seen for $^2J_{CC}$ in (**1b**)—(**1f**), where the geminal coupling constant to the γ_{anti} carbon atom can be resolved only in (**1b**). The effect is less apparent in the three-bond couplings to the δ carbon atoms: $^3J_{CC}$ to the δ_{syn} carbon atoms are, in all cases, larger than to the δ_{anti} carbon atoms. Furthermore all ^{13}C–^{13}C coupling constants in this system seem to be dependent on the substituent. The less the substituent is disturbing the adamantane system as judged from the chemical shift value of the α carbon atom the smaller are the coupling constants. These findings indicate that directional effects of bond polarization[8] may play an important role in the scalar coupling mechanisms of aliphatic systems.

(*Received*, 6*th May* 1976; *Com.* 502.)

† The same assignment has recently been reported by H. Duddeck and W. Dietrich, *Tetrahedron Letters*, 1975, 2925.

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