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EXPERIMENTAL AND THEORETICAL STUDY OF SUBSTITUENT EFFECTS ON $^3J(^{13}C1-^1H)$ COUPLING CONSTANTS IN 1-X-BICYCLO[1.1.1]PENTANES

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A series of 23 bridgehead-substituted bicyclo[1.1.1]pentanes were synthesized and the ^3J(C1–H) coupling constants determined from their proton-coupled ^{13}C NMR spectra. It was found that the values of the couplings are strongly dependent upon the type of substituent present, with powerful effects exerted by the halogens in particular. The IPPP–CLOPPA–INDO theoretical approach, which was employed to provide a measure of the extent of through-bond versus through-space transmission of coupling information, was found to give ^3J(C1–H) values in good agreement with experimental data. Empirical substituent parameter regressions were performed and found to be consistent with the CLOPPA description of the increase in both the through-bond and through-space contributions to the coupling. The substituent parameter regressional analyses also demonstrated that electronegativity effects play a predominant role in determining the magnitude of the couplings, particularly in those substrates in which the substituent is attached to the ring system by a second-row element.

INTRODUCTION

Carbon couplings in polycycloalkanes have been the subject of intense study[1] for many years. Polycycloalkanes are thought to be excellent model compounds for measuring how different factors affect NMR parameters because of their well defined geometries, the varying degree of strain associated with the different member of the series, the different types of pathways connecting the bridgehead atoms and the small internuclear distance for the bridgehead carbon atoms in the smaller members of the series. Selected works include the study of (i) through-space transmission of coupling information via non-bonded interactions between bridgehead carbon atoms in substrates with different substituents at the bridgehead position[2] using both the NNBI[3] and the IPPP[4] approaches, (ii) the effect of strain on the magnitude of one-bond coupling between a bridgehead carbon and a side-chain atom[1b–d] and (iii) the question of multipath additivity for several coupling constants between bridgehead carbon atoms and/or atoms attached to them.[5]

So far, however, the effect of substituents at the bridgehead position on substrate couplings has not been subjected to systematic study. Of particular interest is the magnitude of vicinal coupling between the substituted carbon atom and the proton at the unsubstituted bridgehead position. Bicyclo[1.1.1]pentane is uniquely placed in this context because spin information can be transmitted via three different through-bond pathways in addition to a through-space component transmitted by a direct interaction between the bridgehead carbon atoms. Accordingly, the effect of the substituent would be expected to be enhanced by the multiple coupling routes connecting the relevant atoms.

In this paper, which represents an extension of our earlier work into the bicyclo[1.1.1]pentyl system,[6] a

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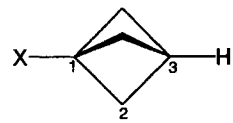
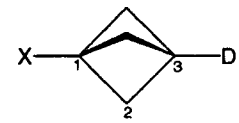




1, X=H	**9, X=$COOCH_3$**	**17, X=NO2**	**2b, X=Ph**
2, X=Ph	**10, X=$SnPh_3$**	**18, X=SePh**	**3b, X=t-Bu**
3, X=t-Bu	**11, X=NH_2**	**19, X=OAc**	**4b, X=$COCH_3$**
4, X=$COCH_3$	**12, X=SO_2Ph**	**20, X=F**	**6b, X=CH_3**
5, X=$SnBu_3$	**13, X=CN**	**21, X=Cl**	**14b, X=OCH_3**
6, X=CH_3	**14, X=OCH_3**	**22, X=I**	**20b, X=F**
7, X=CD_2OH	**15, X=NH_3^+**	**23, X=Br**	
8, X=COOH	**16, X=SPh**		

series of 1-X-bicyclo[1.1.1]pentanes (**1–23**) were synthesized and their ^3J(C1–H) coupling constants measured. The data were subjected to empirical analysis on the basis of substituent electronic effects and this was combined with a study of multipath transmission for this type of coupling using the IPPP–CLOPPA–INDO method.[7] The theoretical approach was also employed to provide insight into the large substituent effects measured for some substituents.

METHOD OF CALCULATION

Within the CLOPPA method (Contributions from Localized Orbitals within the Polarization Propagator Approach),[8] a given coupling constant, J(NN′), can be written as a sum of contributions as in the equation

$$J(\mathrm{NN'}) = \sum_{ia,jb} j_{ia,jb} \tag{1}$$

where i and j stand for occupied localized molecular orbitals (LMOs) representing bonds or lone pairs; and a and b stand for vacant LMOs representing antibonding orbitals.

The $J_{ia,jb}$ terms of equation (1) are in general made up from three different contributions associated with Fermi contact and the spin–dipolar and paramagnetic spin–orbital interactions, respectively. In the present paper, only the first contribution is taken into account since it is by far the main one in couplings of type ^3J(C1–H).[9]

Each $J_{ia,jb}$ term corresponding to the Fermi contact interaction can be written as[10]

$$J_{ia,jb}^{(\mathrm{N,N'})} = \Omega V_{ia,\mathrm{N}} W_{ia,jb} V_{jb,\mathrm{N'}} \tag{2}$$

where Ω is a constant which involves, among other factors, the magnetogyric ratios of the coupled nuclei, $W_{ia,jb}$ are the elements of the triplet polarization propagator matrix $V_{ia,\mathrm{N}}$ and are the elements of the 'perturbators' column matrix, i.e. the matrix elements of the Hamiltonian describing the Fermi contact interaction:

$$V_{ia,\mathrm{N}} = \langle a \mid \delta(\bar{R}_{\mathrm{N}}) \mid i \rangle \tag{3}$$

where $\delta(\bar{R}_{\mathrm{N}})$ is the Dirac delta function whose argument is the position vector with respect to nucleus N.

Within the INDO approximation, the matrix elements of equation (3) are calculated within the monocentric approximation.[11] This approximation gives the following equation for the $V_{ia,\mathrm{N}}$ matrix elements:

$$V_{ia,\mathrm{N}} = C_s^a(N) C_s^i(\mathrm{N}) S_{\mathrm{N}}^2(\mathrm{O}) \tag{4}$$

where $C_s^{i(a)}(\mathrm{N})$ are the LCAO coefficients corresponding to the s atomic orbital of atom N for the ith occupied (a vacant) LMO, and $S_{\mathrm{N}}^2(\mathrm{O})$ are semiempirical atomic parameters which correspond to the atomic electronic density at the site of nucleus N.

If the CLOPPA and IPPP methods are used in combination,[4a] then the contribution to the total coupling originating in a molecular fragment can be obtained in terms of LMOs. In such a case, the following equation holds rather than equation (1):

$$J^L(\mathrm{NN'}) = \sum_{ia,jb}^{\mathrm{Local}} J_{ia,jb}^L \tag{5}$$

where L stands for the contribution to J originating in the particular molecular fragment. It is essential to recognize that the sum must be carried out on all LMOs (occupied and vacant) belonging to that molecular fragment.

$J_{ia,jb}^{L(\mathrm{NN'})}$ is now given by equation (6), which differs from equation (2) since in the present case the polarization propagator is inner projected[4a] on to the LMOs belonging to the chosen molecular fragment, $W_{ia,jb}^L$:

$$J_{ia,jb}^{L(\mathrm{N,N'})} = \Omega V_{ia,\mathrm{N}} W_{ia,jb}^L V_{jb,\mathrm{N'}} \tag{6}$$

Geometries were optimized using the AM1 method[12] within the AMPAC program.

RESULTS AND DISCUSSION

Experimental values

Values of ^3J(C1–H) in the majority of the bicyclo[1.1.1]pentanes **1–23** were obtained directly from their proton-coupled ^{13}C spectra. This was a relatively simple operation because although the carbon signal appears as a doublet of septets, the vicinal coupling constant could be identified and measured readily in view of the much weaker two-bond C1–H coupling. As anticipated, however, analysis of the C1 signal for the bicyclo[1.1.1]pentanes containing substituents such as CH_3, $COCH_3$, C_6H_5, *tert*-Bu and OCH_3 was complicated by additional coupling to the substituent protons. In these cases the 3-deutero analog was synthesized and its proton-decoupled carbon spectrum recorded. Values of ^3J(C1–H) were derived by multiplication of the ^3J(C1–D) data by the H/D gyromagnetic ratio.

The ^3J(C1–H) coupling constants of the 1-X-bicyclo[1.1.1]pentanes are assembled in Table 1. Entries are given in increasing order of magnitude for the coupling which is seen to span the range from 10·0 Hz, for the parent **1**, to 33·8 Hz in 1-bromobicyclo[1.1.1]pentane (**23**); in fact, the most spectacular couplings are seen to occur in the 1-halobicyclo[1.1.1]pentanes **20–23** for which ^3J(C1–H) is *ca* three times as large as that in the parent **1**. To our knowledge, this type of enhancement of coupling is unprecedented and is indicative of the unique behaviour of the bicyclo[1.1.1]pentyl system. The effect of the halogen is in the order I ≈ Br > Cl > F, which is essentially the reverse of their electronegativities. Karabatsos and co-workers[13,14] also noted unusually large vicinal CH couplings in 1-substituted propanes in which the carbon was attached to halogen, and that the magnitude of the couplings decreased in the order I > Br > Cl, i.e. in the reverse order of their electronegativities. In contrast, only a small difference was found to exist between the effect of F, Cl, Br and I on the ^3J(CH) couplings in the halobenzenes.[15] Another feature of interest in the bicyclo[1.1.1]pentanes is the variation between the stannanes **5** and **10** in which a value of 11·2 Hz is associated with the tributyltin substituent whereas ^3J(C1–H) in the case of triphenyltin is 13·5 Hz.

The large variation in vicinal coupling in the case of the bicyclo[1.1.1]pentanes **1–23** has analogies in open-chain and aromatic compounds, although the effect of the substituents in these systems is considerably diminished. Thus, we find, for example, that the values of ^3J(C1–H) measured in a variety of 1-substituted propanes[16] [Figure 1(a)] and monosubstituted benzenes[15] [Figure (1b)] show very good correlation ($r^2 = 0{\cdot}92$ and 0·96, respectively) with those of the 1-substituted bicyclo[1.1.1]pentanes. It is also of interest to compare the values of ^3J(C1–H) in the bicyclo[1.1.1]pentanes **1–23** with the analogous ^{4}J(C4–F) couplings measured in a series of 4-substituted cubyl fluorides **24**.[17] In the latter system, the halogen substituents are also found to lead to considerable enhancement of the ^{4}J(C4–F) coupling, although in this case fluorine has the largest effect. Figure 2 shows the excellent correlation ($r^2 = 0{\cdot}98$) observed when the cross-ring couplings between the common substituents for these two systems are plotted against each other and when the sole outlier, fluorine, is

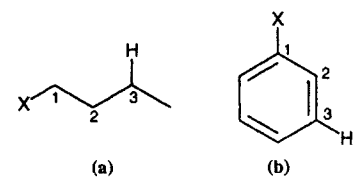
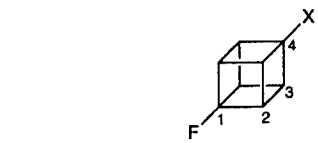


Figure 1. Vicinal coupling pathway between C1 and H3 in (a) 1-substituted propanes, and (b) monosubstituted benzenes

Table 1. ^3J(C1–H) coupling constants (Hz) in the 1-X-bicyclo[1.1.1]pentanes **1–23**

Compound	X	^3J(CH)	Δ^3J(CH)	Compound	X	^3J(CH)	Δ^3J(CH)
1	H	10·0	0·0	**13**	CN	18·1	8·1
2	Ph	10·8[a]	0·8	**14**	OCH_3	20·8[a]	10·8
3	*t*Bu	11·0[a]	1·0	**15**	NH_3^+	21·4	11·4
4	$COCH_3$	11·0[a]	1·0	**16**	SPh	21·9	11·9
5	$SnBu_3$	11·1	1·1	**17**	NO_2	21·9	11·9
6	CH_3	11·3[a]	1·3	**18**	SePh	22.9	12.9
7	CD_2OH	11·4	1·4	**19**	OAc	25·6	15·6
8	CO_2H	13·2	3·2	**20**	F	27·4[a]	17·4
9	CO_2CH_3	13·2	3·2	**21**	Cl	31·5	21·5
10	$SnPh_3$	13·5	3·5	**22**	I	33·3	23·3
11	NH_2	17·1	7·1	**23**	Br	33·8	23·8
12	SO_2Ph	17·4	7·4				

[a] Value obtained from the 3-deuteride.



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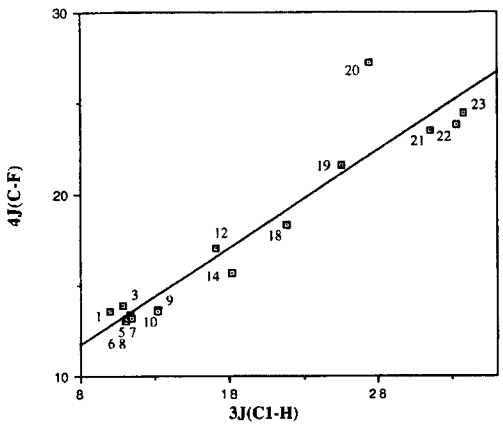

Figure 2. Plot of ^3J(C1–H) in the 1-X-bicyclo[1.1.1]pentanes **1**, **2**, **6–9**, **11**, **13**, **17**, and **19–23** versus ^4J(C4–F) in the corresponding 4-X-cubyl fluorides

removed from the analysis. We believe that these observations have implications in the mechanisms of transmission of coupling information in the bicyclo[1.1.1]pentanes; considering the types of systems under comparison, it would appear that the substituent affects both the through-bond and through-space contributions in bicyclo[1.1.1]pentane to about the same extent.

Empirical regressional analyses

A cursory examination of the entries for the bicyclo[1.1.1]pentanes **1–23** in Table 1 suggests a distinct trend corresponding to an increase in the value of ^3J(C1–H) with increasing electronegativity of the substituent, consistent with the observations by Karabatsos and co-workers[13,14] and Ernst *et al.*[15] described above. In practice, however, analysis of the data using multi-parameter regression shows (Table 2, entries 1 and 2) that, if the values for X = NH_2, SO_2Ph and OAc are eliminated, there is good correlation ($r^2 = 0{\cdot}98$) when the substituent electronic parameters σ_I (field)[18] and σ_R (resonance)[19] are included with ι (electronegativity).[20] The coefficients of the substituent parameters (Table 2, entry 2) and their associated *p*-values suggest that all three effects are important. There is little correlation between the values of ^3J(CH) and these parameters singly, or in groups of two. Regressional analysis using Adcock's σ_F (field) parameter[21] in place of σ_I, gave a similar result (entries 3 and 4).

We have used the iota values[20] of electronegativity in preference to alternative electronegativity constants[21,22] because they cover a wider range of substituents. As the data in Table 2 (entry 5) reveal, use of the σ_χ[22] electronegativity scale in place of ι gives a poor correlation ($r^2 = 0{\cdot}82$), again with unacceptable *p*-values. It is significant, however, that exclusion of the outlying point, chlorine, leads to a dramatic improvement (entry 6, $r^2 = 0{\cdot}94$) in this regression. Attention is drawn to two important features of this new relationship. First, the coefficients and the *p*-values of the three terms demonstrate that the value of ^3J(C1–H) is dominated by the electronegativity effect of the substituent; confirmation for this is obtained when the analysis of ^3J(C1–H) against σ_χ alone affords a good correlation (entry 7, $r^2 = 0{\cdot}93$) if the point for X = Cl is excluded. Second, and of considerable significance we believe, the improved regressions can be seen to cover only compounds where the substituent is attached directly to the bridgehead carbon by hydrogen or a second-row element. A good linear correlation ($r^2 = 0{\cdot}9$) is also obtained (Figure 3) when the values of ^3J(C1–H) of the 15 'second-row' substrates are plotted against the substituent electronegativity values (ι) of Inamoto and Masuda.[20] Removal of the outlying substituents, OAc and Ac, gives an excellent correlation ($r^2 = 0{\cdot}95$) (entries 8 and 9, Table 2). Inclusion of σ_R and σ_I in this regression again shows that they are unimportant (entry 10, Table 2). It is noteworthy that Spoormaker and de Bie[16] have observed a strong dependence of ^3J(C1–H) on the electronegantivity of second-row elements in the series of 1-substituted propanes; a similar relationship has been reported to exist between ^1J(C1–C2) and the electronegativity of second-row elements in a series of monosubstituted benzenes.[22]

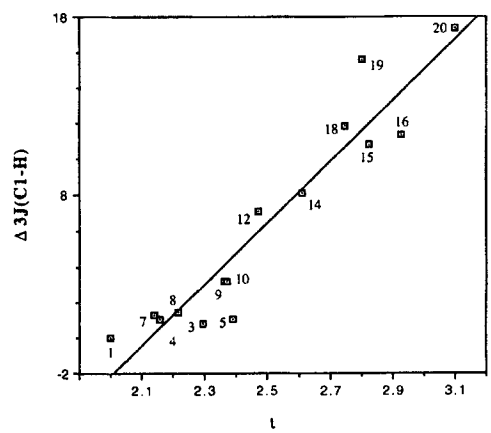

Figure 3. Plot of Δ^3J(C1–H) in the 1-X-substituted bicyclo[1.1.1]pentanes **1**, **2–4**, **6–9**, **11**, **13**, **14**, **17**, **19** and **20** versus electronegativity (ι) of the substituent

Table 2. Regressional analysis of Δ^3J(C1–H) against substituent electronic parameters[a]

Entry	Regression equations				r^2	n[b]
1	Δ^3J(C1–H) = $-7{\cdot}8\iota$ (0·002)	$+48{\cdot}1\sigma_I$ (0·000)	$-32{\cdot}4\sigma_R$ (0·000)	+34·5 (0·003)	0·84	18
2[c]	Δ^3J(C1–H) = $-23{\cdot}0\iota$ (0·000)	$+54{\cdot}0\sigma_I$ (0·000)	$-37{\cdot}3\sigma_R$ (0·000)	+45·2 (0·000)	0·98	15
3	Δ^3J(C1–H) = $-13{\cdot}6\iota$ (0·014)	$+50{\cdot}1\sigma_F$ (0·000)	$-30{\cdot}4\sigma_R$ (0·000)	+25·1 (0·024)	0·82	17
4[d]	Δ^3J(C1–H) = $-15{\cdot}4\iota$ (0·001)	$+52{\cdot}0\sigma_F$ (0·000)	$-39{\cdot}0\sigma_R$ (0·000)	+28·7 (0·003)	0·90	16
5	Δ^3J(C1–H) = $-7{\cdot}6\sigma_\chi$ (0·659)	$+31{\cdot}6\sigma_I$ (0·015)	$-20{\cdot}7\sigma_R$ (0·039)	−1·67 (0·399)	0·82	14
6[e]	Δ^3J(C1–H) = $27{\cdot}4\sigma_\chi$ (0·032)	$+6{\cdot}82\sigma_I$ (0·368)	$-2{\cdot}86\sigma_R$ (0·619)	−3·01 (0·015)	0·94	13
7[f]	Δ^3J(C1–H) = $36{\cdot}1\sigma_\chi$ (0·000)	−3·15 (0·003)			0·93	14
8[f]	Δ^3J(C1–H) = $17{\cdot}1\iota$ (0·000)	−36·4 (0·000)			0·90	15
9[f,g]	Δ^3J(C1–H) = $15{\cdot}9\iota$ (0·000)	−33·5 (0·000)			0·95	13
10[f]	Δ^3J(C1–H) = $13{\cdot}0\iota$ (0·150)	$+6{\cdot}4\sigma_I$ (0·594)	$-5{\cdot}64\sigma_R$ (0·436)	−28·2 (0·128)	0·91	13

[a] Values in parentheses are the *p*-values.
[b] Number of data points in regression.
[c] X = NH_2,SO_2Ph and OAc omitted.
[d] X = NH_2 omitted.
[e] X = Cl omitted.
[f] Regression using second row substituents and hydrogen.
[g] X = OAc, $COCH_3$ omitted.

We interpret these observations as evidence that the electronegativity of the substituent is, indeed, the predominant factor determining the magnitude of vicinal coupling between C1 and H3 in the 1-X-bicyclo[1.1.1]pentanes **1**, **2–4**, **6–9**, **11**, **13–15**, **17**, **19** and **20**, i.e. in those cases in which X is attached to the bridgehead carbon by a second-row element. It is generally accepted that electronegativity effects in saturated systems are transmitted essentially via the σ-bond framework, although the effect is greatly diminished beyond one bond, and most authors in the field agree that the σ-inductive mechanism is essentially ineffective beyond two carbon atoms.[23] As noted above, however, bicyclo[1.1.1]pentane possesses the unusual property that there are now three equivalent through-bond pathways available for transmission of spin information and it would therefore not be unreasonable to suggest that electronegativity effects are likely to be significantly enhanced in this system. Thus, the analyses suggest that for those bicyclo[1.1.1]pentanes attached to the substituent by a second-row element, contributions to the transmission of coupling information from other mechanisms associated with electrostatic field and/or resonance effects appear to be of lesser importance. The correlative analyses indicate, moreover, that in the other substrates in which the substituent is bonded to the ring system via a third-, fourth- or fifth-row element, viz. **5**, **10**, **12**, **16**, **18** and **21–23**, the factors responsible for ^3J(C1–H) coupling appear to be more complex and to include a blend of electronegativity, field and resonance effects. It appears that in these substrates the mechanism may involve a greater contribution from a through-space component involving direct orbital interaction between the bridgehead carbon atoms.

Molecular orbital calculations

Molecular orbital calculations were carried out for a selected range of 1-X-bicyclo[1.1.1]pentanes, viz. those in which X = H, Me, CH_2OH, COOH, CN, NH_2, OH and Cl. Although experimental data for ^3J(C1–H) in 1-bicyclo[1.1.1]pentanol are unavailable, it seems reasonable to employ the value for X = OMe in place of that for X = OH in view of their similar substituent effects.

The geometries for the model compounds were optimized at the AM1 level of approximation using the AMPAC program[12] and IPPP–CLOPPA–INDO[7]

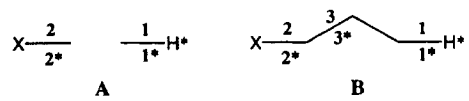

Figure 4. Coupling routes A (through-space) and B (through-bond) for transmission of spin information between the bridgehead carbon atoms. The numbering of the localized molecular orbitals (LMO) is also shown.

analyses were carried out using the AM1 structural data. The coupling routes A and B depicted in Figure 4 were considered.[2,5c] The contribution calculated using the route A is considered to be the component transmitted through-space between the bridgehead carbon atoms. Coupling route B′ is the component transmitted through-bond and corresponds to $B' = B - A$, i.e. the through-space component is subtracted from the total coupling pathways. Figure 4 also depicts the numbering of localized molecular orbitals, LMOs. Occupied LMOs represent bonds and vacant LMOs (marked with asterisks) correspond to antibonding orbitals.

Table 3 depicts the analysis of multipath additivity for the model compounds. The sum of contributions transmitted through routes A and B′, $\Sigma = A + 3B'$, is compared with the total RPA INDO coupling and also with the experimental value taken from Table 1. It can be seen that total calculated couplings for all compounds, with the exception of the parent itself, are in reasonable agreement with the experimental values. We do not have a satisfactory explanation as to why the calculations overestimate the value of J in bicyclo[1.1.1]pentane. For the substituents CH_2OH, COOH, NH_2 and OH the three B coupling routes are not exactly equivalent and therefore all three values of B′ are shown. In order to distinguish between geometrical and electronic effects, both the through-space component (route A) and the total coupling were also calculated using the experimental substrate geometry of the parent compound.[24] Results are shown in parentheses in Table 3. It is observed that a shorter distance between bridgehead carbon atoms does not imply a larger through-space component which is largely determined by electronic effects and not by the geometry of the substrate.

Table 4 displays the main $J^L_{ia,jb}$ terms of the through-space component calculated with the optimized AM1 geometries [See equation (5)]. The corresponding inner projected propagator and 'perturbator' terms are also shown [see equation (6)], together with the LCAO coefficients entering in the V_{11^*,C^*}. 'perturbator', equation (4). Changes in the corresponding inner projected propagator term, $W^L_{11^*,11^*}$, and in the 'perturbator' V_{11^*,H^*}., are insufficient to account for the variation of the coupling term which must, therefore,

Table 3. IPPP INDO analysis of multipath additivity in ^3J(C1–H) for selected substituents in the 1-X-bicyclo[1.1.1]pentanes[a]

X	TS[b]	D(C1C3)[c]	One path[d]	Σ[e]	Total[f]	Exp.[g]
H	3·05 (3·05)	1·8725	4·81	17·48	17·51 (17·55)	10·0
Me	2·15 (2·30)	1·8805	4·07	14·36	12·87 (14·21)	11·3
CH_2OH	2·13 (2·20)	1·8763	4·27	14·21	13·07 (14·02)	11·4
			3·97			
			3·84			
CO_2H	2·12 (2·28)	1·8725	3·56	13·68	13·29 (14·55)	13·2
			4·23			
			3·77			
NH_2	4·08 (3·99)	1·8846	6·02	21·48	20·08 (19·91)	17·1
			5·82			
			5·56			
CN	2·51 (2·73)	1·8721	4·05	14·66	14·49 (15·88)	18·1
OH	5·06 (5·56)	1·8637	6·91	25·27	24·20 (27·01)	20·8[h]
			6·89			
			6·42			
Cl	6·84 (7·42)	1·8681	8·24	31·56	34·81 (36·66)	31·5

[a] All coupling constants in Hz. Values in parentheses were calculated using the parent substrate experimental geometry in which the distance between the bridgehead carbon atoms is 1·8444 Å.[1b]
[b] Through-space contribution calculated with path A (see figure 4).
[c] Bridgehead carbon–carbon distance as obtained in the AM1 optimized geometry.
[d] Contribution from path $B' = B - A$ (see figure 4).
[e] $\Sigma = A + 3B'$.
[f] Total RPA INDO value.
[g] See Table 1.
[h] Value for OMe.

Table 4. The main $J^L_{11^*,11^*}$ contribution to the through-space component of ^3J(C–H); the corresponding propagator and perturbator terms are also compared along the series of substituents quoted in Table 3[a]

X	$J^L_{11^*,11^*}$	$W^L_{ia,jb}$	V_{11^*,H^*}	V_{11^*,C^*}	C^1_s(C1)[b]	$C^{1^*}_s$(C1)[b]
H	7·63	1·778	0·1760	0·0320	0·0547	0·1451
CH_3	4·18	1·757	0·1784	0·0175	0·0271	0·1601
CH_2OH	4·31	1·759	0·1785	0·0180	0·0279	0·1598
CO_2H	3·63	1·765	0·1790	0·0151	0·0221	0·1693
CN	4·18	1·756	0·1784	0·0175	0·0267	0·1624
NH_2	5·58	1·781	0·1794	0·0229	0·0351	0·1616
OH	6·28	1·794	0·1800	0·0255	0·0389	0·1627
Cl	8·62	1·821	0·1807	0·0344	0·0538	0·1584

[a] J terms are given in Hz; see equations (4) and (6).
[b] LCAO coefficients of the 2s AO of carbon C1 in the occupied LMO 1 and vacant LMO 1*, respectively.

Table 5. The main $J^L_{ia,jb}$ terms transmitted through each path B contributing to ^3J(C1–H) for the series of substituents quoted in Table 3[a,b]

i	a	j	b	H	CH_2OH	CO_2H	CN	CH_3	NH_2	OH	Cl
1	1*	3	1*	4·65	4·74	4·64	6·27	2·59	3·05	5·62	5·85
				(0·251)	(0·255)	(0·246)	(0·330)	(0·146)	(0·150)	(0·251)	(0·253)
3	1*	3	1*	1·62	1·75	1·68	2·25	1·56	1·71	1·91	1·92
				(1·182)	(1·230)	(1·201)	(1·403)	(1·273)	(1·298)	(1·207)	(1·209)
3	3*	1	1*	0·30	0·17	0·20	0·56	0·09	0·45	0·85	1·86
				(0·004)	(0·003)	(0·003)	(0·010)	(0·002)	(0·007)	(0·012)	(0·026)
3	2*	1	1*	3·25	1·60	1·59	1·90	1·09	1·41	2·14	3·07
				(0·054)	(0·029)	(0·028)	(0·034)	(0·026)	(0·020)	(0·043)	(0·074)

[a] $J^L_{ia,jb}$ terms are given in Hz. The $J^L_{11^*,11^*}$ and $J^L_{21,21}$ terms are omitted (see Table 6). The numbering of occupied and vacant localized molecular orbitals is shown in Figure 4.
[b] The corresponding propagator terms, $W^L_{ia,jb}$, are given in parentheses [see equation (6)].

originate in the 'perturbator' V_{11^*,C^*}. In turn, this trend is determined by the C^1_s(C1) coefficient, which corresponds to the coefficient of the 2s atomic orbital of the substituted carbon atom to the occupied LMO corresponding to the C—H bond attached to the unsubstituted bridgehead carbon atom occupied LMO 1. Therefore, the increase in this coefficient along the subset of the model series Me, NH_2, OH and Cl corresponds to an increase in the size of the rear lobe of that C—H bond. This enlargement of the rear lobe can be rationalized as originating in a through-space interaction with the substituent, possibly through an electric field effect.

In Table 5 the main $J^L_{ia,jb}$ terms defining the trend of the component transmitted through the coupling route B in the model compounds are displayed. The corresponding inner projected propagator terms, $W^L_{ia,jb}$, are given in parentheses. The J_{11^*,H^*} term is omitted since its trend is displayed in Table 4 although the actual values are different since, in the present case, the polarization propagator is inner projected on to the LMOs defining the coupling route B, and in the former case it was projected on to the LMOs defining the coupling route A. The following comments are pertinent for the values displayed in Table 4. Changes in the propagator term take into account only part of the variation along the series. Therefore, a closer look at the 'perturbators' should provide deeper insight into the factors defining the substituent effects. Terms of entries 3 and 4 involve the 'perturbator' V_{11^*,C^*} whose behavior was discussed above in connection with the main term of the through-space component which increases, although not monotonically, along the series of model compounds in accordance with the increase in the size of the rear lobe

Table 6. 'Perturbators' $V_{31^*,H}$ and $V_{31^*,C}$ and LCAO coefficients C^3_s(C1) and $C^{1^*}_s$(C1)[a]

X	$V_{31^*,H}$	$V_{31^*,C}$	C^3_s(C1)	$C^{1^*}_s$(C1)
H	0·0134	0·1348	0·3336	0·0999
CH_3	0·0120	0·1346	0·2874	0·1161
CO_2H	0·0134	0·1366	0·2875	0·1178
CN	0·0153	0·1376	0·2758	0·1237
CH_2OH	0·0139	0·1344	0·2832	0·1177
NH_2	0·0113	0·1535	0·3119	0·1220
OH	0·0129	0·1608	0·3200	0·1246
Cl	0·0126	0·1653	0·3334	0·1229

[a] C^3_s(C1) and $C^{1^*}_s$(C1) are the LCAO coefficients of the 2s AO of carbon C1 in the occupied LMO 3 and vacant LMO 1*, respectively (see figure 4)

of the bridgehead C—H bond. Terms of entries 1 and 2 involve the 'perturbator' V_{31^*,C^*}, while that of entry 1 involves also $V_{31^*,H}$. These two 'perturbators' are compared in Table 6, where the corresponding LCAO coefficients C_s^3(Cl) and C_s^1 (Cl) are also displayed. It is observed that relative changes in $V_{31^*,H}$ are notably smaller than those of V_{31^*,C^*}, which, in turn, originate mainly in the LCAO coefficient C_s^3(C1). The latter corresponds to the contribution of the C1 2s atomic orbital to the LMO representing the C1—C2 bond.

CONCLUSION

The exceptionally large substituent effects on ^3J(C1–H) couplings in the 1-X-bicyclo[1.1.1]pentanes measured in this work constitute interesting experimental evidence of the additivity of the multipath transmission of the Fermi contact term for this type of couplings.

Empirical substituent parameter regressional analyses demonstrate that electronegativity effects play an important role in determining the magnitude of the couplings particularly in the case of those systems in which the substituent is attached to the bridgehead carbon by a second-row element. Indeed, in these instances the electronegativity of the substituent X appears to be the dominant influence with a far less significant contribution from the substituent field/inductive and resonance effects.

IPPP–CLOPPA–INDO analysis of the above-mentioned substituent effects suggests that three different factors contribute to the observed trend. They are: (a) a larger efficiency of each coupling pathway for certain substituents through the polarization propagator factor; (b) the effect of substituent electronegativity which appears to play a major role as supported by the empirical correlations; and (c) a non-bonded interaction between the substituent and the C3—H bond which increases the size of its rear lobe. The three effects are not necessarily independent of each other, although in some instances some of them are noticeably enhanced. For example, effect (c) is enhanced in the bicyclo[1.1.1]pentyl system owing to the collinearity of the X—C1 and C3—H bonds. This effect increases the through-space component transmitted between the two bridgehead carbon atoms, although the calculations suggest that through-bond transmission of coupling information is still the major contributor to the magnitude of ^3J(C1–H).

EXPERIMENTAL SECTION

NMR spectra were recorded on a Varian Gemini–300 NMR spectrometer operating at 300 MHz (for ^{1}H spectra) and 75·462 MHz (for ^{13}C spectra). Carbon-proton coupling constants were obtained from proton-coupled ^{13}C spectra measured at 200/300 Hz spectral width. Deuterochloroform was employed as solvent for NMR measurements unless specified otherwise. General experimental procedures were as described previously.[25] [1.1.1]Propellane,[26] bicyclo[1.1.1]pentane-1,3-dicarboxylic acid,[26] dimethylbicyclo[1.1.1]pentane-1,3-dicarboxylate,[26] 1-bromobicyclo[1.1.1]pentane (**23**),[27] 1-chlorobicyclo[1.1.1]pentane (**21**),[27] 1-iodobicyclo[1.1.1]pentane (**22**),[28] 1-phenylselenobicyclo[1.1.1]pentane (**18**),[28] 1-aminobicyclo[1.1.1]pentane (**11**)[6g] and its hydrochloride (**15**)[6g,29], methyl-3-iodobicyclo[1.1.1]pentane-1-carboxylate,[25] 1-nitrobicyclo[1.1.1]pentane (**17**),[6j] 1,3-diiodobicyclo[1.1.1]pentane,[30] 3-phenylbicyclo-[1.1.1]pentane-1-carboxylic acid,[31] 1-cyanobicyclo[1.1.1]pentane (**13**),[6i] bicyclo[1.1.1]pentane-1-carboxylic acid (**9**)[29,32] and 3-deuterobicyclo[1.1.1]pentane-1-carboxylic acid (**8b**)[33] were prepared according to literature procedures.

1-Phenylbicyclo[1.1.1]pentane (**2**). 3-Phenylbicyclo[1.1.1]pentane-1-carboxylic acid was converted into the corresponding thiohydroxamic ester as described.[27] The Barton ester (0·23 g, 0·78 mmol) was dissolved in benzene (10 ml) under a nitrogen atmosphere. Azobisisobutyronitrile (AIBN) (catalyst) and pentaerythritol tetrakis(3-mercaptopropionate) (0·76 g, 2 equiv.) were added and the solution was heated at reflux for 3 h whilst being irradiated (300 W tungsten lamp). The solution was washed with 20% sodium hydroxide solution (2 × 20 ml) and then dried ($MgSO_4$), filtered and the benzene removed at atmospheric pressure. Distillation (120 °C/100 mm Hg) of the residue afforded a colorless liquid which was identified as the title compound **2** (58 mg, 52%). ^{1}H NMR (60 MHz), δ 2·07, s, 6H; 2·54, s, 1H; 7·22, s, SH. ^{13}C NMR, δ 26·72; 47·2; 52·18; 125·96, 126·34, 128·13 141·73 (lit.[32] NMR).

3-Deutero-1-phenylbicyclo[1.1.1]pentane (**2b**). The thiohydroxamic ester of 3-phenylbicyclo[1.1.1]-pentane-1-carboxylic acid (327 mg, 1·74 mmol) was dissolved in benzene (32 ml) containing AIBN (catalyst) and the solution maintained under a nitrogen atmosphere. Thiophenol-*d* (3 ml, 16 equiv.) was added and the reaction mixture was heated at reflux and irradiated (300 W tungsten lamp) with stirring for 3·5 h. The reaction mixture was washed with NaOH (15%, 2×) and was then dried ($MgSO_4$), after which the solvent was removed at atmospheric pressure. Distillation of the residue (110 °C/100 mm Hg) afforded the deuterated compound **2b** (0·143 g, 57%) as a colorless liquid whose spectral data were consistent with those of the protio analog. ^{1}H NMR, δ 2·06, s, 6H; 7·26, s, 5H. ^{13}C NMR, δ 26·67, t, J = 25·39 Hz; 47·2; 52·0; 125·91; 126·28; 128·08; 141·8.

3-Deutero-1-tert-butyl-bicyclo[1.1.1]pentane (**3b**). 1,3-Diiodobicyclo[1.1.1]pentane (2·0 g, 6·25 mmol)

was dissolved in dry diethyl ether (15 ml) and dry pentane (5 ml) under nitrogen and cooled to −80 °C. A 1·7 M solution of *tert*-BuLi (12 ml, 3·2 equiv.) in pentane was added over 5 min. After 15 min, methanol-d_4 (1 ml) in dry diethyl ether (5 ml) was added and the reaction was allowed to reach room temperature. The reaction mixture was washed with water (2×) and then dried ($MgSO_4$) before being filtered. Gentle removal of the solvent at atmospheric pressure and distillation of the residue (90 °C/760 mm Hg) afforded the title compound **3b** (329 mg, 42%) as a colorless liquid whose spectral data were consistent with those reported[34,35] for the protio analog. ^{1}H NMR, δ 0·87, s, 9H, CH_3; 1·61, s, 6H, CH_2. ^{13}C NMR, δ 25·73; 25·88; 30·07; 46·57; 53·73.

1-Acetyl-3-deuterobicyclo[1.1.1]pentane (**4b**). 3-Deuterobicyclo[1.1.1]pentane-1-carboxylic acid (566 mg, 5·0 mmol) was dissolved in tetrahydrofuran (40 ml) under a nitrogen atmosphere with stirring at 0 °C. A 1·4 M solution of methyllithium (14 ml, 4 equiv.) in diethyl ether was added rapidly and the mixture stirred for 2 h before being treated with trimethylchlorosilane (5·1 ml, 8 equiv.). The reaction mixture was stirred for 18 h at room temperature after which 1 M hydrochloric acid (30 ml) was added and the mixture stirred for 30 min and then extracted with diethyl ether (3 × 50 ml). The combined extracts were dried ($MgSO_4$) and the solvent removed at atmospheric pressure. Distillation (90 °C/35 mm Hg) afforded a colorless liquid which was identified by comparison of its spectral properties with those of known[36] 1-acetylbicyclo[1.1.1]pentane (**4**). ^{1}H NMR, δ 2·0, s, 6H, CH_2; 2·04, s, 3H, CH_3. ^{13}C NMR, δ 25·77; 26·84, t, J = 25·6Hz; 49·61; 51·00; 205·65.

1-(Tributylstannyl)bicyclo[1.1.1]pentane (**5**). [1.1.1]Propellane [from 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (5·05 g, 17 mmol)] in diethyl ether (50 ml) was treated with tributyltin hydride (14·5 ml, 3·3 equiv.) and AIBN (catalyst) under nitrogen whilst being irradiated (300 W tungsten lamp) for 40 min. The volatile contents of the vessel were retained during irradiation by use of an acetone–liquid nitrogen condenser. The solvent was removed under reduced pressure to leave a colorless liquid, which was dissolved in iodomethane (40 ml) containing AIBN (catalyst) and exposed to irradiation (300 W tungsten lamp) for 75 min. Removal of the volatile constituents and purification of the resulting colorless liquid by silica gel chromatography (70–230 mesh, eluent hexane) afforded the known[37] title compound **5** as the first fraction (3·42 g, 52%). ^{1}H NMR, δ 0·80, t, 6H, J = 8·0 Hz; 0·89, t, 9H, J = 7 Hz; 1·28, sextet, 6H; 1·42–1·54, m, 6H; 2·88, s, 1H, CH with tin magnetic isotope satellites $^4J(^{119}Sn-H)$ = 179·3 Hz, $^4J(^{117}Sn-H)$ = 171·2 Hz; 1·97, s, 6H. ^{13}C NMR δ 8·90, Bu–C1 with tin magnetic isotope satellites $^1J(^{119}Sn-C)$ = 314·0 Hz, $^1J(^{117}Sn-C)$ = 300·0 Hz; 13·79, Bu–C4; 27·46, Bu–C2 with tin magnetic isotope satellites $^2J(^{119}Sn-C)$ = 50.44 Hz, $^2J(^{117}Sn-C)$ = 48·21 Hz; 29·33, Bu–C3; 37·12, C1 with tin magnetic isotope satellites $^1J(^{119}Sn-C)$ = 301·76 Hz, $^1J(^{117}Sn-C)$ = 288·34 Hz; 39·16, C3 with tin magnetic isotope satellites $^3J(^{119}Sn-C)$ = 119·21 Hz, $^3J(^{117}Sn-C)$ = 114·17 Hz; 56·13, C2.

3-Deutero-1-methylbicyclo[1.1.1]pentane (**6b**). [1.1.1]Propellane [from 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (12·03 g, 40·5 mmol)] in diethyl ether (110 ml) was distilled into a Pyrex photolysis vessel. Iodomethane (4·03 g, 0·7 equiv.) was added and the mixture was irradiated (450 W Hanovia medium-pressure mercury lamp) for 75 min at 0 °C under argon. The solvent was removed *in vacuo* at 0 °C to afford a viscous yellow liquid (4·16 g). Distillation (90 °C/50 mm Hg) afforded a white solid (collected at 0 °C, which rapidly melted when warmed to room temperature) which was identified as 1-iodo-3-methylbicyclo[1.1.1]pentane (2·9 g, 40%). ^{1}H NMR, δ 1·21, s, 3H, CH_3; 2·21, s, 6H, CH_2. ^{13}C NMR, δ 7·04; 18·33; 44·61; 62·11. (lit.[38] NMR). The iodide (0·15 g, 0·72 mmol) was reduced and trapped as described above for the synthesis of **14** to afford 3-deutero-1-methylbicyclo[1.1.1]pentane (**6b**) (0·03 g, 50%). ^{1}H NMR, δ 1·10, s, 3H, CH_3; 1·65, s, 6H, CH_2. ^{13}C NMR, δ 19·10; 26·96, t, J = 25·2 Hz; 42·08; 52·00. (lit.[6d] NMR).

1-(Hydroxydideuteromethyl)bicyclo[1.1.1]pentane (**7**). Bicyclo[1.1.1]pentane-1-carboxylic acid (214 mg, 1·91 mmol) was dissolved in dry diethyl ether (10 ml) and added slowly with stirring to a solution of lithium aluminium deuteride (160 mg, 2 equiv.) in dry diethyl ether (10 ml) under nitrogen. The mixture was heated at reflux for 2 h and then stirred at room temperature for 16 h before being quenched by the addition of saturated sodium sulfate solution (1 ml). The solution was dried ($MgSO_4$) and filtered. Most of the diethyl ether was removed under reduced pressure and the remainder by distillation (40 °C/760 mm Hg), leaving the title compound **7** (71 mg, 37%) whose identity was confirmed by comparison of its spectral data with literature values for the unlabelled[29] and ^{13}C-labelled[1e] analogs. ^{1}H NMR, δ 1·73, s, 6H; 2·51, s, 1H; 2·78, s, 1H. ^{13}C NMR, δ 27·79; 45·32; 48·56; 62·39.

Methyl bicyclo[1.1.1]pentane-1-carboxylate (**9**). Methyl 3-iodobiyclo[1.1.1]pentane-1-carboxylate in Bu_3SnH (1·5 equiv.) was irradiated (300 W tungsten lamp) with stirring while a stream of nitrogen was bubbled through the solution and into a trap cooled to −40 °C. The colorless volatile liquid which collected in the trap was identified as methyl bicyclo[1.1.1]pentane-1-carboxylate (**9**). ^{1}H NMR, δ 2·08, s, 6H, CH_2; 2·42,

s, 1H, CH; 3·64, s, 3H, CH3. ^{13}C NMR, δ 27·76; 42·50; 51·40; 51·50; 169·97 (lit.[36] NMR).

1-(Triphenylstannyl)bicyclo[1.1.1]pentane (**10**). The procedure used above for the corresponding tributylstannane (**5**) was employed. Silica gel chromatography (70–230 mesh, eluent 3% diethyl ether–hexane) of the crude product afforded a white solid, which was identified by comparison of spectral data with literature[37] values as 1-(triphenylstannyl)bicyclo[1.1.1]-pentane (**10**). (4·2 g, 73%). ^{1}H NMR (300 MHz), δ 2·26, s, 6H, CH_2; 2·94, s, 1H, CH, tin magnetic isotope satellites $^4J(^{119}Sn-H) = 225·3$ Hz, $^4J(^{117}Sn-H) = 215·3$ Hz; 7·25–7·35, m, 9H, ArH; 7·45–7·60, m, 6H, ArH. ^{13}C NMR, δ 37·21, C1, tin magnetic isotope satellites $^1J(^{119}Sn-C1) = 395·2$ Hz, $^1J(^{117}Sn-C1) = 377·8$ Hz; 40·39, C3, tin magnetic isotope satellites $^3J(^{119}Sn-C3) = 140·7$ Hz, $^3J(^{117}Sn-C3) = 134·5$ Hz; 56·72, C2; 128·45, tin magnetic isotope satellites $J(^{119}Sn-C) = 48·4$ Hz, $J(^{117}Sn-C) = 46·3$ Hz; 128·80, tin magnetic isotope satellites $J(^{119/117}Sn-C) = 10·9$ Hz; 137·10, tin magnetic isotope satellites $J(^{119}Sn-C) = 36·0$ Hz, $J(^{117}Sn-C) = 34·5$ Hz; 138·99 ArC1, tin magnetic isotope satellites $J(^{119}Sn-C) = 481·4$ Hz, $J(^{117}Sn-C) = 460·1$ Hz.

1-Bicyclo[1.1.1]pentyl phenyl sulfone (**12**). 1-Bicyclo[1.1.1]pentyl phenyl sulfide (**16**) (1·74 g, 9·9 mmol) was combined with acetic acid (4 ml, 7 equiv.) and acetic anhydride (3·7 ml, 4 equiv.) at 0 °C, then 30% hydrogen peroxide (3·4 ml, 3 equiv.) was added slowly to the solution, which was stirred for 16 h at room temperature before being quenched with water (40 ml). The mixture was extracted with dichloromethane (3×) and the organic extracts washed with saturated hydrogencarbonate solution (2×) and water (1×) before being dried ($MgSO_4$) and evaporated. The residue was distilled (135 °C/0·1 mm Hg) to give white crystals of 1-bicyclo[1.1.1]pentyl phenyl sulfone (**12**) (1·85 g, 90%), m.p. 55–56 °C. ^{1}H NMR (300 MHz), δ 2·06, s, 6H, CH^2; 2·71, s, 1H, CH; 7·54–7·61, m, 2H, *m*-ArH; 7·63–7·70, m, 1H, *p*-ArH; 7·82–7·88, m, 2H, *o*-ArH. ^{13}C NMR, δ 26·68, 50·29, 54·95, 128·48, 129·02, 133·55, 136·71; mass spectrum, *m/z* (relative intensity, %) 209 ($M^+ + 1$, 14·5), 208 (0·7), 143 (65·1), 125 (93), 83 (38), 78 (58), 77 (82), 67 (100); HRMS, calculate for $C_{11}H_{12}O_2S$ 208·0558, found 208·0583. Analysis, calculated for $C_{11}H_{12}O_2S$, C 63·44, H 5·81; found C 63·49, H 5·89%.

3-Deutero-1-methoxybicyclo[1.1.1]pentane (**14b**). 1,3-Diiodobicyclo[1.1.1]pentane (1·8 g, 5·63 mmol), NaOH (0·9 g, 4 equiv.) and methanol (48 ml) were combined in a sealed vessel and stirred at room temperature in the dark for 72 h, after which water (50 ml) was added and the solution extracted with pentane (5 × 50 ml). The combined pentane extracts were back-extracted with water (1×), dried ($MgSO_4$) and the solvent was removed *in vacuo* (<5 °C) to afford a clear liquid (880 mg), which was shown by spectral comparison[39] to be a 92:8 mixture of 3-iodo-1-methoxybicyclo[1.1.1]pentane (^{1}H NMR, δ 2·33, s, 6H, CH_2; 3·27, s, 3H, OCH_3) and its solvolysis product, 3,3-dimethoxy-1-methylenecyclobutane (^{1}H NMR, δ 2·8, t, 4H, CH_2; 3·18, s, 6H, OCH_3; 4·95, m, 2H, $=CH_2$). The crude mixture was added to Bu_3SnD (2·8 ml) containing AIBN (catalyst) and the mixture irradiated (300 W tungsten lamp) with stirring for 2 h whilst being swept with nitrogen. The effluent was led into a cold trap (<−30 °C) and then dissolved in deuterochloroform. Bromine (4 drops) was added and the solution was washed with sodium metabisulfite solution (1 × 1 ml) and dried ($MgSO_4$). The $CDCl_3$ solution was swept by nitrogen and the volatile constituents trapped below −30 °C. The contents of the trap were analysed (^{1}H and ^{13}C NMR) and found to consist of 3-deutero-1-methoxybicyclo[1.1.1]pentane (**14b**) and deuterochloroform. The yield was not determined. ^{1}H NMR, δ 1·86, s, 6H, CH_2; 3·28, s, 3H, CH_3. ^{13}C NMR, δ 17·95, t, $J = 26·74$ Hz; 50·40; 53·55; 68·93. HRMS, calculated for C_6H_9DO 99·0794, found 99.0806.

1-Bicyclo[1.1.1]pentyl phenyl sulfide (**16**). [1.1.1]Propellane [from 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (20·0 g, 67·4 mmol)] in diethyl ether (50 ml) was treated with thiophenol (6·9 ml, 1 equiv.) at −40 °C as described.[33] The product obtained after chromatography was distilled (80 °C/4·5 mm Hg) and afforded the sulfide **16** as a colorless liquid (5·89 g, 50%). ^{1}H NMR, δ 1·92, s, 6H, C_2; 2·68, s, IH, CH; 7·1–7·5, m, 5H, ArH. (lit.[34] ^{1}H NMR). ^{13}C NMR, δ 28·63, 45·57, 53·92, 127·33, 128·65, 133·42, 134·04.

1-Acetoxybicyclo[1.1.1]pentane (**19**). Bicyclo[1.1.1]pentane-1-carboxylic acid was converted into 1-acetylbicyclo[1.1.1]pentane (**4**) as described above for the deutero analog. The ketone **4** (510 mg, 4·6 mmol) dissolved in chloroform (11 ml) containing 50% *m*-chloroperbenzoic acid (1·6 g, 1 equiv.) was allowed to stand at room temperature for 27 days. The mixture was filtered, and the filtrate washed successively with saturated sodium metabisulfite solution, 10% sodium hydrogencarbonate solution, and water, before being dried ($MgSO_4$) and carefully evaporated (30 °C/110 mm Hg). The residue was distilled (100 °C/30 mm Hg) to give the volatile acetate **19**. Mass spectrum *m/z* (relative intensity, %) 111 ($M^+ - CH_3$), 83 (32), 43 (100). ^{1}H NMR, δ 2·0, s, 3H, CH_3, 2·2, s, 6H, CH_2; 2·5, s, 1H, CH. ^{13}C NMR, δ 20·88; 21·35; 53·23; 64·28; 170·37.

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