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Steric Effects on Carbon-13 NMR Shifts: Carbon–Hydrogen Bond Polarization Contributions

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ABSTRACT: The shielding observed in the chemical shifts of carbon atoms subjected to steric compression was originally attributed to carbon–hydrogen bond polarization. There is increasing evidence that this is not universally the case and theoretical studies reveal that changes in dihedral angles may be responsible for many steric effects. Hydrogen shifts, bond lengths and charge distributions were used as probes for these effects in methylnorbornanes and similar tetracyclic norbornyl hydrocarbons. Carbon–hydrogen bond polarization can make a significant contribution to shielding and can be distinguished from effects caused by changes in dihedral angles due to steric congestion. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: steric effects; carbon–hydrogen bond polarization; ^{13}C NMR chemical shifts

INTRODUCTION

The widespread use of carbon-13 NMR in the determination of the stereochemistry of organic compounds is based on changes in chemical shifts caused by groups that are close in space. Their interactions result in shielding of the carbon nuclei involved. Such effects are generally attributed to carbon–hydrogen bond polarization. Nevertheless, as one recent textbook[1] has pointed out: 'it seems that further theoretical and experimental work is necessary in order to substantiate this argument.'

The interpretation of carbon-13 and hydrogen spectra of tetracyclododecanes[2] confirmed some of the earliest work[3] related to steric effects on chemical shifts. Comparison of tetracyclic norbornyl systems such as **1**–**5** (Fig. 1) with their bicyclic counterparts clearly shows that, in all cases in which significant van der Waals interactions might be expected, shielding is observed for carbon atoms and deshielding is observed for hydrogen atoms. Force field calculations reveal a significant shortening of the compressed C—H bond,[2] in line with the theoretical analysis of strain in cyclic hydrocarbons since, in CH_2 groups subjected to strain, charge is transferred from hydrogen to carbon, increasing the s-character of the C—H bond.[4,5] On the other hand, the *ab initio* IGLO MO work of Barfield and collaborators[6–10] on paramagnetic bond contributions to carbon-13 chemical shifts has shown their strong sensitivity to changes in dihedral angles formed by carbon–carbon and carbon–hydrogen bonds. Fisher and Gradwell[11] have similarly noted a correlation between dihedral angles and substituent effects on hydrogen chemical shifts. How, then, can these dihedral angle and stereochemical influences on carbon and hydrogen chemical shifts be distinguished and evaluated?

Part of the problem lies in the choice of appropriate model systems. Rotation about carbon–carbon bonds in linear hydrocarbons introduces several steric interactions that would lead to carbon–hydrogen bond polarization in addition to effects due to changes in dihedral angles. Ring strain in cyclobutanes and bicyclo[1.1.1]pentanes also affects chemical shifts.[6] Substituents may introduce additional effects such as those due to contributions by electric fields, anisotropy, hyperconjugation, etc. Even methyl groups may disturb a system's geometry[12] and charge distribution[13] and would be expected to affect its chemical shifts also.

The use of ultrasound radiation in the dechlorination of hexachlorinated polycyclic compounds[14] provided access to some of the structures we had assigned[2] from data in the literature, permitting the unambiguous interpretation of carbon and hydrogen chemical shifts for two tetracyclic hydrocarbons where significant inductive and field effects are absent, and steric contributions could be more clearly analysed. Particular interest in these molecules arises from the fact that the [2.2.1] bicyclic (or norbornyl) systems (Fig. 2) that were extensively investigated in order to establish steric effects on carbon-13 chemical shifts are fused in different geom-

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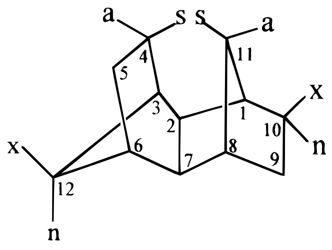

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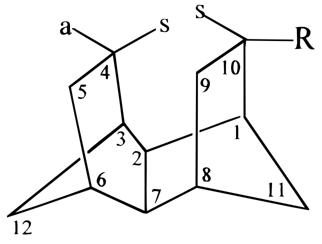
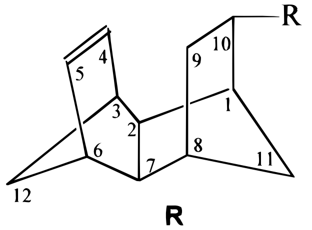
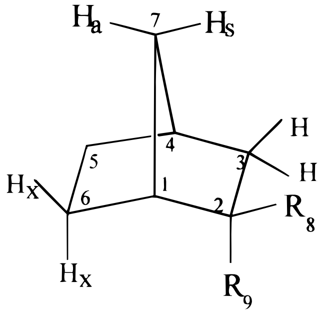


	R
2	H_a
3	OH



	R
4	H
5	OH

Figure 1. Tetracyclic systems.



	R_8	R_9
6	H_x	H_n
7	CH_3	H_n
8	H_x	CH_3

Figure 2. Bicyclic systems.

etries in tetracyclic *exo–endo* and *endo–endo* systems **1** and **2**, respectively. Particularly in the *exo–endo* system **1**, there is one methylene and one ethylene segment which suffer severe steric strain and one of these segments which is in a situation very similar to that of the bicyclic hydrocarbon norbornane (**6**). Its carbon-13 and hydrogen spectra (which were reported without interpretation in the literature[15]) are assigned and used as probes for steric effects. Results for **1** and **2** are compared with those for 2-*exo* (**7**) and 2-*endo* (**8**) methyl-substituted norbornane (**6**). It is clear that carbon–hydrogen bond polarization represents one of the most important contributions to carbon and hydrogen chemical shifts but it is not the only one. It can be unambiguously identified by hydrogen chemical shifts and distinguished from other factors that are responsible for stereochemical effects by the use of probes for bond polarization such as lengths and charge distributions.

RESULTS AND DISCUSSION

Interpretation of Spectra

Carbon-13 chemical shifts for norbornane (**6**) and its 2-methyl derivatives (**7** and **8**) have been compiled, checked and, in some cases, reassigned from the literature,[16] while their hydrogen shifts were recently unambiguously assigned.[11] With regard to tetracyclic molecules **1** and **2**, our original[2] carbon-13 chemical shift assignments were confirmed and hydrogen chemical shifts of **1** were assigned as described below.

There are four absorptions in the carbon-13 spectrum of **2**, the *endo–endo* tetracyclic dodecane. According to the literature,[15] these appear at 47.9, 46.9, 41.3 and 25.2 ppm. Assignments of C-4/C-5/C9/C-10 at 25.2 ppm and C-1/C-3/C-6/C-8 at 41.3 ppm, are immediate and C-2/C-7 at 46.9 ppm, C-11/C-12 at 47.9 ppm should follow from analogy with **4**.[17] Since **3** was easily accessible by hydrogenation of **5** we made a complete assignment of its spectra (Table 1; the numbering scheme follows the previously published structures), APT being used to distinguish C-12 at 47.8 ppm, C-11 at 43.6 ppm, C-9 at 38.2 ppm, C-5 at 25.8 ppm and C-4 at 25.2 ppm. Assignment of the carbon-13 spectrum for **3** is consistent with that of **2** and supports the choice of C-11/C-12 as the absorption corresponding to the largest chemical shift.

The carbon-13 spectrum of the *exo–endo* tetracyclic hydrocarbon **1** shows absorptions at 50.1, 42.1 41.2, 36.2, 34.2, 31.2 and 24.4 ppm, those at 50.1, 41.2 and 36.2 corresponding to tertiary carbons by APT. The relative intensities of absorptions at 31.2 and 24.4 ppm are approximately double those of all others and must correspond to C-4/C-5 and C-9/C-10.

There are absorptions around 2.2 (2H), 2.05 (2H), 1.55 (3H), 1.45 (4H), 1.25 (3H), 1.15 (1H) and 0.95 (3H) ppm in the hydrogen spectrum of **1**. A HETCOR experiment shows that the carbon atoms (50.1 ppm) with the largest

Table 1. Carbon-13 and proton chemical shifts

	Structure								
	1		2	3	4	5	6[a]	7[a]	8[a]
Atom	^{1}H δ (ppm)	^{13}C δ (ppm)	^{13}C δ (ppm)						
1	2.05	36.2	41.3	50.3	39.8	48.0	36.3	43.0	41.7
2	1.55	50.1	46.9	46.4	47.1	46.4	29.6	36.4	34.0
3	2.20	41.2	41.3	40.9	44.7	44.2	29.6	39.8	38.4
4	—	24.4	25.2	25.2	131.6	131.9	36.3	36.9	37.7
4a	1.25	—	—	—	—	—	—	—	—
4s	1.45	—							
5	—	24.4	25.2	25.8	131.6	132.6	29.6	28.7	30.2
5a	1.25	—	—	—	—	—	—	—	—
5s	1.45	—	—	—	—	—	—	—	—
6	2.20	41.2	41.3	41.1	44.7	44.4	29.6	30.0	22.1
7	1.55	50.1	46.9	45.0	47.1	45.8	38.3	34.8	40.2
8	2.05	36.2	41.3	40.5	39.8	39.0	—	—	—
9	—	31.2	25.2	38.2	24.8	37.4	—	—	—
9n	0.95	—	—	—	—	—	—	—	—
9x	1.45	—	—	—	—	—	—	—	—
10	—	31.2	25.2	70.3	24.8	71.0	—	—	—
10n	0.95	—	—	—	—	—	—	—	—
10x	1.45	—	—	—	—	—	—	—	—
11		34.2	47.9	43.6	48.7	43.5	—	—	—
11a	0.95	—	—	—	—	—	—	—	—
11s	1.55	—	—	—	—	—	—	—	—
12	—	42.1	47.9	47.8	59.2	58.7	—	—	—
12n	1.15	—	—	—	—	—	—	—	—
12x	1.25	—	—	—	—	—	—	—	—

[a] Ref. 16

chemical shifts correlate with the hydrogens around 1.55 ppm, carbons at 42.1 ppm with hydrogens at 1.15 and 1.25 ppm, carbons at 41.2 ppm with hydrogens at 2.2 ppm, carbons at 36.2 ppm with hydrogens at 2.05 ppm, carbons at 34.2 ppm with hydrogens at 1.55 and 0.95 ppm, carbons at 31.2 ppm with hydrogens at 1.45 ppm and 0.95 ppm and carbons at 24.4 ppm with hydrogens at 1.45 and 1.25 ppm. Our previous tentative carbon-13 shift assignments[2] are in agreement with these results and are confirmed by COSY experiments. Complete interpretation is given in Table 1.

Carbon and Hydrogen Chemical Shifts

The *exo–endo* tetracyclic hydrocarbon **1** has two pairs of methylene and ethylene segments that are similar to those of norbornane (**6**). The 'inside' hydrogens on C-4 and C-5 and on C-11 are close in space, introducing severe steric interactions, which are absent for C-9 and C-10 of the other ethylene segment and C-12 of the other methylene segment and their respective hydrogens. Correspondingly, C-4 and C-5 are shielded by 6.8 ppm relative to C-9 and C-10 while C-11 is shielded by 7.9 ppm relative to C-12. Chemical shifts for pairs of hydrogens on these carbons also reflect the effects of steric crowding. There is a 0.7 ppm difference between the 'inside' (11s) and 'outside' (11a) methylene hydrogens and a 0.2 ppm difference between the inside (4s, 5s) and outside (4a, 5a) hydrogens on the ethylene carbons. Since the corresponding *exo* hydrogens (2x, 3x and 5x, 6x) on norbornane absorb at 0.3 ppm higher frequency than the respective *endo* hydrogens (2n, 3n and 5n, 6n) while the uncongested *exo* ethylene hydrogens 9x, 10x absorb at a −0.5 ppm higher frequency than their *endo* counterparts (9n, 10n) this difference should be estimated as *ca.* −0.7 ppm.

These results are consistent with carbon–hydrogen bond polarization due to steric repulsions among hydrogens. Charge is shifted from hydrogen to carbon, deshielding the former and shielding the latter. Force field calculations show a shortening of the corresponding carbon–hydrogen bonds and STO-3G calculations reveal an increase in the charge on carbon and a decrease in the charge on hydrogen, as discussed in the next section.

It is instructive to compare these results with methyl group-induced chemical shifts on norbornane. The introduction of substituents in 2-*exo* and *endo* positions of norbornane is taken as a classical example of steric interactions and is often used to illustrate the γ-effect on carbon-13 chemical shifts, i.e. when the substituent is *exo* C-7 is shielded by 3.5 ppm whereas when it is *endo* it is C-6 that is shielded by 7.5 ppm. This simplistic interpretation does not account for the 0.9 ppm shielding of C-5 in *exo*-2-methylnorbornane relative to norbornane or its 1.3 ppm shielding relative to C-6.

Hydrogen chemical shifts can be used in order to verify this interpretation. Whereas in *endo*-2-methylnorbornane the hydrogen under strain, H-6n, is deshielded by 0.3 ppm relative to norbornane and 0.4 ppm relative to its *exo*-isomer, H-7s in *exo*-2-methyl norbornane is deshielded by only 0.1 ppm relative to norbornane and absorbs at about the same frequency as the corresponding hydrogen on the *endo* isomer. Hence it appears that although C-6 in *endo*-2-methylnorbornane is mainly shielded by carbon–hydrogen bond polarization, this does not seem to be the case with C-7 in *exo*-2-methylnorbornane.

Carbon–hydrogen Bond Polarization

Carbon–hydrogen bond polarization should be reflected by a shortening of the respective bond and a transfer of charge from hydrogen to carbon. We therefore calculated the molecule's geometries (MM2) and charge distributions (STO-3G).

Inspection of Table 2 reveals that carbon–hydrogen bond lengths closely parallel the trends in their respective chemical shifts. Taking norbornane as a model, it is immediately clear that for the tetracyclic hydrocarbons 1 and 2, only congested carbon–hydrogen bonds show any significant ($>0.1\%$) deviation from values calculated for the corresponding methylene or ethylene segment. For the *exo–endo* hydrocarbon **1**, for example, it is obvious that bonds corresponding to hydrogens under steric strain are considerably shortened. The carbon–hydrogen bond on the methylene bridge which is 'inside' (H-11s) is almost 1% shorter than the 'outside' one (H-11a), the methylene hydrogens on norbornane, or the hydrogens on the methylene group of **1** that are not subject to strain (H-12s, H-12a). The 'inside' hydrogens on the ethylene bridge under strain (H-4s, H-5s) are shortened to a lesser extent (*ca.* 0.4%) compared with norbornane, the respective 'outer' hydrogens (H-4a, H-5a), or hydrogens on the ethylene segment that is not under strain (H-9s, H-9a, H-10s, H-10a). Similar considerations apply to the ethylene bridges of the *endo–endo* hydrocarbon **2**.

Charge distributions are also in line with this interpretation. From Table 3 it is clear that for **1** the methylene carbon atom suffering steric compression (C-11) has considerably (*ca.* 4%) more negative charge than the carbon in which compression is absent (C-12). Hydrogen atoms reflect effects more strongly, since there is almost 15% more positive charge on H-11s than on H-11a. As was the case with bond lengths, the ethylene carbons under compression (C-4, C-5) have considerably more charge than the ones that are not (C-9, C-10) whereas the 'inside' hydrogens (H-4s, H-5s) have *ca.* 5% more positive charge than the 'outside' ones (H-4a, H-5a).

Taken together with the shielding observed for the respective carbons and deshielding observed for the respective hydrogens, these results make a very strong case for carbon–hydrogen bond polarization as a source of steric effects on carbon and hydrogen chemical shifts. This is, however, an extraordinary case of compression along a carbon–hydrogen bond. The extent to which it is also present in other cases may be probed by applying similar criteria to 2-methyl-substituted norbornanes.

Table 2. Carbon–hydrogen bond lengths

Bond	Structure				
	1	**2**	**6**	**7**	**8**
C-1—H-1	1.1158	1.1168	1.1169	1.1163	1.1168
C-2—H-2	1.1175	1.1196	—	—	—
C-2—H-2x	—	—	1.1162	—	1.1188
C-2—H-2n	—	—	1.1153	1.1174	—
C-3—H-3	1.1168	1.1168	—	—	—
C-3—H-3x	—	—	1.1162	1.1154	1.1162
C-3—H-3n	—	—	1.1153	1.1153	1.1146
C-4—H-4	—	—	1.1169	1.1169	1.1168
C-4—H-4x	—	—	—	—	—
C-4—H-4n	—	—	—	—	—
C-4—H-4s	1.1124	1.1078	—	—	—
C-4—H-4a	1.1165	1.1168	—	—	—
C-5—H-5	—	—	—	—	—
C-5—H-5x	—	—	1.1162	1.1153	1.1162
C-5—H-5n	—	—	1.1153	1.1162	1.1153
C-5—H-5s	1.1124	1.1077	—	—	—
C-5—H-5a	1.1165	1.1168	—	—	—
C-6—H-6	1.1168	1.1168	—	—	—
C-6—H-6x	—	—	1.1162	1.1163	1.1164
C-6—H-6n	—	—	1.1153	1.1153	1.1136
C-6—H-6s	—	—	—	—	—
C-6—H-6a	—	—	—	—	—
C-7—H-7	1.1175	1.1196	—	—	—
C-7—H-7s	—	—	1.1158	1.1150	1.1158
C-7—H-7a	—	—	1.1158	1.1158	1.1159
C-8—H-8	1.1158	1.1168	—	—	—
C-8—H-8s	—	—	—	—	—
C-8—H-8a	—	—	—	—	—
C-9—H-9x	1.1164	—	—	—	—
C-9—H-9n	1.1153	—	—	—	—
C-9—H-9s	—	1.1077	—	—	—
C-9—H-9a	—	1.1168	—	—	—
C-10—H-10x	1.1164	—	—	—	—
C-10—H-10n	1.1153	—	—	—	—
C-10—H-10s	—	1.1078	—	—	—
C-10—C-10a	—	1.1168	—	—	—
C-11—H-11x	—	1.1164	—	—	—
C-11—H-11n	—	1.1163	—	—	—
C-11—H-11s	1.1055	—	—	—	—
C-11—H-11a	1.1163	—	—	—	—
C-12—H-12x	1.1161	1.1164	—	—	—
C-12—H-12n	1.1161	1.1163	—	—	—

The 3.5 ppm shielding of C-7 in *exo*-2-methylnorbornane is taken as a classical example of the γ-effect.[1,16] Using hydrogen chemical shifts as probes, it would appear that this contribution would be very slight since the hydrogen on the same side of the methylene bridge as the methyl group, H-7s is deshielded by only *ca.* 0.1 ppm relative to norbornane. The change in the corresponding bond length (C-7—H-7s) is also small ($<0.1\%$) compared with norbornane or the *anti*-

Table 3. Charge distributions

	Structure				
Atom	**1**	**2**	**6**	**7**	**8**
C-1	−0.0347	−0.0346	−0.0307	−0.0354	−0.0333
C-2	−0.0456	−0.0470	−0.1082	−0.0261	−0.0266
C-3	−0.0310	−0.0346	−0.1082	−0.1128	−0.1131
C-4	−0.1125	−0.1122	−0.0307	−0.0318	−0.0307
C-5	−0.1125	−0.1122	−0.1082	−0.1070	−0.1088
C-6	−0.0310	−0.0346	−0.1082	−0.1085	−0.1103
C-7	−0.0456	−0.0470	−0.1094	−0.1107	−0.1113
C-8	−0.0347	−0.0346	—	—	—
C-9	−0.1071	−0.1122	—	—	—
C-10	−0.1071	−0.1122	—	—	—
C-11	−0.1167	−0.1073	—	—	—
C-12	−0.1124	−0.1073	—	—	—
H-1	0.0464	0.0470	0.0488	0.0486	0.0468
H-2	0.0429	0.0429	—	—	—
H-2x, R-8	—	—	0.0510	−0.1863	0.0442
H-2n, R-9	—	—	0.0507	0.0436	−0.1877
H-3	0.0442	0.0470	—	—	—
H-3x	—	—	0.0510	0.0505	0.0500
H-3n	—	—	0.0507	0.0504	0.0498
H-4	—	—	0.0488	0.0497	0.0490
H-4a	0.0519	0.0510	—	—	—
H-4s	0.0546	0.0559	—	—	—
H-5a, x	0.0519	0.0510	0.0510	0.0512	0.0504
H-5s, n	0.0546	0.0559	0.0507	0.0493	0.0505
H-6	0.0442	0.0470	—	—	—
H-6x	—	—	0.0510	0.0512	0.0509
H-6n	—	—	0.0507	0.0506	0.0524
H-7s	—	—	0.0495	0.0496	0.0502
H-7a	—	—	0.0495	0.0496	0.0504
H-7	0.0429	0.0429	—	—	—
H-8	0.0464	0.0470	—	—	—
H-9x, a	0.0510	0.0510	—	—	—
H-9n, s	0.0496	0.0559	—	—	—
H-11x, s	0.0583	0.0489	—	—	—
H-11n, a	0.0496	0.0484	—	—	—
H-12x, s	0.0501	0.0489	—	—	—
H-12n, a	0.0516	0.0484	—	—	—

hydrogen (H-7a). The charge distribution likewise fails to reflect any bond polarization since charge on H-7s is about the same as that on H-7a. Clearly bond polarization has no major role in this 'γ-effect.'

On the other hand, H-6n in 2-*endo*-methylnorbornane is deshielded by *ca.* 0.3 ppm relative to the parent compound (0.2 ppm relative to the *exo*-hydrogen, H-6x, and 0.4 ppm relative to the other *endo* hydrogen, H-5n, that is distant from the methyl group). The corresponding carbon–hydrogen bond is noticeably shortened (*ca* 0.15%) and C-6 has more negative charge (*ca.* 0.13%) than C-5 and H-6n has more positive charge (*ca.* 3%) than H-6x, although in norbornane *endo*-hydrogens have slightly less positive charge than the *exo*-hydrogens. Here carbon bond polarization is playing a role, but it cannot be solely responsible for 7.5 ppm shielding of C-6 (this is the magnitude of shielding of compressed carbons in **1**, but bond polarization seems to contribute less according to the criteria applied here).

Clearly, some other factor must be mainly responsible for the upfield shifts observed for *exo*-2-alkyl-substituted norbornanes. An inspection of the hydrogen spectra of *exo*- and *endo*-2-methyl-substituted norbornane[11] may provide some indications. Excluding vicinal substituent chemical shifts (SCS), H-6n of the *endo*-isomer is the hydrogen atom that is the most deshielded on introduction of a methyl group in the 2-position of norbornane. This observation is consistent with the 'classical' C—H bond polarization previously discussed since charge transfer from hydrogen to carbon should have a deshielding effect. On the other hand, although C-7 is considerably shielded in the *exo*-isomer, the SCS observed for H-7s of the *exo*-isomer is of the same order as that observed for H-7s of the *endo*-isomer where no bond polarization effect is present.

A more detailed investigation into the origin of these effects is beyond the scope of the present paper, but as Fisher and Gradwell[11] have pointed out, there is a correlation between dihedral angles and substituent-induced shifts of hydrogens. This is also the case for carbons[6–10] since the *exo*-methyl group of **7** twists the methylene carbon (C-7) relative to the C_{2v} plane of norbornane, opening the C-2—C-1—C-7 angle and closing the C-3—C-4—C-7 angle slightly. There is also reasonable torsion around C-5 [the C-5—H-5x bond is approximately 4° out of alignment with C-6—H-6x in **3** whereas in norbornane (**6**) these bonds lie in the same plane]. There must also be a contribution from the change in the dihedral angle in *endo*-methylnorbornane (**8**). Here interactions occur below the bridge and the C-6—H-6n bond is pushed out of alignment with C-5—H-5n (over 4°) so the steric effect must have a bond polarization and an angular component. Table 3 in Ref. 10 is consistent with this interpretation since the γ-effect attributed to dihedral angle contributions for **8** is almost 3 ppm too small.

There is obviously more than one origin of the shielding observed for carbon atoms under steric strain. One of them is the 'classical' bond polarization originally proposed by Grant and Cheney,[18,19] which is analogous to that observed for protons,[3] whereas the other is probably related to the angles formed by the carbon–hydrogen bonds that are under strain. If this is the case, it also is similar to that observed for protons. We are currently investigating these contributions in other systems.

EXPERIMENTAL

The *endo–endo* saturated tetracyclic alcohol **3** was obtained by hydrogenation of the tetracyclic alcohol **5**[2] over platinum oxide. The *exo–endo* saturated tetracyclic hydrocarbon **1** was prepared by dechlorination of aldrin with lithium in tetrahydrofurane–*tert* butanol in an ultrasonic bath[14] followed by hydrogenation over palladium–charcoal at 5 atm.

NMR spectra were measured on a Varian VXR-200 spectrometer at a magnetic field of 4.7 T and temperature of 295 K. Chemical shifts are expressed as δ (ppm) relative to TMS as an internal standard for ^{1}H spectra and the central signal of $CDCl_3$ for ^{13}C spectra. Samples were prepared by dissolving 20 mg of tetracyclic compounds in 0.5 ml of $CDCl_3$ in 5 mm tubes. The APT, COSY and HETCOR experiments are based on the standard sequences described in the literature[20–25] and found in the spectrometer software.

Molecular mechanics MM2 calculations were used to optimize geometries and calculate bond distances and angles. Charge distributions were calculated by the GAMESS program.[26]

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