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Substituent effects in ^{13}C NMR spectra. Part II[†]—Alicyclic rigid systems[‡]

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ABSTRACT: It is shown that the ^{13}C NMR chemical shifts of the α-, β- and γ-carbon atoms in various subtituted polycycloalkanes yield correlations of very good quality with the sets of substituent **X** increments common for all of them. For the β-carbon atoms the slope of the correlation line depends on the angle between the X—Cα and Cα—Cβ bonds, whereas for the γ-carbon atoms it depends on the dihedral angle of the X—Cα and Cβ—Cγ bonds. The differences between the slopes of correlation lines provide satisfactory explanation for differences in the values of increments for the same sets of substituent in individual types of polycycloalkanes. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{13}C NMR; substituent polar effects; polycycloalkanes; bicycloheptane; twistane; camphene; fenchone; norbornane; adamantane

INTRODUCTION

In semiempirical methods, the chemical shifts of carbon atoms in a compound containing given substituent are calculated by addition of certain constant values (additivity parameters, increments) to the chemical shifts of the carbon atoms in the parent unsubstituted compound or to that containing a methyl group at this site. These methods are still widely applied[2–6] and are considered very useful in the interpretation of ^{13}C NMR spectra.[7]

These parameters are characteristic for the substituent, for the type of compound and its position with respect to the carbon atom in question.

The chemical shifts of carbon atoms in monosubstituted benzene derivatives are calculated[4,8] from the equation

$$\delta\mathrm{C}(k) = 128.5 + \Sigma A_l(\mathrm{R}) \tag{1}$$

where 128.5 is the chemical shift of all carbon atoms in the unsubstituted benzene ring and $A_l(\mathrm{R})$ are additivity parameters of substituents R in the position l, i.e. *ipso, ortho, meta* or *para* with respect to the carbon atom C(k), which tells how much the chemical shift of carbon atom k is changed as a result of substitution of the carbon atom l by the group R.

A similar relation is applied for other kinds of compounds. This approach, however, implies that for each type of heterocyclic ring and, moreover, for each site of substitution a separate set of parameters has to be used. The chemical shifts of carbon atoms in pyridine derivatives are calculated[4,8] from the equation

$$\delta\mathrm{C}(k) = C_k + \Sigma A_{ik}(\mathrm{R}_i) \tag{2}$$

where δC(k) is the chemical shift of the carbon atom k in the pyridine ring containing substituents R_i, C_k is the chemical shift of the same atom in an unsubstituted pyridine, and A_{ik} is the corresponding additivity parameter.

For pyridine derivatives there are three sets of parameters, for α-, β- and γ-substituted compounds, and moreover each set contains separate additivity parameters for each carbon atom.[8] Other six-membered heterocycles require larger amounts of the sets. The values of these parameters for a given substituent, even for an analogous substitution site (e.g. for a carbon atom bonded to a substituent), are considerably different. Additivity parameters for six-membered heteroaromatic rings differ considerably from those for corresponding carbon atoms in benzene derivatives. For example, for the atom C-2 in 2-substituted pyridine derivatives their values are equal to about 0.5 of these for benzene.

It is obvious that the changes of chemical shifts of carbon atoms in a substituted compound with respect to an unsubstituted compound depends mainly on the polarity of the substituent (which is constant), on the

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distance (in bonds) from the substituent to the carbon atom in question and on the kind of the parent compound. Any substituent, however, has definite electron-donating or electron-withdrawing properties. Hence it seemed reasonable to assume that the polar effects (electron-donating or electron-withdrawing) exerted by a given substituent are always the same. Other values of the changes in chemical shifts of carbon atoms in analogous positions with respect to the substituent involved by the same group in various structural systems are due to differences in transmission of these effects through the bonds in the ring and to differences in the susceptibility of a certain carbon atom to the polar effects of a substituent. The result of the same polar effects on a certain site of a molecule depends on the site of substitution and the geometry of that site.

Some support for this assumption was provided by studies of the relations between basicity and substitution,[9–13] where it was shown that the polar effects of a substituent in a conjugated system can be considerably altered by changes in the electron density in the system, influencing transmission of these effects through the bonds.

Stronger support for this hypothesis was provided by the work of Gronowitz and co-workers,[14,15] where it was shown that there is a good correlation between the ^{13}C NMR chemical shifts of corresponding carbon atoms in monosubstituted derivatives of furan, selenophene and tellurophene with those in thiophene, and that it can be used for the assignments of the chemical shifts of carbon atoms in these series of compounds.

The above hypothesis was confirmed in Part I,[1] where it was shown that the ^{13}C NMR chemical shifts of carbon atoms in substituted six-membered heteroaromatic compounds such as pyridines, pyrazines or pyrimidines correlate with the corresponding 'additivity parameters' for substituted benzene derivatives, and that for precalculation of the chemical shifts in such compounds just one common set of parameters can be used, but instead of the additivity principle, the general correlation Eqn (3) should be applied for this purpose:

$$\delta\mathrm{C}(k) = \delta^{\circ}\mathrm{C}(k) + a_s^g\, A_\mathrm{g}(\mathrm{X}) \tag{3}$$

where $\delta^{\circ}\mathrm{C}(k)$ is the chemical shift of carbon atom k in an unsubstituted six-membered ring, $A_\mathrm{g}(\mathrm{X})$ is a so-called additivity parameter of a substituent X derived from the chemical shift in the corresponding monosubstituted phenyl derivative and a_s^g is a coefficient specific for the substitution s and its geometric position g, corresponding to the position *i*- (*ipso*), *o*- (*ortho*), *m*- (*meta*) or *p*- (*para*) with respect to the substituent X in a certain aromatic or heteroaromatic ring.

The values of the term a_s^g are considerably different from unity provided a satisfactory explanation for variety of so-called 'additivity parameters' for pyridine derivatives reported in the literature.[2,8] As a consequence, the chemical shifts of carbon atoms in all aromatic and heteroaromatic rings should correlate with just one common set of parameters, but these parameters will be multiplied by a certain factor depending on the nature of the ring and the position of the substituent.

Moreover, it was shown that the analysis of the differences between experimental chemical shifts and those calculated from Eqn (3) with a common set of parameters may be a convenient tool for the detection of effects not reported earlier in the literature occurring in various derivatives and involving intermolecular interactions, such as association, hydrogen bonds or solvation effects. The occurrence of separate correlations for certain groups of substituents, e.g. for iodine or bromine and alkyl groups (bulky substituents), may indicate that in these cases a change in the geometry of a molecule occurs, causing changes in the transmission of polar effects.

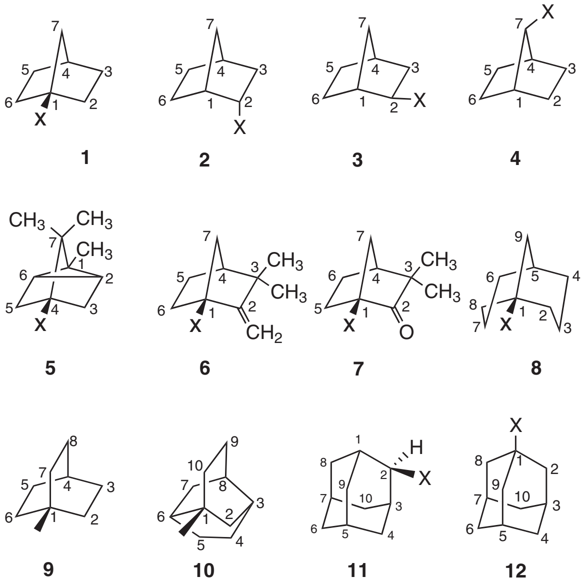
All these findings led to the assumption that a similar approach should be used also for saturated hydrocarbons, and in such a case also just one common set of parameters can be applied for precalculation of their ^{13}C NMR chemical shifts. According to this assumption, the changes in the ^{13}C NMR chemical shifts in saturated hydrocarbons caused by polar effects of a substituent can be described by the general equation

$$\delta\mathrm{C}(k) = \delta^{\circ}\mathrm{C}(k) + a_s A_g(\mathrm{X}) \tag{4}$$

where A_g is an additivity parameter characteristic for the substituent X and its position g (α, β or γ) with respect to carbon atom in question, and a_s is a coefficient specific for the substitution site s in a given structure.

Each open-chain or cyclic saturated hydrocarbon exists as a mixture of all possible conformations, hence the chemical shifts observed under standard conditions are usually averaged. Therefore, to check the above hypothesis we considered polycycloalkanes as the best suited for the purpose, because their rigid skeletons do not allow any conformational changes causing averaging of the chemical shifts.

In this work, to check this hypothesis, we collected from the literature[4,16] the ^{13}C NMR chemical shifts of carbon atoms in monosubstituted polycycloalkane derivatives of norbornane (**1**–**4**), trimethylnortricyclane (**5**), camphene (**6**), fenchone (**7**), bicyclononane (**8**), bicyclooctane (**9**), twistane (**10**) and adamantane (**11** and **12**). Each series contained compounds with substituents X of the same set, i.e. F, Cl, Br, OH, NH_2 and COOH. To find out whether for prediction of the changes in all these compounds just one common set of parameters is needed, and whether certain deviations (if any) may serve as an indication of phenomena not yet reported, we attempted to correlate these chemical shifts with one common set of parameters.



Scheme 1

STUDIED SERIES OF COMPOUNDS

The compounds studied are shown in Scheme 1: **1**, 1-substituted bicyclo[2.2.1]heptane (norbornane); **2**, 2-*endo*-substituted bicyclo[2.2.1]heptane (norbornane); **3**, 2-*exo*-substituted bicyclo[2.2.1]heptane (norbornane); **4**, 7-substituted bicyclo[2.2.1]heptane (norbornane); **5**, 4-substituted 1,7,7-trimethyltricyclo[2.2.1.$0^{2,6}$]heptane (trimethylnortricyclane); **6**, 1-substituted camphene; **7**, 1-substituted fenchone; **8**, 1-substituted bicyclo[3.3.1]nonane; **9**, 1-substituted bicyclo[2.2.2]octane; **10**, 1-substituted tricyclo[4.4.0.$0^{3.8}$]decane (twistane); **11**, 2-substituted tricyclo[3.3.1.13.7]decane (adamantane); **12**, 1-substituted tricyclo[3.3.1.13.7]decane (adamantane).

RESULTS AND DISCUSSION

On the assumption that the polar effects exerted by a substituent in any aliphatic or alicyclic molecule on the chemical shift is the same, the chemical shifts of carbon atoms bonded to a substituent, according to Eqn (4), can be correlated with the A_α parameters, those of all carbon atoms two bonds away from a substituent, i.e. in a β-position, with the A_β parameters, whereas for all carbon atoms three bonds away the A_γ parameters should be applied.

As the most appropriate we considered additivity parameters derived either from the 1-substituted adamantane or from 1-substituted bicyclooctane because of their high symmetry, but the number of derivatives of bicyclooctane for which the ^{13}C NMR chemical shifts are reported in the literature is much smaller. The first attempts at correlations, however, revealed that experimental points for bulky halogens, namely Cl, Br and I, in the case of norbornane and related compounds (**1**–**8**) would form a line separate from other points and of different slope (a_s). For example, in the case of the C-2 atoms in 2-*exo*-substituted norbornane (Fig. 1), the value of a_s for these halogen derivatives is 1.63, whereas for remaining substituents it is 1.04. For the C-7 atoms in 7-substituted norbornane (Fig. 2) they are 1.55 and 0.99, respectively, for the C-2 atoms in 1-substituted norbornane (Fig. 3) 1.64 and 1.18 and for the C-2 atoms in 2-substituted adamantane (Fig. 4) 1.44 and 0.91. This means that in each case the slope of the correlation line of the chemical shifts of the α-carbon atoms in the halogen derivatives is about 50% higher than that for the others. In the case of other series of norbornane-related compounds, where only one or two of these halogens are reported, it was impossible to estimate reliable values of a_s, but the patterns of the experimental points were very similar (Fig. 5).

This similarity indicated that in the case of compounds with a strained ring, a second set of parameters should be used. As the most appropriate we considered those obtained from derivatives of compounds containing a strained norbornane moiety. Among them only the series

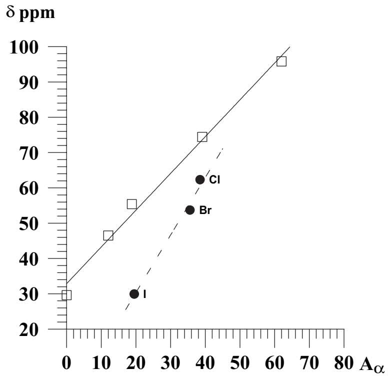


Figure 1. Correlation of the chemical shifts of the C-2 atoms in 2-*exo*-substituted norbornane (**2**) with the A_α parameters derived from 1-substituted adamantane

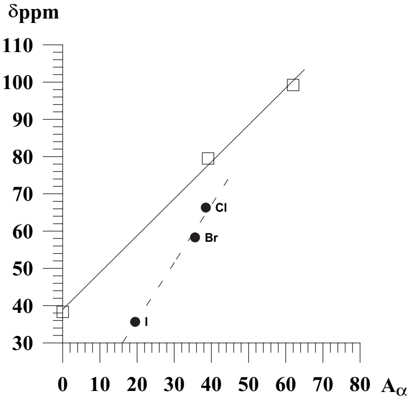


Figure 2. Correlation of the chemical shifts of the C-7 atoms in 7-substituted norbornane (**4**) with the A_α parameters derived from 1-substituted adamantane

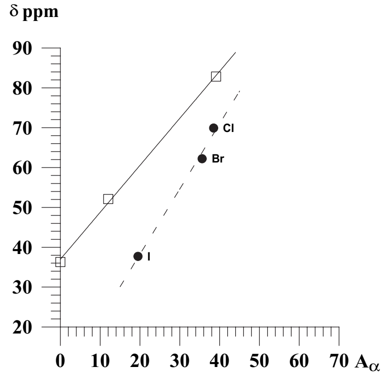


Figure 3. Correlation of the chemical shifts of the C-2 atoms in 1-substituted norbornane (**1**) with the A_α parameters derived from 1-substituted adamantane

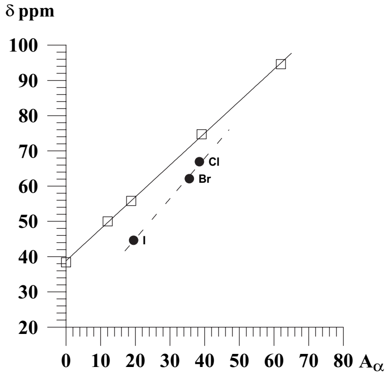


Figure 4. Correlation of the chemical shifts of the C-2 atoms in 2-substituted adamantane (**11**) with the A_α parameters derived from 1-substituted adamantane

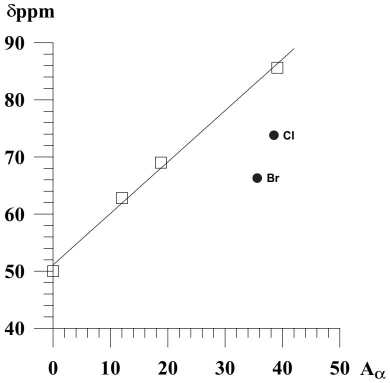


Figure 5. Correlation of the chemical shifts of the C-1 atoms in 1-substituted fenchone (**7**) with the A_α parameters derived from 2-*exo*-substituted norbornane

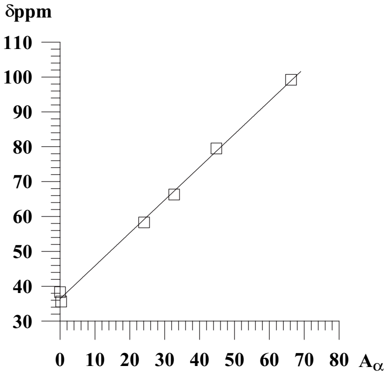


Figure 6. Correlation of the chemical shifts of the C-7 atoms in 7-substituted norbornane (**4**) with the A_α parameters derived from 2-*exo*-substituted norbornane

of 2-*exo*-substituted norbornanes contained the whole set of derivatives considered, therefore it was used for the calculation of the second set of substituent parameters. This appeared to be a good choice, because one very good common correlation was obtained in all cases where the experimental points corresponding to the halogen derivatives deviated considerably from the correlation line for other derivatives, as can be seen from comparison of Figs 2 and 6, illustrating correlations of the C-7 carbon atom in 7-substituted derivatives of norbornane with the two sets of parameters.

The parameters of the Eqn (4) found by the least-squares method for the α-, β- and γ-carbon atoms in the studied compounds are summarized in Tables 1, 2 and 3, respectively.

We found that, as in the previously studied case of correlations of the chemical shifts in six-membered heterocyclic compounds with one common set of parameters,[15] in this case also correlations with the same sets of parameters for various compounds enable us to find relations not accessible by any other methods.

Carbon atoms bonded to the substituent (in the α-position)

Very large ranges of both the chemical shifts of the α-carbon atoms in the studied compounds and the A_α parameters ($\sim$50 ppm) enable us to draw the most reliable conclusions based on the correlation parameters.

All obtained correlations of chemical shifts of carbon atoms bonded to a substituent with the corresponding A_α parameters are of excellent quality, as indicated by the correlation coefficients r ($\geq$0.99), thus justifying our hypothesis that the ^{13}C NMR chemical shifts in all polycycloalkanes correlate with common sets of parameters (cf. Table 1). The large range of the values of the a_s parameters, from 0.78 for 1-substituted fenchones (**7**) to 1.12 for 1-substituted bicyclooctanes (**9**), provides a good explanation for the diversity of the values of the increments for the same substituent in various compounds. This diversity of the a_s values shows that for each substituent in a certain series its increment for a given site will be a_s times higher (or lower) than the increment for the corresponding site in the 1-substituted adamantane or in 2-*exo*-substituted norbornane.

Table 1. Parameters of linear regressions [Eqn (4)] of the chemical shifts of carbon atoms bonded to the substituent with the A_α parameters derived from 1-substituted adamantane or 2-*exo*-substituted norbornane

Series	Atom	a_s	$\delta\,°\mathrm{C}(k)$	r	n[a]
1-Substituted norbornane (**1**)[b]	C-1	1.027	36.49	0.999	6
2-*endo*-Substituted norbornane (**2**)[b]	C-2	0.956	29.77	0.999	6
7-Substituted norbornane (**3**)[b]	C-7	0.944	36.41	0.999	6
4-Substituted trimethylnorbicyclane (**5**)[b]	C-4	0.989	35.99	0.997	4
1-Substituted camphene (**6**)[b]	C-1	0.911	43.63	0.999	4
1-Substituted fenchone (**7**)[b]	C-1	0.780	49.17	0.995	6
1-Substituted bicyclononane (**8**)[c]	C-1	1.090	29.46	0.990	7
1-Substituted bicyclooctane (**9**)[c]	C-1	1.120	24.52	1.000	6
1-Substituted twistane (**10**)[c]	C-1	1.110	28.38	1.000	4
2-Substituted adamantane (**11**)[b]	C-2	0.802	39.75	0.985	8

[a] Number of experimental points.
[b] Correlated with parameters derived from norbornane.
[c] Correlated with parameters derived from adamantane.

Table 2. Parameters of linear regressions [Eqn (4)] of the chemical shifts of carbon atoms two bonds away from the substituent (β-position) with the A_β parameters derived from 1-substituted adamantane or 2-*exo*-substituted norbornane

Series	Atom	a_s	$\delta°\mathrm{C}(k)$	r	n[a]
1-Substituted norbornane (**1**)[b]	C-2/6	0.933[d]	29.37	0.999	5
1-Substituted norbornane (**1**)[b]	C-7	0.875[d]	38.18	0.999	5
2-*endo*-Substituted norbornane (**2**)[b]	C-1	0.358	40.45	0.995	5
2-*endo*-Substituted norbornane (**2**)[c]	C-3	1.327	28.08	0.971	6
2-*exo*-Substituted norbornane (**3**)[b]	C-3	1.411	29.63	0.970	5
7-Substituted norbornane (**4**)[b]	C-1/4	0.557	36.25	0.988	6
1-Substituted camphene (**6**)[b]	C-7	0.602	40.05	0.977	4
1-Substituted fenchone (**7**)[b]	C-6	0.913[d]	24.18	0.993	5
1-Substituted fenchone (**7**)[b]	C-7	0.902	34.68	0.990	5
1-Substituted bicyclononane (**8**)[b]	C-2/8	1.014	32.29	0.999	7
1-Substituted bicyclononane (**8**)[b]	C-9	1.032	35.72	0.996	7
1-Substituted bicyclooctane (**9**)[b]	C-2/5/7	1.000	26.17	0.997	6
1-Substituted twistane (**10**)[b]	C-2	1.172	29.09	0.996	4
1-Substituted twistane (**10**)[b]	C-6	1.104	29.82	0.990	4
1-Substituted twistane (**10**)[b]	C-10	1.120	24.84	0.990	4
2-Substituted adamantane (**11**)[b]	C-2/7	0.624	29.64	0.981	8

[a] Number of experimental points.
[b] Correlated with parameters derived from adamantane.
[c] Correlated with parameters derived from norbornane.
[d] Calculated without the COOH derivative.

Table 3. Parameters of linear regressions [Eqn (4)] of the chemical shifts of carbon atoms four bonds away (γ-position) from substituent with the A_γ parameters derived from 1-substituted adamantane

Series	Atom	a_s	$\delta°\mathrm{C}(k)$	r	n[a]
1-Substituted norbornane (**1**)	C-3/5	0.45	29.73	0.941	6
1-Substituted fenchone (**7**)	C-5	0.44	23.86	0.903	5
1-Substituted bicyclononane (**8**)	C-3/7	0.67[b]	22.31	0.898	7
1-Substituted bicyclooctane (**9**)	C-3/6	0.78	25.60	0.948	6
1-Substituted twistane (**10**)	C-7	0.57	28.79	0.989	4
1-Substituted twistane (**10**)	C-9	0.91	24.56	0.987	4
2-*exo*-Substituted norbornane (**3**)	C-4	0.98	36.32	0.986	8

[a] Number of experimental points.
[b] Calculated without the COOH derivative.

The ^{13}C NMR chemical shifts of the α-carbon atoms in 1-substituted bicyclononane (**8**), 1-substituted bicyclooctane (**9**) and 1-substituted twistane (**10**) were correlated with the A_α parameters derived from adamantane. In **8**–**10** and also in adamantane the substituent was bonded to tertiary carbon atom and all their rings are free of any strain. Therefore, the values of a_s are very similar and close to unity. In the 2-substituted adamantane there is no strain in any ring, but the substituent is bonded to a secondary carbon atom and most probably this is the reason for the different susceptibility to the polar effects of a substituent and, as a consequence, that a good correlation is obtained only if the parameters from 2-substituted norbornane (derived also from the chemical shifts of secondary carbon atoms) are applied.

The chemical shifts of the α-carbon atoms in the remaining compounds were correlated with the A_α parameters derived from norbornane. The lowest values of a_s (0.91 and 0.78) are observed for the α-carbon atoms in 1-substituted camphene (**6**) and fenchone (**7**), where these atoms are in a vicinal position with respect to the C=C or C=O double bond. It should be noted that there is a discernible difference between the polar effect of a substituent in the axial and equatorial orientation. The second set of substituent parameters A_α was derived from the 2-*exo*-substituted norbornanes (**3**), where the substituent is equatorial. For the derivatives with an axial substituent (2-*exo*-substituted), the value of a_s is slightly smaller (0.956). The smaller slope of the correlation line means that the decrease in the value of the increment for a substituent in an axial position is about 0.96 times lower than that for a substituent in an equatorial position.

Carbon atoms in the *β*-position with respect to the substituent

The values of both the chemical shifts of the β-carbon atoms in studied compounds and the A_β parameters vary in much smaller range ($\sim$20 ppm), but still enabling one to draw reliable conclusions based on the correlation parameters. The ^{13}C NMR chemical shifts of the β-carbon atoms of C-3 in 2-*endo*-substituted norbornane (**2**) and C-3 in 2-*exo*-substituted norbornane (**3**) were correlated with the A_β parameters derived from norbornane. In this case also the value of a_s for derivatives with an axial substituent (**2**) is slightly smaller than that for derivatives containing the substituent in an equatorial position (**3**).

The ^{13}C NMR chemical shifts of the β-carbon atoms in remaining compounds were correlated with the A_β parameters derived from adamantane. In most cases the correlations obtained are excellent, as indicated by the correlation coefficient $r > 0.99$. For C-1 and C-3 in 2-*endo*-substituted norbornane (**2**), C-3 in 2-*exo*-substituted norbornane (**3**) C-1/4 in 7-substituted norbornane (**4**), C-7 in 1-substituted camphene (**6**) and C-1/3 in 2-substituted adamantane (**11**) the correlations are of good quality ($r > 0.95$).

The high quality of the correlations obtained and the range of values of a_s, ranging from 0.36 for C-1 in 2-*endo*-substituted norbornane (**2**) to 1.17 for C-2 in 1-substituted twistane (**10**), which is about four times larger than that for the α-carbon atoms, provide further and stronger support for our hypothesis and a further explanation for the diversity of the increment values in various compounds.

For compounds without strained rings, i.e. bicyclononane (**8**), bicyclooctane (**9**) and twistane (**10**), the a_s values are very close to unity. For those with strained rings (norbornane and related compounds), they are smaller than unity. In the case of 1-substituted fenchone (**7**), the experimental value of the ^{13}C NMR chemical shift for C-6 is about 4 ppm higher than that resulting from the correlation line. This can be rationalized by the changes in distribution of electron density in the carboxyl group caused by hydrogen bonding with the carbonyl group. However, similar deviations for C-2 and C-7 in 1-substituted norbornane for carboxyl derivatives still require some explanation.

The results obtained show that the transmission of polar effects of a substituent X through the bonds (the slope a_s of the correlation line) depends markedly on the angle between the X—Cα and Cα—Cβ bonds. The best example is provided (Table 2) by the a_s values for C-2/6 and C-7 in the 1-substituted norbornane (**1**) and C-2,5,7 in the 1-substituted bicyclooctane (**9**). In bicyclooctane the X—C-1—C-2, X—C-1—C-5 and X—C-1—C-7 angles are the same as the X—C-1—C-2, X—C-1—C-8 and X—C-1—C-9 angles in adamantane taken as the standard for calculation of the A_β parameters, hence the a_s value for C-2/5/7 is equal to unity. In 1-substituted norbornane, however, the X—C-1—C-7 angle is larger and this is the most probably the reason for the lower a_s value.

Carbon atoms in the *γ*-position with respect to the substituent

In all series of compounds studied, the changes in chemical shifts of carbon atoms three bonds away from substituent, i.e. in the γ-position, are much smaller. The mean value of these changes is about 3.5 ppm, and in some instances even below 2.5 ppm, which is of the same order as often encountered differences between the ^{13}C NMR chemical shifts for the same carbon atom reported in various sources. Moreover, the values of the substituent parameters A_γ vary in a very narrow range of 7.2 ppm for the increments derived from adamantane and 3.5 ppm for the increments derived from norbornane. Therefore, the relations between chemical shifts of the γ-carbon atoms and the A_γ parameters are less evident; however, in some instances, the tendency is still noticeable (cf. Table 3).

For the ^{13}C NMR chemical shifts of C-4 in 2-*exo*-substituted norbornane (**3**), and also for C-7 and C-9 in 1-substituted twistane (**10**), the correlations are of excellent quality ($r = 0.99$), for C-3/6/8 in 1-substituted bicyclooctane (**9**) of good quality ($r \approx 0.95$), but for C-3/5 in 1-substituted *norbornane* (**1**), C-3,5 in 1-substituted fenchone (**7**) and C-3/7 in 1-substituted bicyclononane (**8**) the correlations are hardly satisfactory. However, the differences in the a_s values for various series are again large, ranging from 0.44 for C-5 in 1-substituted fenchone (**7**) to 0.91 for C-10 in 1-substituted twistane (**10**).

CONCLUSIONS

On the basis of the presented results, the following general conclusions can be drawn.

The differences between increments of the same substituent in various polycycloalkanes is due to the susceptibility of a certain carbon atom in the ring to polar effects of a substituent and to the difference in transmission of these effects through the bonds in the rings.

The ^{13}C NMR chemical shifts of the α-, β- and γ-carbon atoms in various subtituted polycycloalkanes rings yield correlations of very good quality with the sets of the substituent **X** increments common for all of them. For the β-carbon atoms the slope of the correlation line depends on the angle between the bonds X—Cα and Cα—Cβ whereas for the γ-carbon atoms it depends on the dihedral angle between the X—Cα and Cβ—Cγ bonds. The differences in the slopes of correlation lines provide a satisfactory explanation for differences in the values of increments for the same sets of substituent in individual types of polycycloalkanes.

Analysis of the parameters of the chemical shifts in a series of related compounds with a common set of parameters may serve as a convenient tool for the detection of specific effects inaccessible by other methods considering the influence of single substituent on the chemical shifts in a given kind of compound.

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