

# Development of a New Set of Additive Parameters for the Estimation of Geometrical Distortion of Cycloalkanes from C-13 NMR Chemical Shifts

Emad A. S. AL-HYALI

*Chemistry Department, College of Education, University of Mosul, Mosul-IRAQ  
e-mail: emadabd2006@yahoo.com*

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A previous model for the calculation of C-13 chemical shifts is modified by replacement of 3 parameters representing the p-character of carbon atom in cyclic systems with a single parameter aiming for the development of a new set of parameters with a wide range of application for the calculation of C-13 NMR chemical shifts. The considered systems are cyclohexanes, trans decalins, and a number of hypothetical polycyclic 6-member ring hydrocarbons. The developed parameters include a combination of quantum mechanical and statistical methods. They are based on 2 factors: through bond (electronic) effect represented by the partial electronic charge on the tested carbon, and long-range (steric) effect expressed in terms of proton-proton interactions. The results of this study are compared to those of previous studies and sometimes are preferable.

**Key Words:** Additivity parameters, C-13 NMR chemical shifts, geometrical distortion, cycloalkanes.

## Introduction

Since the early years of the use of NMR spectroscopy for structural elucidation, the effect on C-13 chemical shifts has been recognized to be largely additive.<sup>1,2</sup> Accordingly, numerous sets of additive parameters have been suggested for the prediction of a large number of substance classes.<sup>3-5</sup> Although the models applied vary considerably, they have some common properties. Most of the models proposed are linear and follow the equation

$$\delta C_{(k)} = B + \sum A_i N_{kj} \quad (1)$$

The C-13 chemical shift of the kth carbon atom is equal to a constant (B) plus additive chemical shift coefficients ( $A_i$ ) multiplied by the number of carbon atoms in the ith position relative to k. Non-linearities have been taken into account by adding some correction factors in several cases.<sup>6</sup> It is thought that the C-13 chemical shift is affected by 2 factors. The first is electronic in nature and represents the p-character that a certain substituent experiences on the carbon under study. The second factor is the steric effect, which is a kind of attraction and/or repulsion force induced by the H-H interactions due to the spatial arrangement of

the molecule. These factors outlined above encouraged the researchers interested in this field to construct different sets of additivity parameters based on them.

Grant and Paul<sup>7</sup> introduced the p-character in terms of the number of carbon atoms at  $\alpha$ ,  $\beta$ ,  $\gamma$ ,...etc. positions and the steric effect as the number of protons at  $\alpha$ ,  $\beta$ ,  $\gamma$ ,...etc. positions. These parameters are developed and refined by other research groups in which correction factors were added.<sup>6</sup> Such parameters have played a major role in the assignment of C-13 NMR absorptions in low molecular weight compounds<sup>6,8</sup> and macromolecules.<sup>9</sup> Most of the mentioned parameters were empirical and no attempt has been made to give them meaning in terms of the theory of C-13 NMR spectroscopy.

In the late 1980s Shahab and Al-Wahab<sup>4</sup> related the p-character to the number of  $\alpha$ -carbons of primary, secondary, tertiary, and quaternary types, and introduced the proton interactions as the number of protons in the  $\alpha$ ,  $\beta$ ,  $\gamma$ ,...etc. positions. Later, Al-Hyali<sup>10</sup> succeeded in developing the work done by Shahab and Al-Wahab by representing the steric factor in terms of the actual number of interacting protons at  $\alpha$ ,  $\beta$ ,  $\gamma$ ,...etc. positions instead of the number of protons, relying on the fact that protons that exist in opposite planes do not interact with each other, and the type of such interactions depends on the distance and angle between the interacting protons. The parameters developed proved to be applicable for different types of cycloalkanes.<sup>11,12</sup>

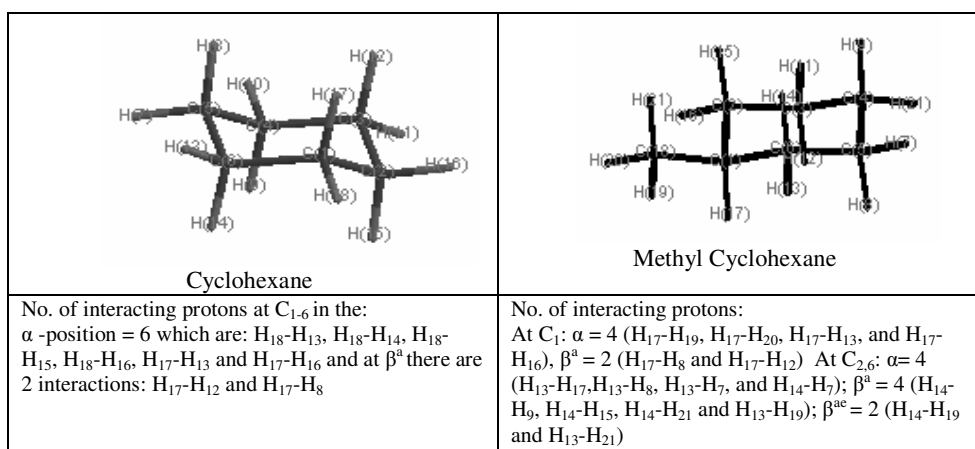
Other studies<sup>13-15</sup> concerning quantum mechanical methods have achieved success for the treatment of H and C-13 databases. Gasteiger and Marsili,<sup>14</sup> Abraham and Grant,<sup>15</sup> and Abraham and Griffiths<sup>13</sup> observed that there is a good correlation between the proton chemical shifts of substituted alkanes and the charge densities on the protons as calculated by their semiempirical modeling schemes. The charge densities were calculated by electronegativity equalization<sup>14</sup> and by reference to experimental dipole moments,<sup>15</sup> which are both completely independent from NMR. Encouraged by such a correlation, in this study we investigated the relation between the charge densities on the carbon atoms of the studied systems with their C-13 chemical shifts and the p-character, aiming to develop a new set of parameters for predicting C-13 chemical shifts.

The importance of such methods lies in the fact that they can give a clear picture of the factors affecting the chemical shifts of C-13 nuclei, they can be used for predicting unknown C-13 chemical shifts of many types of organic compounds, and the deviation between the observed and calculated chemical shifts may give an indication of the geometry distortion that occurs as a result of the spatial interactions, especially when the constructed parameters for regression analysis start with compounds of definite conformations and least strain. Only a few experimental methods can describe such distortion quantitatively.

## Experimental

The parameters used for the calculation of C-13 NMR chemical shifts of the studied systems are based on 2 factors. The first one is electronic in nature and is represented by the partial electronic charge (EC) on the studied carbons. The charge is estimated by the extended Hückel method. The Chem. Office program of Cambridge University (version 2000) is employed for this purpose. The second factor is the steric effect induced by the hydrogen-hydrogen interactions (electrostatic attraction and/or repulsion) resulting from the spatial arrangement of the molecule. It is introduced in terms of proton interactions between those present on the considered carbon and the other carbons of the molecule at  $\alpha$ ,  $\beta$ ,  $\gamma$ ,...etc. positions. The  $\beta$ -interactions are divided into 2 types depending on the distance and angle between the interacting protons (Figure 1). The first type is assigned as  $\beta^a$  and refers to the interactions between 2 protons located in

the same plane, either 2 axial or equatorial protons. The other is given the symbol  $\beta^{ae}$  and represents the interaction between 2 protons, one of them in the axial position and the other equatorial.



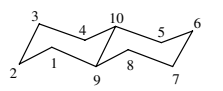
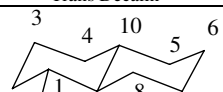
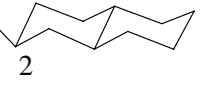
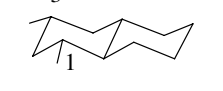
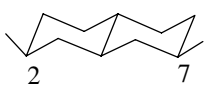
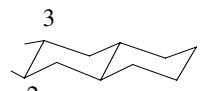
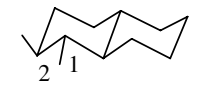
**Figure 1.** Example of the calculation of (H-H) interactions.

The number of interacting protons is calculated manually by constructing a model compound. All the studied compounds exist in one energetically favored conformation, and so a single model is used for calculation of each compound. The numbers of interacting protons calculated manually are listed in Tables 1-3. Multiple

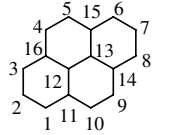
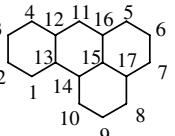
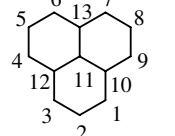
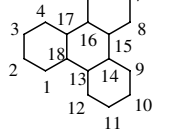
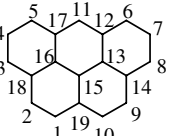
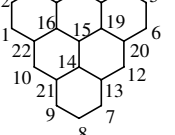
**Table 1.** The electronic charge and number of interacting protons at  $\alpha$ ,  $\beta$ , and  $\gamma$  positions used in the regression analysis of cyclohexanes.

Compound	C.No.	$\delta C^{d3}_{obs}$ (16)	Charge on C	$\alpha$	$\beta^a$	$\beta^{ae}$	$\gamma$
 Cyclohexane	1-6	27.06	-0.057	6	2	0	0
 Cis-1,3-DMC	1,3	32.82	0.017	4	2	0	0
	2	44.7	-0.068	2	6	4	0
	4,6	35.37	-0.062	4	4	2	0
	5	26.45	-0.060	6	2	0	0
 1-Cis-3-cis-5-TMC	CH <sub>3</sub> <sup>(1,3)</sup>	22.81	-0.136	2	4	4	0
	1,3,5	32.68	0.016	4	2	0	0
	2,4,6	44.2	-0.068	2	6	4	0
 1-MC	CH <sub>3</sub> <sup>(1,3,5)</sup>	22.81	-0.136	2	4	4	0
	1	33.06	0.018	4	2	0	0
	2,6	35.77	-0.063	4	4	2	0
	3,5	26.55	-0.058	6	2	0	0
 Trans-1,4-DMC	4	26.4	-0.057	6	2	0	0
	CH <sub>3</sub> <sup>(1)</sup>	22.72	-0.136	2	4	4	0
	1,4	32.61	0.018	4	2	0	0
	2,3,5,6	35.63	-0.064	4	4	2	0
 Trans-1,2-DMC	CH <sub>3</sub> <sup>(1,4)</sup>	22.81	-0.137	2	4	4	0
	1,2	39.55	0.010	3	3	1	0
	3,6	36.03	-0.062	4	4	2	0
	4,5	26.85	-0.059	6	2	0	0
CH <sub>3</sub> <sup>(1,2)</sup>	20.22	-0.139	2	3	3	1	

**Table 2.** The electronic charge and number of interacting protons at  $\alpha$ ,  $\beta$ , and  $\gamma$  positions used in the regression analysis of trans decalins.

Compound	C <sub>No.</sub>	$\delta C^{13}_{obs}^{(8)}$	Charge on C	$\alpha$	$\beta^a$	$\beta^{ae}$	$\gamma$
 Trans Decalin	9,10	44.22	0.003	2	4	0	0
	1,4,5,8	34.74	-0.066	4	4	2	0
	2,3,6,7	27.17	-0.058	6	2	0	0
 Trans-anti-1-M-decalin	9	50.60	-0.006	1	5	1	0
	10	44.05	0.004	2	4	0	0
	1	38.42	0.007	3	3	1	0
	2	37.12	-0.061	4	4	2	0
	4,5	35.39	-0.065	4	4	2	0
	8	31.02	-0.069	4	3	1	1
	3	27.45	-0.060	6	2	0	0
	6	27.16	-0.059	6	2	0	0
	7	26.82	-0.057	6	2	0	0
CH <sub>3</sub>	19.74	-0.139	2	3	3	1	
 Trans-syn-2-M-decalin	9	43.49	0.002	2	4	0	0
	10	43.39	0.004	2	4	0	0
	1	43.31	-0.071	2	6	4	0
	3	35.66	-0.064	4	4	2	0
	4,5	34.3	-0.067	4	4	2	0
	8	34.15	-0.066	4	4	2	0
	2	33.06	0.017	4	2	0	0
	6,7	27.02	-0.058	6	2	0	0
	CH <sub>3</sub>	22.85	-0.137	2	4	4	0
 Trans-anti-1-syn-3-DM-decalin	9	49.44	-0.006	1	5	1	0
	2	45.42	-0.067	2	6	4	0
	10	43.67	0.002	2	4	0	0
	4	42.99	-0.070	2	6	4	0
	1	37.71	0.006	3	3	1	0
	5	34.63	-0.065	4	4	2	0
	3	32.44	0.015	4	2	0	0
	8	30.63	-0.069	4	3	1	1
	6	27.16	-0.059	6	2	0	0
	7	26.91	-0.057	6	2	0	0
	CH <sub>3</sub> <sup>(3)</sup>	22.84	-0.137	2	4	4	0
CH <sub>3</sub> <sup>(1)</sup>	19.74	-0.139	2	3	3	1	
 Trans-syn-2-syn-7-DM-decalin	1,8	43.05	-0.071	2	6	4	0
	9	42.84	0.001	2	4	0	0
	10		0.004				
	3,6	35.6	-0.064	4	4	2	0
	4,5	34.05	-0.067	4	4	2	0
	2,7	32.89	0.017	4	2	0	0
	CH <sub>3</sub> <sup>(2,7)</sup>	23.0	-0.136	2	4	4	0
9,10	44.18	0.002	2	4	0	0	
 Trans-syn-2-syn-3-DM-decalin	1,4	44.18	-0.070	2	6	4	0
	2,3	39.78	0.008	3	3	1	0
	5,8	34.32	-0.066	4	4	2	0
	6,7	27.14	-0.058	6	2	0	0
	CH <sub>3</sub> <sup>(2,3)</sup>	20.30	-0.139	2	3	3	1
	9	49.36	-0.007	1	5	1	0
 Trans-1-syn-2-DM-decalin	1	44.34	-0.001	2	4	2	0
	10	43.3	0.004	2	4	0	0
	2	39.27	0.009	3	3	1	0
	3	35.82	-0.062	4	4	2	0
	4	35.8	-0.066	4	4	2	0
	5	34.51	-0.065	4	4	2	0
	8	30.96	-0.070	4	3	1	1
	6	27.14	-0.059	6	2	0	0
	7	26.58	-0.057	6	2	0	0
	CH <sub>3</sub> <sup>(2)</sup>	20.94	-0.139	2	3	3	1
	CH <sub>3</sub> <sup>(1)</sup>	16.1	-0.145	2	2	2	2

**Table 3.** The electronic charge and number of interacting protons at  $\alpha$ ,  $\beta$ , and  $\gamma$  positions used in the regression analysis of polycyclic compounds.

Compound	C <sub>No.</sub>	$\delta C^{1,3 (5)}$	Charge on C	$\alpha$	$\beta^a$	$\beta^{ac}$	$\gamma$
	12,13	57.21	-0.031	0	6	0	0
	11,14,15,16	43.20	0.001	2	4	0	0
	1,3,6,8	34.93	-0.066	4	4	2	0
	4,5,9,10		-0.067				
	2,7	27.14	-0.060	6	2	0	0
	15	57.21	-0.011	0	6	0	0
	13	49.02	-0.009	1	5	1	0
	14		-0.011				
	12		0.003				
	16	43.20	0.00	2	4	0	0
	17		0.001				
	11	42.73	-0.074	2	6	4	0
	4,5,7,8	34.93	-0.066	4	4	2	0
	1,10	30.80	-0.070	4	3	1	1
	2	27.14	-0.057	6	2	0	0
	9		-0.058				
	3		-0.059				
6	-0.060						
	11	57.21	-0.010	0	6	0	0
	10,12,13	43.20	0.001	2	4	0	0
	1,3,4,6,7,9	34.93	-0.066	4	4	2	0
	2,8,5	27.14	-0.060	6	2	0	0
	13,14,15,16,17,18	49.02	-0.009	1	5	1	0
	1,4,5,8,9,12	30.80	-0.070	4	3	1	1
	2,3,6,7,10,11	27.14	-0.057	6	2	0	0
	15	57.21	-0.016	0	6	0	0
	13,16		-0.013				
	14,18,19	43.20	0.001	2	4	0	0
	12,17		0.00				
	11		42.73				
	1,2,9,10	34.93	-0.067	4	4	2	0
	3,5,6,8		-0.066				
4,7	27.14	-0.060	6	2	0	0	
	15	57.21	-0.019	0	6	0	0
	14,16,18		-0.013				
	13,17,19,20,21,22	43.20	-0.001	2	4	0	0
	10,11,12	42.73	-0.074	2	6	4	0
	1,3,4,6,7,9	34.93	-0.066	4	4	2	0
	2,5,8	27.14	-0.060	6	2	0	0

regression analysis is then used for the estimation of the coefficients of the parameters suggested for this study by employing the well-known statistical program SPSS. The value and sign of the coefficient refer to the weight and type of influence (shielding or de-shielding) of the parameter, respectively.

The matrix used for the representation of the molecule is generated on the basis of a linear model (as illustrated in Tables 1-3) according to the following equation:

$$Y = B + a_1X_1 + a_2X_2 + \dots + a_nX_n \quad (2)$$

In this method the observed chemical shifts ( $\delta_{C-13\text{obs}}$ ) are considered as the dependent variable (Y), and the parameters representing the charge and the proton interactions (Tables 1-3) as independent variables ( $X_1, X_2, \dots, X_n$ ). The coefficients of the parameters ( $a_1, a_2, \dots, a_n$ ) and the constant (B) are obtained as a result of the regression analysis. The success of the selected parameters is estimated in terms of the correlation coefficient (R) and standard deviation (SD).

## Results and Discussion

Systems considered in this study include cyclohexanes, trans decalins, and a number of hypothetical polycyclic hydrocarbons. The importance of studying such types of compounds lies in that their derivatives are extensively treated in the chemical literature. They are similar in structure to the most commonly encountered backbone of natural products of the steroid type. All the investigated compounds exist in the trans form, which is the energetically favored conformation.

Our previous model,<sup>12</sup> which was developed for the calculation of C-13 chemical shift of substituted cycloalkanes, based upon p-character and steric interactions, has been modified. The p-character represented by the number of  $\alpha$ -carbon atoms of primary ( $\alpha$ -pri), secondary ( $\alpha$ -sec), and tertiary ( $\alpha$ -ter) types is replaced by one single parameter. This parameter is introduced as the electronic charge present on the tested carbon and is calculated by employing the Chem. Office program of Cambridge University.

In a preliminary test an attempt was made to correlate the C-13 chemical shift to the electronic charge. The results obtained, listed in Table 4, showed a very poor relation.

**Table 4.** The correlation results between the C-13 chemical shifts and electronic charges.

	Cyclohexanes	Decalins
Correlation coefficient (R)	0.9705	0.9367
Standard deviation (SD)	5.804	6.651

We assumed that, since the p-character is representing somehow the through bond (electronic) effect of the substituents on a specific carbon, it should be well related to the electronic charge present on it. Accordingly, regression analysis is carried out to test this assumption. The electronic charge (as a dependent variable) is related to the number of ( $\alpha$ -pri), ( $\alpha$ -sec), and ( $\alpha$ -ter) carbons (as independent variables) for all the studied systems. The output of the regression is given in Table 5.

The results in Table 5 exhibited high correlation coefficients and acceptable standard deviations, which proved that this factor (electronic charge) could be introduced as the electronic effect (p-character) and suggested that the 3 parameters (of the p-character) employed previously<sup>4,12</sup> could be replaced by this single parameter. Encouraged by these results and in order to test the applicability of the suggested parameters on the studied systems, multiple regression analysis was carried out to correlate the C-13 chemical

shifts (as a dependent variable) versus the electronic charge and the number of interacting protons at  $\alpha$ ,  $\beta$ ,  $\gamma$ ,...etc. positions (which are listed in Tables 1-3) as the independent variables for cyclohexanes, decalins, and polycyclic compounds. The results obtained are listed in columns A, B, and C in Table 6 for the 3 systems respectively.

**Table 5.** Results of the correlation between the charge on carbon and p-character.

Parameter*	Coefficients of parameters of the		
	Cyclohexane (A)	Decalins (B)	Polycyclic comp. (C)
No. of carbon: $\alpha$ -pri	0.07431	0.07321	-
$\alpha$ -sec	0.07381	0.06885	0.06734
$\alpha$ -ter	0.06846	0.06819	0.05935
Constant	-0.205	-0.200	-0.194
R	1.0	0.9955	0.9993
SD	0.001	0.014	0.003
No. of observations	46	80	28

\* Electronic charge (EC) is the dependent variable

**Table 6.** Regression analysis results using the charge on carbon instead of the p-character of the studied compounds.

Parameters*	Coefficients of parameters for		
	Cyclohexanes (A)	Decalins (B)	Polycyclic comp. (C)
Electronic Charge (EC)	131.186	119.166	-74.635
No. of interacting protons			
$\alpha$	1.621	0.555	-4.322
$\beta^a$	6.425	6.271	1.856
$\beta^{ae}$	LC	-1.062	-2.467
$\gamma$	4.188	1.989	-5.070
Constant	11.749	17.720	44.834
R	0.9996	0.9994	0.9999
SD	$\pm 0.61$	$\pm 0.92$	$\pm 0.39$
No. of observations	46	80	105

\*C-13 chemical shifts is the dependent variable

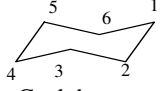
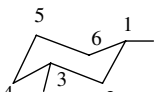
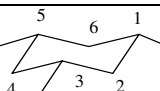

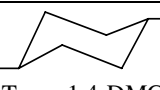
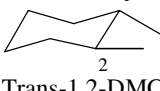
The results in Table 6 indicate the following:

1. The C-13 chemical shifts are more influenced by the through bond effect than the long-range effect (proton interactions).
2. The values of the coefficients of the proton interaction's parameters vary according to the distance and angle between the interacting protons.
3. The values of R and SD are good indications of the correct choice of the parameters.

## Cyclohexanes

The results of column A in Table 6 are used to calculate the C-13 chemical shifts of the cyclohexane compounds selected for this study. A comparison between the observed<sup>16</sup> and calculated chemical shifts is portrayed in Table 7.

**Table 7.** Comparison between the calculated and observed<sup>16</sup> chemical shifts of cyclohexane compounds.

Compound	C <sub>No.</sub>	$\delta C^{13}_{obs.}$	$\delta C^{13}_{cal}$	Res*
 Cyclohexane	1-6	27.06	26.85	-0.21
 Cis-1,3-DMC	1,3	32.82	33.31	0.49
	2	44.7	44.62	-0.08
	4,6	35.37	35.80	0.43
	5	26.45	26.45	0.0
	CH <sub>3</sub> <sup>(1,3)</sup>	22.81	22.85	0.04
 1-Cis-3-cis-5-TMC	1,3,5	32.68	33.18	0.50
	2,4,6	44.2	44.62	0.42
	CH <sub>3</sub> <sup>(1,3,5)</sup>	22.81	22.85	0.04
	1	33.06	33.44	0.38
 1-MC	2,6	35.77	35.67	-0.10
	3,5	26.55	26.72	0.17
	4	26.4	26.85	0.45
	CH <sub>3</sub> <sup>(1)</sup>	22.72	22.85	0.13
	1,4	32.61	33.44	0.83
 Trans-1,4-DMC	2,3,5,6	35.63	35.54	-0.09
	CH <sub>3</sub> <sup>1,4</sup>	22.81	22.72	-0.09
	1,2	39.55	37.20	-2.35
 Trans-1,2-DMC	3,6	36.03	35.80	-0.23
	4,5	26.85	26.59	-0.26
	CH <sub>3</sub> <sup>(1,2)</sup>	20.22	20.22	0.0

\* Res.=  $\delta C^{13}_{cal} - \delta C^{13}_{obs.}$ 

The results in Table 7 show a good agreement between the observed and calculated chemical shifts. Isolated rings and equatorial methyl carbon show negligible deviations, regardless of the degree of substitution. Deviations are observed only on carbons involved in large steric interactions. Such interactions influence the chemical shift of carbons through distortion of their tetrahedral symmetry. An example of the deviation is seen on the adjacent ring carbons in 1,2-dimethyl substituted cyclohexanes. The interesting point is that the deviation is observed only at the ring carbons and not on the carbons of the methyl substituents. This may be attributed to the fact that the methyl substituents have more freedom to rotate and reduce the strain arising from great proton interactions, restoring their tetrahedral symmetry as a result. The deviations are then transferred to the ring carbons attached to them.

Since the construction of the additivity parameters employed for the regression analysis starts with chemical shifts belonging to methyl cyclohexanes with definite conformations and least strain, the deviation between the observed and calculated chemical shifts can provide a measure of the geometry distortions occurring as a result of the spatial interactions. The importance of treating the C-13 chemical shifts by the statistical method lies in its ability in predicting such deviation quantitatively.



## Decalins

Decalins exist in 2 stereo isomeric forms, cis and trans. In trans decalin, one ring is attached to the other by 2 equatorial or axial bonds. Trans decalin is the more stable one. The relative stability of such fused systems is easily understood in terms of  $\gamma$ -gauche interaction.<sup>17</sup> A number of methyl substituted trans decalins are selected for this study.

The values of the coefficients of the suggested parameters that emerged from the regression analysis of trans decalins (Table 6, column B) are employed to calculate the C-13 chemical shifts for these compounds according to the following equation:

$$\begin{aligned} \delta C_{cal}^{13} = & 19.749 + 77.646 \times EC - 0.0593 \times \alpha - \text{protons} + 6.246 \times \beta^a - \text{protons} \\ & - 2.376 \times \beta^{ae} - \text{protons} - 0.00797 \times \gamma - \text{protons} \end{aligned} \quad (3)$$

The comparison between the calculated ( $\delta C_{cal}^{13}$ ) and the observed ( $\delta C_{obs}^{13}$ ) chemical shifts is listed in Table (8).

A close inspection of Table 8 shows that the trans decalins exhibit the same trend in deviation as that observed in the cyclohexane compounds. The experimental and predicted C-13 chemical shifts of the sterically unhindered carbon atoms are in excellent agreement. Deviations are observed on the 1,2-disubstituted tertiary carbons (C-2,3 of comp. 6 and C-1,2 of comp. 7) and on the bridge head carbons (C-9,10) which are analogues to ring carbons of 1,2-disubstituted methyl cyclohexane. The value of deviation varies with respect to the steric congestion (C-1 of comp. 2 suffers from greater deviation than C-2 because it is locked between fused carbon and another substituent). In cases of the existence of large steric interferences, the deviation may transfer into the neighboring carbons (C-2 in comps. 2 and 4). This can be attributed to ring flattening, which arises from great proton interactions.<sup>1,16</sup>

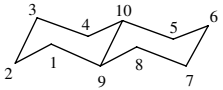






## Polycyclic hydrocarbons

The investigation is extended to apply the developed parameters on a number of hypothetical polycyclic alkanes of 6-member rings. These rings are present in the chair form and fused as in the trans conformation. The C-13 chemical shifts of these compounds employed in the regression analysis as the dependent variable (Table 3) were calculated previously.<sup>5</sup> The coefficient values of the developed parameters obtained from regression analysis and listed in column C of Table 6 are used for the estimation of C-13 chemical shifts of these compounds. The comparison between the calculated and observed values is given in Table 9.

The calculated chemical shifts tabulated in Table 9 are in excellent agreement with the observed values. No deviations, similar to those seen in the cyclohexane and decalin compounds, are observed since the selected polycyclic are unsubstituted compounds. This proves that this method is not just good for prediction of unknown chemical shifts but also good for estimation of the geometrical distortion.

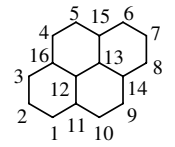
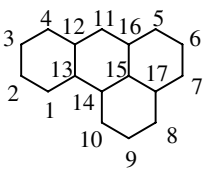
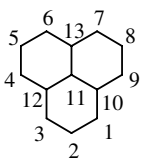
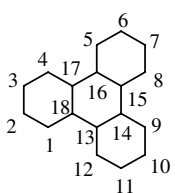
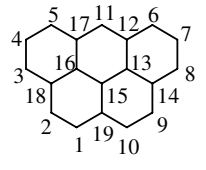
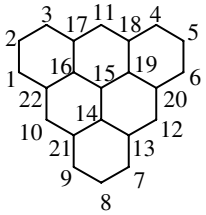
The use of electronic charge in the developed parameters discriminates some absorptions that could not be observed by the previous method.<sup>5</sup> An additional point worth mentioning here is that the coefficients obtained from the regression analysis of any of the investigated systems can be used to calculate C-13 chemical shifts, with acceptable error, for the other systems and vice versa.

**Table 8.** Comparison between the calculated and observed<sup>8</sup> chemical shifts of trans decalin compounds.

Itm	Compound	C <sub>No.</sub>	$\delta C^{13}_{obs}$	$\delta C^{13}_{calc}$	Res*
1	 Trans Decalin	9,10	44.22	44.27	0.05
		1,4,5,8	34.74	35.04	0.30
		2,3,6,7	27.17	26.68	-0.49
2	 Trans-anti-1-M-decalin	9	50.60	47.85	-2.75
		10	44.05	44.39	0.34
		1	38.42	37.97	-0.45
		2	37.12	35.63	-1.49
		4,5	35.39	35.15	-0.24
		8	31.02	31.46	0.44
		3	27.45	26.44	-1.01
		6	27.16	26.56	-0.6
		7	26.82	26.80	-0.02
3	 Trans-syn-2-M-decalin	CH <sub>3</sub>	19.74	19.88	0.14
		9	43.49	44.15	0.66
		10	43.39	44.39	1.00
		1	43.31	43.75	0.44
		3	35.66	35.27	-0.39
		4,5	34.3	34.92	0.62
		8	34.15	35.04	0.89
		2	33.06	34.51	1.45
		6,7	27.02	26.68	-0.34
4	 Trans-anti-1-syn-3-DM-decalin	CH <sub>3</sub>	22.85	23.34	0.49
		9	49.44	47.85	-1.59
		2	45.42	44.22	-1.20
		10	43.67	44.15	0.48
		4	42.99	43.87	0.88
		1	37.71	37.85	0.14
		5	34.63	35.15	0.52
		3	32.44	34.27	1.83
		8	30.63	31.46	0.83
		6	27.16	26.56	-0.60
		7	26.91	26.80	-0.11
		CH <sub>3</sub> <sup>(3)</sup>	22.84	23.34	0.52
5	 Trans-syn-2-syn-7-DM-decalin	CH <sub>3</sub> <sup>(1)</sup>	19.74	20.12	0.38
		1,8	43.05	43.75	0.70
		9	42.84	44.03	1.19
		10	42.84	44.39	1.55
		3,6	35.6	35.27	-0.33
		4,5	34.05	34.92	0.87
		2,7	32.89	34.51	1.62
6	 Trans-syn-2-syn-3-DM-decalin	CH <sub>3</sub> <sup>(2,7)</sup>	23.0	23.46	0.46
		9,10	44.18	44.15	-0.03
		1,4	44.18	43.87	-0.31
		2,3	39.78	38.09	-1.69
		5,8	34.32	35.04	0.72
		6,7	27.14	26.68	-0.46
7	 Trans-1-syn-2-DM-decalin	CH <sub>3</sub> <sup>(2,3)</sup>	20.30	19.88	-0.42
		9	49.36	47.73	-1.63
		1	44.34	41.67	-2.67
		10	43.3	44.39	1.09
		2	39.27	38.21	-1.06
		3	35.82	35.51	-0.31
		4	35.8	35.04	-0.76
		5	34.51	35.15	0.64
		8	30.96	31.34	0.38
		6	27.14	26.56	-0.58
		7	26.58	26.80	0.22
		CH <sub>3</sub> <sup>(2)</sup>	20.94	19.88	-1.06
CH <sub>3</sub> <sup>(1)</sup>	16.1	15.95	-0.15		

\*Res.=  $\delta C^{13}_{calc} - \delta C^{13}_{obs}$ .

**Table 9.** Comparison between the calculated and observed chemical shifts of polycyclic rings compounds.

Compound	C <sub>No.</sub>	$\delta C^{13(5)}$	$\delta C^{13}_{cal}$	Res
	12,13	57.21	58.28	1.07
	11,14,15,16	43.20	43.54	0.34
	1,3,6,8	34.93	34.96	0.03
	4,5,9,10		35.04	0.11
	2,7	27.14	27.09	-0.05
	15	57.21	56.79	-0.42
	13	49.02	47.99	-1.03
	14		48.15	-0.88
	12	43.20	43.39	0.19
	16		43.61	0.41
	17		43.54	0.34
	11	42.73	42.98	0.25
	4,5,7,8	34.93	34.96	0.03
	1,10	30.80	30.80	0.0
	2	27.14	26.87	-0.27
	9		26.94	-0.2
	3		27.02	-0.12
	6		27.09	-0.05
	11	57.21	56.72	-0.49
	10,12,13	43.20	43.54	0.34
	1,3,4,6,7,9	34.93	34.96	0.03
	2,8,5	27.14	27.09	-0.05
	13,14,15,16,17,18	49.02	48	-1.02
	1,4,5,8,9,12	30.80	30.80	0.0
	2,3,6,7,10,11	27.14	26.87	-0.27
	15	57.21	57.16	-0.05
	13,16		56.94	-0.27
	14,18,19	43.20	43.54	0.34
	12,17		43.61	0.41
	11		42.98	0.25
	1,2,9,10	34.93	35.04	0.11
	3,5,6,8		34.96	0.03
	4,7	27.14	27.09	-0.05
	15	57.21	57.39	0.18
	14,16,18		56.94	-0.27
	13,17,19,20,21,22	43.20	43.69	0.49
	10,11,12	42.73	42.98	0.25
	1,3,4,6,7,9	34.93	34.96	0.03
	2,5,8	27.14	27.09	-0.05

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