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Linear free energy relationships of the ^{1}H and ^{13}C NMR chemical shifts of 3-methylene-2-substituted-1,4-pentadienes

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Abstract

Linear free energy relationships (LFER) were applied to the ^{1}H and ^{13}C NMR chemical shifts (δ_N, N = ^{1}H and ^{13}C, respectively) in the unsaturated backbone of cross-conjugated trienes 3-methylene-2-substituted-1,4-pentadienes. The NMR data were correlated using five different LFER models, based on the mono, the dual and the triple substituent parameter (MSP, DSP and TSP, respectively) treatment. The simple and extended Hammett equations, and the three postulated unconventional LFER models obtained by adaptation of the later, were used. The geometry data, which are needed in Karplus-type and McConnell-type analysis, were obtained using semi-empirical MNDO-PM3 calculations.

In correlating the data the TSP approach was more successful than the MSP and DSP approaches. The fact that the calculated molecular geometries allow accurate prediction of the NMR data confirms the validity of unconventional LFER models used. These results suggest the *s-cis* conformation of the cross-conjugated triene as the preferred one. Postulated unconventional DSP and TSP equations enable the assessment of electronic substituent effects in the presence of other interfering influences.

Keywords: LFER models; Substituent effects; Anisotropy of the aromatic ring; Angle-dependent substituent effects; MNDO-PM3 calculations

1. Introduction

The NMR theory distinguishes between short-range substituent effect over one, two and tree bonds, which are attributed to the electronic effects of the substituents, and long-range effects, due to the electric fields, steric effects and anisotropy of the substituents [1]. Substituents containing magnetically anisotropic chemical bonds, e.g. double bonds, triple bonds or the aromatic phenyl ring, influence the shielding any nucleus in the molecule by their anisotropy effects dependent on their spatial arrangement [2]. The anisotropy effect is independent of the nuclei being observed. The shift due to the anisotropy for protons and ^{13}C nuclei are therefore equal in magnitude (they amount to several ppm). However, since the total range of chemical shift in ^{13}C NMR spectroscopy is much greater than for protons, the fraction attributable to magnetic anisotropy of ^{13}C is relatively small, although not negligible [3].

One particularly fruitful area of research has been the use of ^{1}H and ^{13}C NMR chemical shifts to examine the transmission of electronic substituent effects in systems where the probe nuclei are located in the sidechain attached to an aromatic ring [4]. In majority of those systems, a small, substituent induced, changes in the chemical shifts of a given probe group can be examined. This class of compounds is of a historic importance because on just these compounds much of the early work on linear free energy relationships (LFER) was developed.

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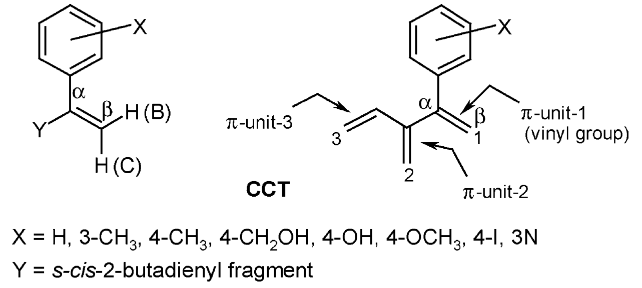

Fig. 1. Structure of the investigated cross-conjugated triene 3-methylene-2-substituted-1,4-pentadiene (CCT) with added nuclei labels used for ^{1}H and ^{13}C NMR data.

In spite of some theoretical limitations, the use of LFER to correlate NMR data with Hammett constants is a helpful technique to determine the transmission of polar and resonance electronic effects through the benzene ring [5,6]. The empirical character of Hammett and related structural parameters renders (makes) them attractive to NMR spectroscopists. The dual substituent parameter non-linear resonance (DSP-NLR) analysis [7] is a successful method in modeling the long-range substituent effects on ^{13}C NMR substituent chemical shifts (in substituted aromatic systems [7–9]) that show deviations from the Hammett-type correlations. The DSP-NLR approach assumes a linear variation of field/inductive effects with changes in the electronic nature of the system (with a resultant fixed σ_I scale) but a non-linear variation of resonance effects. The latter variation is accommodated by having a non-linear resonance scale.

Recently Pytela [10–12] published a qualitatively new approach to description of substituent effects denoted as Alternative Interpretation of Substituent Effects (AISE). This method suggested starts from the presumption that a substituent only possesses a single property described (in terms of quantitative description of substituent effects) by a single substituent constant, irrespective to type of the basis skeleton and position of substitution. The substituent property is transferred to the reaction center by three different ways depending on the interaction type in the triad reaction center-basic skeleton-substituent. The use of AISE parameters in correlation the NMR data represents an interesting alternative as compared with the correlation models involving greater numbers of parameters.

The aim of the present investigation was to apply LFER to the ^{1}H and ^{13}C NMR chemical shifts (δ_H and δ_C, respectively) in the unsaturated chain of cross-conjugated triene 3-methylene-2-substituted-1,4-pentadiene (CCT) (see Fig. 1) to get insight into the factors determining chemical shifts and to use these chemical shifts as a empirical measure of substituent effects in this system. To achieve this goal we have used five different correlation models. Being fully aware of the complexity of determining factors especially for ^{1}H NMR shifts, we have tried to adopt the conventional extended Hammett equation as a basis to postulate three new unconventional LFER models that provides estimation of electronic substituent effects regardless of other interfering influences and provides a good method for accurate prediction of the NMR data as well.

Since the semi-empirical MNDO-PM3 calculations suggests that investigated cross-conjugated triene CCT prefers the *s-cis* conformation [13], a contribution from both the electronic substituent effects and the other factors that determine the chemical shifts were discussed corresponding to such molecular geometry. The *s-cis* and some other conformers of 3-methylene-2-phenyl-1,4-pentadiene are shown in Fig. 2.

2. Experimental

2.1. NMR spectra

The NMR chemical shifts of both unsaturated chain carbons-13 and protons of 3-methylene-2-substituted-1,4-pentadienes, were previously determined [13,14]. ^{13}C NMR chemical shifts were not available for 3-methylene-2-(4-hydroxyphenyl)-1,4-pentadiene (see Fig. 1).

2.2. Method of calculation

In our work we used the MNDO-PM3 method that proved to be highly reliable for investigating the molecular

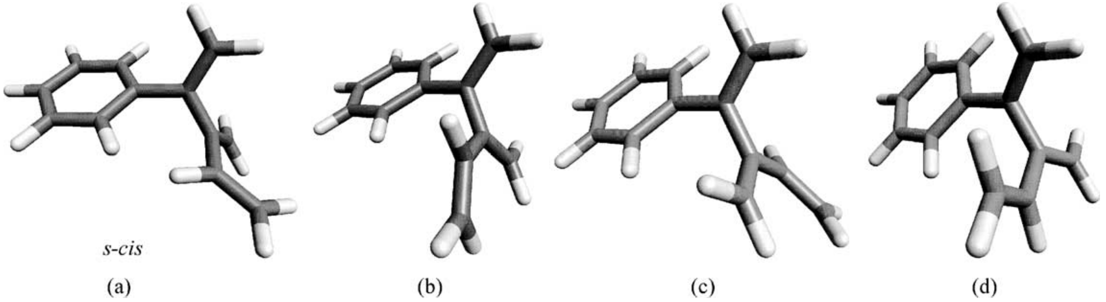

Fig. 2. *s-Cis* and some other conformers of 3-methylene-2-phenyl-1,4-pentadiene [13]. Corresponding calculated heats of formation, $\Delta H°$: (a) 70.984 kcal mol^{-1}, (b) 71.797 kcal mol^{-1}, (c) 71.690 kcal mol^{-1}, (d) 72.317 kcal mol^{-1}.

properties of molecules, ions [15–23], and zwitterions [24]. The MOPAC program package, Version 7.01 was used. The initial structures of compounds were generated by PC MODEL, version 4.0 [25], that involves an MMX force field [26,27] and were saved as MOPAC input files for MNDO-PM3 semi-empirical calculations [17,18]. The geometries of all molecular species, corresponding to the energy minima in vacuum, were optimized by the PM3 method. When needed, the structures obtained were refined by Bartel's method (non-linear least squares gradient minimization routine-NLLSQ), and further proved by vibrational analysis showing no negative vibration. The simulation of polar medium was performed using COSMO facility [28,29].

3. Results and discussion

The effects of substituents in the aromatic ring on the NMR data of investigated compounds could be correlated by two conventional LFER models, based on the mono and the dual substituent parameter (MSP and DSP, respectively) treatment. The first LFER model is MSP equation, so called simple Hammett equation, which we used in the following form:

$$\delta_N = \rho\sigma + h \qquad (1)$$

where δ_N is the chemical shift (N = ^{13}C or ^{1}H) induced by the substituent X, and σ is the substituent parameter reflecting the electronic effects. Parameters h (the intercept on the ordinate), ρ (measure of the sensitivity of the chemical shift to the electronic effects of the substituents), are obtained by regression analysis.

The second one is the DSP equation, so called extended Hammett equation, which we used in the following form:

$$\delta_N = \rho_I\sigma_I + \rho_R\sigma_R + h \qquad (2)$$

where σ_I and σ_R are substituent parameters reflecting the polar and resonance electronic effects, respectively. Parameters ρ_I and ρ_R (measures of the sensitivity of the chemical shift to the polar and resonance electronic effects of the substituents, respectively), are obtained by regression analysis.

From the viewpoint of semi-empirical MO theory, it is known that the following ground-state properties of a substituted benzenes vary approximately as $\cos^2\theta$ (θ is dihedral angle) [30]: resonance energy, π-electronic charge densities, ring C–C bond orders and the π-electronic dipole moment. Parameter θ increases as the substituent is twisted. By analogy, since the suggested *s-cis* geometry of CCT [13] (see Fig. 2) one should expect that the π-conjugative substituent effects at the probe nuclei in this system should vary as $\cos^2\theta$ (θ is the torsion angle between aromatic ring plane and the π-unit plane of interest). To test this hypothesis, we decided to use adopted DSP Eq. (2) in the sense of resonance substituent effects dependence on the coplanarity of the double bonds in investigated CCT. We used this adopted DSP equation in the following form:

$$\delta_N = \rho_I\sigma_I + \rho_R(\sigma_R\cos^2\theta) + \mathrm{h} \qquad (3)$$

where θ is the torsion angle between aromatic ring plane and the π-unit plane of interest in CCT.

The chemical shift is often divided into contributions stemming from purely empirical components, such as local atomic properties or the influence of neighboring atoms and groups. Considering the influence of neighborhood, those originating from the presence of delocalized electrons or from the presence of a magnetically anisotropic group are most relevant. McConnell's equation [31], based on the anisotropy of the magnetic susceptibility, quantified these proximity effects and predicted the long-range shielding influences. This treatment gives rise to the familiar 'shielding cone' over functional groups represented in NMR spectroscopy textbooks [3,32].

Since the NMR probe nuclei in unsaturated chain of *s-cis* CCT may in some extent be influenced by anisotropy of the aromatic ring in position 2, we decided to amend DSP Eq. (2) by the additional term δ_{an} accounting for the contributions to chemical shifts from anisotropy effects of the aromatic ring. This new LFER model is based on the triple substituent parameter (TSP) treatment. We used this TSP Eq. in the following form:

$$\delta_N = \rho_I\sigma_I + \rho_R\sigma_R + \rho_{an}\delta_{an} + h \qquad (4)$$

where ρ_{an} is adjustable parameter obtained by polylinear regression analysis. The term δ_{an} is given by expression:

$$\delta_{an} = (3L_0r^3)^{-1}(3\cos^2\varphi - 1)$$

where L_0 is Avogadro's constant, r is the distance of the NMR probe nucleus from the benzene ring center, φ the angle of the r vector with the ring symmetry axis (see Fig. 3).

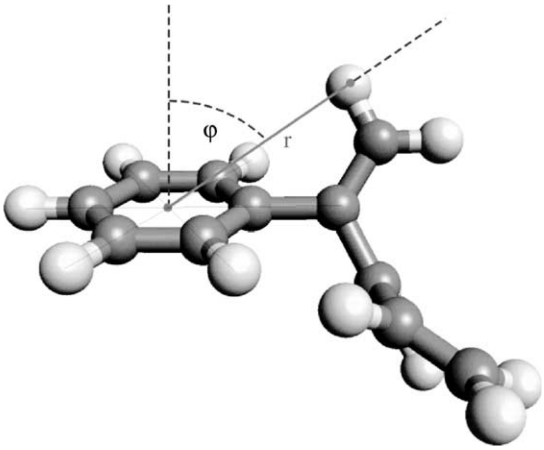

Fig. 3. Definition of distance r and angle φ in term δ_{an} in TSP Eqs. (4) and (5) for proton H(B) in 3-methylene-2-phenyl-1,4-pentadiene.

By combining the Eqs. (3) and (4) we obtained the new LFER model based on TSP treatment in the form of Eq. (5):

$$\delta_N = \rho_I\sigma_I + \rho_R(\sigma_R \cos^2\theta) + \rho_{an}\delta_{an} + h \qquad (5)$$

The specific nature of additional term δ_{an} precludes its absorption in σ_I and σ_R. Corollary, the Eqs. (4) and (5) do provide a means to quantify these effects in the presence of other interfering influences.

Application of MSP, DSP and TSP analyses to the NMR probes nuclei in the unsaturated chain in CCT using Eqs. (1)–(5) yields the results that are given in Tables 1–5. Following substituent constants were taken from the literature: σ and σ_I for all groups [33–38] as well as σ_R [34,35] except for both 3N[2] and 4-CH_2OH group. As the σ_R constant for 3N substituent has not been found in the literature, and having in mind that for 3N substituent in the aromatic ring stands $\sigma_m = \sigma_I$, σ_R constant for this substituent was taken as zero. By analogy, having in mind that for *para* substituents in the aromatic ring stand $\sigma_p = \sigma_R + \sigma_I$, σ_R constant for 4-CH_2OH substituent was calculated from $\sigma_R = \sigma_p - \sigma_I$. The parameters $\cos^2\theta$ and δ_{an} in Eqs. (3)–(5) were calculated on the basis of geometry data (torsion angle θ, distance r and angle φ) that have been determined by semi-empirical MNDO-PM3 calculations.

The DSP method represents a general approach for the correlation of substituents effects over large range of different data sets. Of course, certain limitations have to be acknowledged. Namely, the minimization of steric or solvent-related effects. For this reason, NMR studies of substituent effects should be carried out in dilute solutions of an inert solvent.

The generality arises because of the independence of the ρ_I and ρ_R transmission coefficients. Since polar and resonance effects are transmitted by different mechanisms [39–41], their relative importance may change from one system to another. This feature cannot be accommodated in the MSP approach.

The MSP correlation with Eq. (1) for $\delta_{H(B)}$ is of fair precision while all the others are satisfactory (Table 1). The observed ρ values for protons H(B) and H(C) indicate a different susceptibilities of their chemical shifts to substituents effects. The $\delta_{H(C)}$ is relatively more influenced with substituent effects than the $\delta_{H(B)}$. According to the observed ρ values for δ_C, it is apparent that chemical shifts of terminal π-unit-1 carbon, $\delta_{C(1)}$, show a relatively increased susceptibility to substituent effects compared with those for more distant carbons C(2) and C(3). Since the MSP treatment contains only one blend of polar and resonance substituent effects the results of the correlations with Eq. (1) (Table 1) cannot yield a precise determination of these effects on δ_H and δ_C of CCT.

Table 1
Results of the correlations with MSP Eq. (1)

Parameter	ρ^a	h^b	R^c	s^d	n^e
$\delta_{H(B)}$	0.142 (±0.023)	5.5135 (±0.006)	0.9305	0.018	8
$\delta_{H(C)}$	0.216 (±0.017)	5.2337 (±0.005)	0.9808	0.014	8
$\delta_{C(1)}$	3.74 (±0.460)	114.62 (±0.123)	0.9643	0.321	7
$\delta_{C(2)}$	0.648 (±0.66)	117.51 (±0.016)	0.9783	0.043	7
$\delta_{C(3)}$	1.06 (±0.130)	118.40 (±0.035)	0.9639	0.091	7

[a] Weighting coefficients for Eq. (1).
[b] Intercept.
[c] Correlation coefficient.
[d] Standard error of estimate for the chemical shift.
[e] Number of the points.

Much better correlation for both δ_H and δ_C was obtained by using the DSP Eq. (2) (Table 2). It should be noted that all the DSP correlations are of excellent precision except for $\delta_{H(C)}$ which only is satisfactory. The observed ρ_I and ρ_R values for δ_H indicate a prevalent resonance effect at both β protons. The value of $\lambda = \rho_R/\rho_I$ for $\delta_{H(C)}$ ($\lambda = 1.41$) is smaller than those for $\delta_{H(B)}$ ($\lambda = 2.29$) revealing the larger influence of the resonance effect at H(B). Owing to the particular geometric arrangement of the vinyl group (π-unit-1) in *s-cis* CCT (see Fig. 2), the vinyl protons H(B) and H(C) should have different sensitivities to polar and resonance effects [14]. This is consistent with the different magnitudes of observed ρ_I and ρ_R values for $\delta_{H(B)}$ and $\delta_{H(C)}$. The values of $\lambda = \rho_R/\rho_I$ for β protons suggests an increased localization of resonance effects in the aromatic ring in CCT compared with those for β protons in ring 4-substituted styrenes ($\lambda = 1.71$ and 3.02 for H(C) and H(B), respectively; scale σ_R^0 [42]).

The trend in the ρ_I and ρ_R values for $\delta_{C(1)}$ indicate a prevalent resonance effect on $\delta_{C(1)}$ while those for $\delta_{C(2)}$ and $\delta_{C(3)}$ indicate a dominant polar effects on $\delta_{C(2)}$ and $\delta_{C(3)}$ (Table 2). The magnitudes of ρ_I and ρ_R values for $\delta_{C(1)}$ are relatively bigger than these for $\delta_{C(2)}$ and $\delta_{C(3)}$ revealing a greater susceptibility of $\delta_{C(1)}$ to the substituent effects. According to the locations of carbons C(2) and C(3) it is to be expected that $\delta_{C(2)}$ will be more influenced by the substituent effects than $\delta_{C(3)}$. In spite of the relatively bigger magnitudes of ρ_I and ρ_R values for $\delta_{C(3)}$ than these for $\delta_{C(2)}$, values of $\lambda = \rho_R/\rho_I$ for $\delta_{C(2)}$ and $\delta_{C(3)}$ are similar ($\lambda = 0.76$). This reveals both the peculiarity of the arrangement of the π electrons in the cross-conjugated chain in CCT and a similarity in the transmission mode of substituent effects on $\delta_{C(2)}$ and $\delta_{C(3)}$. The value of $\lambda = \rho_R/\rho_I$ for $\delta_{C(1)}$ ($\lambda = 1.63$) suggests an increased localization of resonance effects in the aromatic ring of CCT compared with those for $\delta_{C(\beta)}$ ($\lambda = 1.80$; scale σ_R^0 [42]) of ring 4-substituted styrenes.

The alternation of polar substituent effects on δ_C in the unsaturated chain of CCT was observed [13]. The extent of observed alternation of polar substituent effects in the unsaturated chain of CCT bears evidence for the transfer of these effects by the π-polarization mechanism in this molecular framework.

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[2] The aza-substituent at position 3 in benzene ring; the replacement of the nitrogen atom for CH in benzene ring was considered as a ‘substitution’.

Table 2
Results of the correlations with DSP Eq. (2)

Parameter	ρ_{I}[a]	ρ_{R}[a]	h[b]	R[c]	s[d]	n[e]
$\delta_{\mathrm{H(B)}}$	0.080 (±0.013)	0.183 (±0.012)	5.5304 (±0.004)	0.9906	0.007	8
$\delta_{\mathrm{H(C)}}$	0.169 (±0.024)	0.239 (±0.022)	5.2436 (±0.008)	0.9840	0.014	8
$\delta_{\mathrm{C(1)}}$	2.95 (±0.128)	4.87 (±0.175)	114.84 (±0.042)	0.9984	0.076	7
$\delta_{\mathrm{C(2)}}$	0.688 (±0.036)	0.523 (±0.049)	117.48 (±0.012)	0.9958	0.021	7
$\delta_{\mathrm{C(3)}}$	1.13 (±0.084)	0.862 (±0.115)	118.35 (±0.027)	0.9915	0.050	7

[a] Weighting coefficients for Eq. (2).
[b] Intercept.
[c] Correlation coefficient.
[d] Standard error of estimate for the chemical shift.
[e] Number of the points.

Table 3
Results of the correlations with DSP Eq. (3)

Parameter	ρ_{I}[a]	ρ_{R}[a]	h[b]	R[c]	s[d]	n[e]
$\delta_{\mathrm{H(B)}}$	0.080 (±0.013)	0.179 (±0.012)	5.5302 (±0.004)	0.9900	0.008	8
$\delta_{\mathrm{H(C)}}$	0.169 (±0.024)	0.233 (±0.022)	5.2434 (±0.008)	0.9837	0.014	8
$\delta_{\mathrm{C(1)}}$	2.96 (±0.132)	4.71 (±0.742)	114.83 (±0.043)	0.9983	0.078	7
$\delta_{\mathrm{C(2)}}$	0.693 (±0.030)	0.416 (±0.033)	117.47 (±0.010)	0.9970	0.018	7
$\delta_{\mathrm{C(3)}}$	1.14 (±0.070)	0.661 (±0.073)	118.34 (±0.022)	0.9941	0.041	7

The parameter $\cos^2\theta$ for appropriate NMR probe nuclei in 3-methylene-2-(substituted phenyl)-1,4-pentadiene is expressed relatively to those for NMR probe nuclei in 3-methylene-2-phenyl-1,4-pentadiene.
[a] Weighting coefficients for Eq. (3).
[b] Intercept.
[c] Correlation coefficient.
[d] Standard error of estimate for the chemical shift.
[e] Number of the points.

From the previous discussion, follows that the *s-cis*-buta-1,3-dien-2-yl group involving π-unit-2 and π-unit-3 (see Fig. 1), behaves as a rather isolated fragment. While the $\delta_{\mathrm{C(1)}}$, $\delta_{\mathrm{H(B)}}$ and $\delta_{\mathrm{H(C)}}$ are dominantly influenced by resonance substituent effects, the $\delta_{\mathrm{C(2)}}$ and $\delta_{\mathrm{C(3)}}$ show a larger susceptibility to the polar effect of the substituents.

Our DSP analyses with Eq. (3) (Table 3) of both δ_{H} and δ_{C} of CCT gave high precision fits. Examination of the data in Tables 2 and 3 reveals that in every correlation listed the DSP analyses with Eq. (3) fits are equal to or better than these of DSP analyses with Eq. (2). The better correlation coefficients were obtained for ^{13}C chemical shifts in the more distant π-units, $\delta_{\mathrm{C(2)}}$ and $\delta_{\mathrm{C(3)}}$. The analyses of both $\delta_{\mathrm{C(2)}}$ and $\delta_{\mathrm{C(3)}}$ with DSP Eq. (3) indicate a somewhat lesser extent of transmission of the resonance effect of the substituents compared with those from analyses with DSP Eq. (2). Whereas the DSP Eq. (3) could not yield the precise determination of electronic substituent effects, it is important to note that pattern of ρ_{I} and ρ_{R} values for $\delta_{\mathrm{C(1)}}$, $\delta_{\mathrm{H(B)}}$ and $\delta_{\mathrm{H(C)}}$ closely matches those obtained by using a conventional DSP Eq. (2). Although we can reach qualitative conclusions based upon the observation of angle-dependent resonance substituent effects on NMR probe nuclei in CCT, it cannot be made quantitative.

Table 4
Results of the correlations with TSP Eq. (4)

Parameter	ρ_{I}[a]	ρ_{R}[a]	ρ_{an}[a]	h[b]	R[c]	s[d]	n[e]
$\delta_{\mathrm{H(B)}}$	0.077 (±0.009)	0.184 (±0.009)	0.322 (±0.140)	5.2066 (±1.415)	0.9959	0.005	8
$\delta_{\mathrm{H(C)}}$	0.240 (±0.018)	0.242 (±0.017)	−2.380 (±0.527)	7.6241 (±0.5296)	0.9927	0.011	8
$\delta_{\mathrm{C(1)}}$	2.86 (±0.145)	4.86 (±0.198)	3.00 (±4.09)	111.84 (±4.11)	0.9985	0.086	7
$\delta_{\mathrm{C(2)}}$	0.689 (±0.040)	0.564 (±0.053)	0.771 (±0.817)	116.71 (±0.822)	0.9962	0.023	7
$\delta_{\mathrm{C(3)}}$	1.24 (±0.094)	1.01 (±0.128)	-4.16 (±2.51)	122.53 (±2.52)	0.9921	0.055	7

The parameter δ_{an} for appropriate NMR probe nuclei in 3-methylene-2-(substituted phenyl)-1,4-pentadiene is expressed relatively to those for NMR probe nuclei in 3-methylene-2-phenyl-1,4-pentadiene.
[a] Weighting coefficients for Eq. (4).
[b] Intercept.
[c] Correlation coefficient.
[d] Standard error of estimate for the chemical shift.
[e] Number of the points.

Table 5
Results of the correlations with TSP Eq. (5)

Parameter	ρ_I[a]	ρ_R[a]	ρ_{an}[a]	h[b]	R[c]	s[d]	n[e]
$\delta_{H(B)}$	0.077 (±0.009)	0.180 (±0.008)	0.339 (±0.140)	5.1889 (±0.141)	0.9959	0.005	8
$\delta_{H(C)}$	0.241 (±0.018)	0.236 (±0.016)	−2.407 (±0.529)	7.6512 (±0.532)	0.9926	0.011	8
$\delta_{C(1)}$	2.90 (±0.151)	4.71 (±0.199)	1.99 (±4.25)	112.84 (±4.27)	0.9984	0.089	7
$\delta_{C(2)}$	0.695 (±0.029)	0.468 (±0.031)	1.24 (±0.602)	116.23 (±0.605)	0.9980	0.017	7
$\delta_{C(3)}$	1.32 (±0.069)	0.842 (±0.072)	−6.80 (±1.85)	125.17 (±1.86)	0.9957	0.041	7

The both parameters $\cos^2\theta$ and δ_{an} for appropriate NMR probe nuclei in 3-methylene-2-(substituted phenyl)-1,4-pentadiene are expressed relatively to these for NMR probe nuclei in 3-methylene-2-phenyl-1,4-pentadiene.

[a] Weighting coefficients for Eq. (5).

[b] Intercept.

[c] Correlation coefficient.

[d] Standard error of estimate for the chemical shift.

[e] Number of the points.

Table 6
Results of the correlations with four different LFER models, with topological correction relative to proton H(B)

Model[a]	Parameter $\delta_{H(B)}$ and $\delta_{H(C)}$						
	ρ_I[b]	ρ_R[b]	ρ_{an}[b]	$T_{H(C)}$[c]	h[d]	R[e]	s[f]
Eq. (2)	0.125 (±0.019)	0.211 (±0.018)	–	−0.280 (±0.008)	5.5270 (±0.007)	0.9957	0.016
Eq. (3)[g]	0.125 (±0.019)	0.713 (±0.061)	–	−0.270 (±0.008)	5.5267 (±0.007)	0.9956	0.016
Eq. (4)	0.116 (±0.019)	0.211 (±0.018)	0.0001 ($\pm 0.8\times10^{-5}$)	−0.389 (±0.008)	5.1601 (±0.032)	0.9960	0.016
Eq. (5)[g]	0.116 (±0.019)	0.714 (±0.061)	0.0001 ($\pm 0.8\times10^{-5}$)	−0.394 (±0.081)	5.1448 (±0.032)	0.9960	0.016

Sixteen point correlations

[a] Type of linear relationship used.

[b] Weighting coefficients for appropriate equation.

[c] Topological parameter for proton H(C).

[d] Intercept.

[e] Correlation coefficient.

[f] Standard error of estimate for the chemical shift.

[g] The parameter $\cos^2\theta$ for appropriate NMR probe nuclei in 3-methylene-2-(substituted phenyl)-1,4-pentadiene is expressed relatively to those for NMR probe nuclei in 3-methylene-2-phenyl-1,4-pentadiene.

Table 7
Results of the correlations with four different LFER models, with topological correction relative to carbon C(1)

Parameter $\delta_{C(1)}$, $\delta_{C(2)}$ and $\delta_{C(3)}$	Model[a]			
	Eq. (2)	Eq. (3)[b]	Eq. (4)	Eq. (5)[b]
ρ_I[c]	1.59 (±0.449)	1.59 (±0.278)	1.02 (±0.401)	1.09 (±0.203)
ρ_R[c]	2.08 (±0.612)	16.23 (±1.92)	2.13 (±0.543)	16.03 (±1.41)
ρ_{an}[c]	–	–	0.0057 ($\pm 2.8\times10^{-5}$)	0.0049 ($\pm 1.4\times10^{-5}$)
$T_{C(2)}$[d]	3.64 (±0.206)	3.10 (±0.127)	43.42 (±0.184)	37.47 (±0.093)
$T_{C(3)}$[d]	2.74 (±0.206)	2.20 (±0.127)	41.07 (±0.184)	35.32 (±0.093)
h[e]	114.76 (±0.172)	115.07 (±0.100)	66.35 (±0.186)	73.24 (±0.091)
R[f]	0.9726	0.9896	0.9796	0.9948
s[g]	0.445	0.275	0.397	0.201

Twenty-one point correlations.

[a] Type of linear relationship used.

[b] The parameter $\cos^2\theta$ for appropriate NMR probe nuclei in 3-methylene-2-(substituted phenyl)-1,4-pentadiene is expressed relatively to those for NMR probe nuclei in 3-methylene-2-phenyl-1,4-pentadiene.

[c] Weighting coefficients for appropriate equation.

[d] Topological parameter for appropriate carbon.

[e] Intercept.

[f] Correlation coefficient.

[g] Standard error of estimate for the chemical shift.

At this point is of interest to compare the results of the correlations with TSP Eq. (4) (Table 4) with those obtained by using DSP Eq. (2) (Table 2). In all correlations of carbon chemical shifts the coefficient ρ_{an} has a large (unacceptable) standard error of estimate indicating that the semi-empirical parameter δ_{an} is not statistically significant in these correlations. By contrast, the parameter δ_{an} is significant in excellent correlations of $\delta_{H(B)}$ and $\delta_{H(C)}$. This suggests that the TSP Eq. (4) does provide a means of quantifying electronic substituent effects on β protons in CCT in the presence of the anisotropy effect of the aromatic ring.

Examination of the data in Tables 2–5 reveals that in every correlation listed the TSP analyses with Eq. (5) yields fits statistically equal to or better than these of multiple parameter analyses with Eqs. (2)–(4). The data in Table 5 show that the parameter δ_{an} is statistically significant in the correlations of $\delta_{H(B)}$, $\delta_{H(C)}$, $\delta_{C(2)}$ and $\delta_{C(3)}$, while the coefficient ρ_{an} has a large standard error of estimate in the correlation of $\delta_{C(1)}$. Fits of the NMR data of CCT to TSP Eq. (5) indicate, in general, that the quantified polar and resonance contributions are mutually comparable in the presence of other contributions.

We tried to fit all 16 δ_H to multiple parameter Eqs. (2)–(5). As a result the four excellent fits to LFER models were obtained and are given in Table 6. Every correlation listed in Table 6 was done with topological correction relative to proton H(B). By analogy with δ_H, the analyses of all 21 δ_C with four LFER models were done. The obtained results are listed in Table 7. The correlations of δ_C were done with topologic correction relative to carbon C(1). It is evident that δ_C were fitted satisfactorily to all Eqs. (2)–(5).

Examination of the data in Tables 6 and 7 reveals that in every correlation listed the TSP analyses with Eq. (5) yields fits statistically equal to or better than these of multiple parameter analyses with Eqs. (2)–(4). The degree of success of TSP Eq. (5) is shown in Figs. 4 and 5 by means of a plot of δ_N experimental versus δ_N calculated ($\delta_N = \delta_H$ or δ_C).

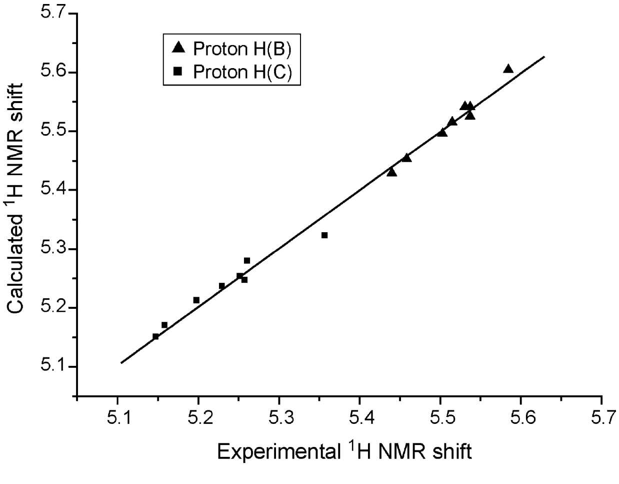

Fig. 4. Plot of δ_H experimental versus δ_H calculated from TSP Eq. (5) for 3-methylene-2-substituted-1,4-pentadienes, with topological correction relative to proton H(B) ($R = 0.9960$, $s = 0.014$, $n = 16$).

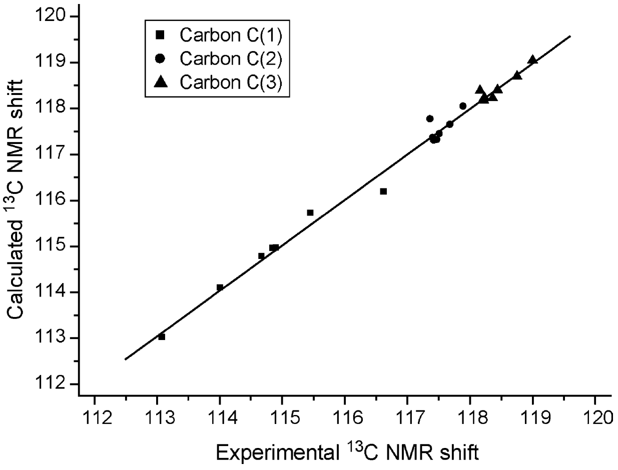

Fig. 5. Plot of δ_C experimental versus δ_C calculated from TSP Eq. (5) for 3-methylene-2-substituted-1,4-pentadienes, with topological correction relative to carbon C(1) ($R = 0.9945$, $s = 0.178$, $n = 21$).

It should be noted that when all δ_H or δ_C are taken into consideration, multiple parameter analyses with Eqs. (2)–(5) yield a new term T_N (N = ^{1}H and ^{13}C, respectively) so called topological parameter [43]. According to the results of the correlation listed in Tables 6 and 7, a type of parameterization that mentioned above is a method that provides a prediction of the NMR data for probe nuclei of different topology in the molecule of CCT.

4. Conclusions

The MSP approach gives a modest correlation of the ^{1}H and ^{13}C NMR data of 3-methylene-2-substituted-1,4-pentadienes. While the conventional DSP approach using extended Hammett Eq. (2) was more superior in analyzing the δ_H and δ_C values to the former, the nature of σ_I and σ_R substituent constants precludes DSP, Eq. (2), to provide any other contribution to chemical shifts except from electronic effects. Both the dual and the triple parameter correlations of the chemical shifts with unconventional LFER models (Eqs. (3)–(5)) gave significant improvement over simple and extended Hammett equation. Application of unconventional LFER models gave a better insight into the factors determining chemical shifts of NMR probe nuclei in the studied molecular framework. The validity of the used unconventional LFER models is confirmed by the fact that the calculated molecular geometries in general allow accurate prediction of the NMR data.

The prevalent influence of resonance substituent effects on $\delta_{C(1)}$, $\delta_{H(B)}$ and $\delta_{H(C)}$ together with the minor influence of these effects on $\delta_{C(2)}$ and $\delta_{C(3)}$ indicate that the *s-cis*-buta-1,3-dien-2-yl group behaves as a rather isolated fragment. Further evidence for this was obtained from the results of the analyses of $\delta_{C(2)}$ and $\delta_{C(3)}$ with both DSP Eq. (3) and TSP Eq. (5). These results show that the resonance component of substituent effect markedly depends on the coplanarity of the double bonds. The superior results of the correlations of δ_H with TSP Eqs. (4) and (5) show that δ_H are not determined solely by electronic substituent effects. Since the π-unit-1 is conjugated to an aromatic ring, $\delta_{H(B)}$ and $\delta_{H(C)}$ are in some extent affected by magnetic anisotropy of the aromatic ring as well.

In spite of obvious peculiarity of the arrangement of the π-electrons in investigated cross-conjugated triene and its geometrical complexity, we have demonstrated that the ^1H and ^{13}C NMR probe nuclei in unsaturated chain can be used as the semi-empirical measure of substituent effects in this system.

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