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Investigation of Substituent Effects on Proton and Carbon-13 Chemical Shifts of 4-Substituted *trans*-Stilbenes

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Proton and carbon-13 chemical shifts of para-substituted stilbenes have been measured. ^{1}H-^{1}H, ^{1}H-^{13}C COSY spectra were obtained to analyze unambiguously the chemical shifts of protons and carbons. A long range coupling between 2-H and α-H was observed in a ^{1}H-^{1}H COSY spectrum. The observed chemical shifts have been correlated with Hammett substituent parameters. Among ethenyl protons and carbons, all but the chemical shifts of α-H show good correlation with both dual substituent parameters and single substituent parameters. In addition to this finding, the excellent linear correlations of C-1, and 4′-H of 4-substituted *trans*-stilbenes are also reported. Besides the correlations of chemical shifts with Hammett parameters, a good correlation between the chemical shifts and the calculated charges of position C-4′ are reported.

INTRODUCTION

By the correlation of chemical shifts in NMR spectra with Hammett substitutent parameters, the systematic changes in electronic properties of organic molecules have been studied.[1-4] Through several decades, many styrene derivatives have been used for the study of correlations of the chemical shifts of vinylic carbons and protons with various substituent parameters.[5-12] To study the substituent effects in NMR chemical shifts of styrenes, either a single-substituent parameter (MSP) treatment or a dual-substituent parameter (DSP) treatment has been used. Four different selectable resonance scales compared to the invariable single-parameter scale make the DSP method more flexible, thus improve correlations. The DSP method has the merit to separate the observed chemical shifts into inductive and resonance contributions as shown in equation 1.[13]

$$\text{Chemical shift} = \rho_I\sigma_I + \rho_R\sigma_R \qquad (1)$$

Good linear correlations of the chemical shifts of β-carbons of styrene derivatives were observed. The correlation of α-carbons are generally good, even though there were controversial reports about the correlation of the chemical shifts of α-carbons in benzenylidenemalononitriles, $XC_6H_5CH=C(CN)_2$.[14,15] In addition to the correlations of the vinylic protons and carbons, the carbons of adjacent carbonyl groups and protons attached to the nitrogens of the ring-substituted styrenes show good linear correlations with various Hammett parameters.[14,16]

For proton chemical shifts of α-carbon, several different observations were reported. Posner et al.[9] and Tan et al.[16] found good correlations for benzylidenemalononitriles, and for (z) 5-arylmethylenehydatoins, respectively. However, Ivin et al.[17] observed no correlation of the α-protons of 5-arylmethylene-2-thiohydantoins. The linearity of correlation of chemical shifts of α-proton is largely determined by the structure of the subsitituent at the β position. Relatively few cases were reported about the correlations of β (α' in the case of stilbene) and α protons in the same molecule of the ring-substituted styrene derivatives. By introducing a single substituent at the β position of styrene, one can study the correlations of chemical shifts of both α and β protons as well as those of carbon atoms. Even though stilbene is a simple example of a monosubstituted styrene, not much attention has been paid to the NMR of stilbene derivatives.[4] The reason is probably that the chemical shifts of the two ethenyl protons, as well as that of the two carbons, are so close to each other that one cannot distinguish them unambiguously.

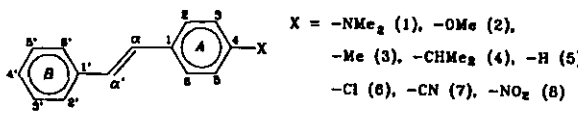
4-Substituted *trans*-stilibenes were chosen in our experiments. Unlike styrenes,[18-21] the order of the chemical shifts of α and α' carbons is reversed according to the substituents, which provide a good clue to the results of numerous chemical reactions occurring at an ethenyl double bond. Besides the reasons mentioned above, it is of interest to investigate the subsitituent effects on the chemical shifts of carbons and protons which are now further down the ethenyl group when a completely conjugated

Dedicated to Professor Sheng-Lieh Liu (劉盛烈) on the occasion of his eightieth birthday.

group is substituted at the β position of styrene. Finally, we report the correlation of NMR chemical shifts with the calculated charges of the 4-substituted stilbenes.

RESULTS AND DISCUSSION

The numbering system of proton and carbon atoms and two phenyl rings of 4-substituted *trans*-stilbenes is shown below.



The substituent chemical shift (SCS: defined as difference between the observed chemical shift and the unsubstituted chemical shift) values of the protons and carbon atoms of 4-substituted *trans*-stilbenes are given in Tables 1 and 2 respectively.

In stilbene, two ethenyl protons are chemically and magnetically equivalent. By the introduction of a substituent in the 4-position of stilbene, two ethenyl protons are changed to AB spin system. To assign peaks unambiguously, the ^{1}H-^{1}H COSY spectrum was obtained for every 4-substituted *trans*-stilbene. The aromatic region of the ^{1}H-^{1}H COSY spectrum of one 4-substituted stilbene (compound **1**) is shown in Fig. 1. The aromatic region of the proton spectrum of 4-*N,N*-dimethylaminostilbene consists of three well-separated multiplet resonance. Starting from the lower left of the spectrum, peak a at δ = 7.47 ppm is coupled to peak c which is coupled in turn to peak d.

Table 1. SCS Values of Protons of 4-Substituted *trans*-Stilbenes[a]

Compd	α-H	α'-H	3-H	2-H	2′-H	3′-H	4′-H	Other[b]
1	-0.06[c]	-0.19	-0.64	-0.11	-0.04	-0.03	-0.06	2.96
2	-0.03[d]	-0.12[d]	-0.44	-0.05	-0.01	0.00	-0.02	3.81
3	-0.02[c]	-0.04	-0.20	-0.11	-0.02	-0.01	-0.02	2.35
4	0.00[c]	-0.03	-0.12	-0.05	0.00	0.00	-0.02	2.92,1.28, 1.26
5[b]	7.10[c]	7.10	7.35	7.51	7.51	7.35	7.25	
6	-0.04[d]	-0.01[d]	-0.01	-0.07	0.01	0.04	0.05	
7	-0.02[c]	0.10	0.27	0.05	0.01	0.02	0.07	
8	0.02[c]	0.15	0.85	0.10	0.03	0.04	0.09	

[a] Proton chemical shifts relative to the unsubstituted stilbene; downfield shifts are positive.
[b] Chemical shifts (in ppm) relative to TMS.
[c] Assignment of this proton was determined by observing a long range coupling between α-H and 2-H; 2-H was unambiguously assigned by ^{1}H-^{1}H COSY spectrum.
[d] Assignment of this proton was determined on the consideration of general trend in the substituent effects upon α'-H and C-α'; the attachment of α'-H and C-α' was deduced from ^{1}H-^{13}C COSY spectrum.

Table 2. SCS Values of Carbons of 4-Substituted *trans*-Stilbenes[a]

Compd	C-α	C-1	C-2[d]	C-3	C-4[d]	Other[b]
1	0.09	-11.41	1.06	-16.18	22.47	40.46
2	-0.48[c]	- 7.20	1.21	-14.55	31.70	55.27
3	-0.05	- 2.77	-0.10	0.70	9.92	21.23
4	-0.05	- 2.37	0.01	- 1.93	20.94	33.88,23.92
5[b]	128.67	137.32	126.49	128.67	127.59	
6	-1.37[c]	- 1.53	1.13	0.11	5.52	
7	-1.96	4.52	0.36	3.80	-17.03	119.00
8	-2.41	6.50	0.33	- 4.57	19.16	

Compd	C-α'	C-1′[d]	C-2′	C-3′	C-4′
1	-4.26	0.82	-0.50	-0.13	-0.95
2	-2.07[c]	0.31	-0.25	-0.05	-0.40
3	-0.98	0.19	-0.10	-0.05	-0.21
4	-0.86	0.21	-0.10	-0.05	-0.22
5[b]	128.67	137.32	126.49	128.67	127.59
6	0.59[c]	-0.40	0.03	0.01	0.23
7	3.73	-1.05	0.40	0.18	1.04
8	4.62	-1.17	0.50	0.20	1.23

[a] Carbon-13 Chemical shifts (in ppm) relative to the unsubstituted stilbene; downfield shifts are positive.
[b] Chemical shifts (in ppm) relative to TMS.
[c] Assignments of chemical shifts of these carbons were done by consideration of trends of substituent effects on the C-α' and α'-H whose direct attachments were traced by ^{1}H-^{13}C COSY spectra.
[d] Assignments of quaternary carbons were based on the comparison of the observed and calculated values.

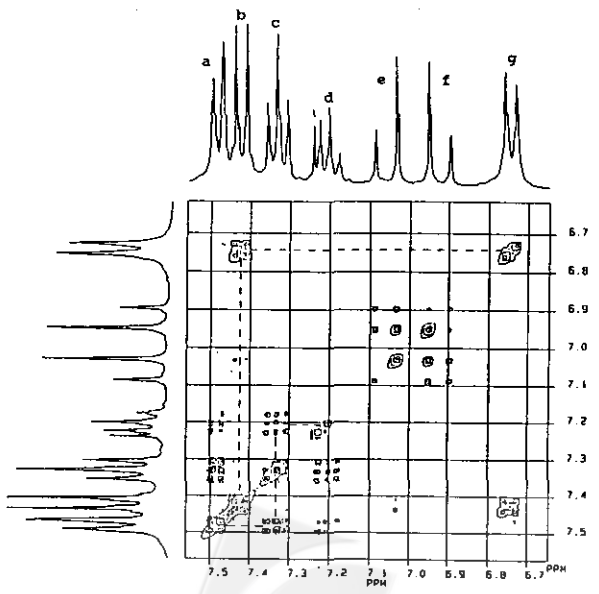


Fig. 1. Aromatic region of ^{1}H-^{1}H COSY spectrum of 4-*N,N*-dimethylaminostilbene.

These doublet, triplet, and triplet peaks correspond to 2′-H, 3′-H and 4′-H, respectively. There is a meta coupling between 2′-H and 4′-H which is shown in the spectrum. Peaks b and g are coupled together and peak b has a long-range coupling to peak e which is the left side doublet of a quartet corresponding to two ethenyl protons. Therefore, peaks b, g, e, and f are assigned to 2-H, 3-H, α-H, and α'-H of 4-*N,N*-dimethylaminostilbene, respectively. By means of the ^{1}H-^{1}H COSY spectrum, all protons are assigned unequivocally; then carbon peaks are assigned through the correlation in the ^{1}H-^{13}C COSY spectrum shown in Fig. 2.

In the same way, the chemical shifts of all carbons to which protons are attached were unambiguously assigned except in methoxy- and chloro-substituted stilbenes in which no long-range coupling between 2-H and α-H was observed. The reason is unavailable. Nevertheless, the assignments of chemical shifts of these ethenyl protons and carbons were done upon the consideration of the general trends of the substituted effects on these protons and carbons of other 4-substituted *trans*-stilbenes. The assignment of three quaternary carbons, C-4, C-1 and C-1′ could not be done through the ^{1}H-^{1}H and ^{1}H-^{13}C COSY spectra. The chemical shift of C-4 is strongly affected by the electronegativity of the atom of the substituent which is directly attached to the phenyl ring A[1] and varies in a larger range in ppm than the other carbons in the stilbene derivatives. The assignment of the chemical shifts of C-1 was done upon considering that the substituent effect is larger in C-1 than in C-1′, and the chemical shift of C-1′ changes only in a more narrow range than that of C-1. This assumption was supported by the fact that the slope of the correlation of the chemical shifts of C-1 is greater than that of C-1′. All the assigned chemical shifts of the quaternary carbons were compared with the calculated values using the additivity rule[22] and found to be close together.

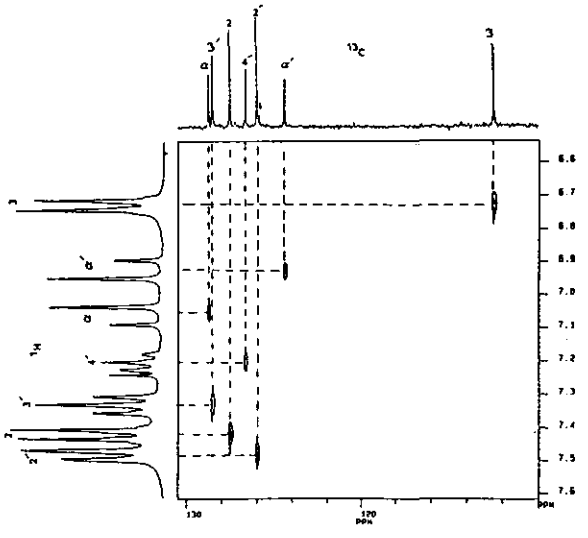


Fig. 2. ^{1}H-^{13}C COSY spectrum of 4-*N,N*-dimethylaminostilbene.

Proton and carbon-13 SCS values were correlated by the MSP method and DSP method. Statistics were carried out on the programs written in a Lotus-123 package. To calculate ρ_I, ρ_R, the correlation coefficient c and its standard deviation (S.D.), the formula given by Swain and Lupton was used.[23] To derive the dispersion, f, we followed the suggestion of Laszlo[14] and a substituent chemical shift (SCS) value was used in every calculation necessary. For the sake of comparison, correlation coefficient, c, for the MSP treatment was calculated in the same way as that used in the case of DSP. The parameters used in the MSP and DSP treatments are from the recent compilation by Exner.[24]

The results of correlations of the carbons are given in Table 3. The correlations of the chemical shifts of C-α' with both MSP and DSP parameters show good linearity. No significant improvement of correlation with DSP parameters can be obselved. However, in either treatment, parameters derived from the benzoic-acid dissociation constants show much improved correlation. These results imply that the phenyl group attached to C-α' has no strong electronic influence on C-α' of a stilbene derivative, in contrast to the results obtained with β,β-dichlorostyrenes in which a strong electron-withdrawing group is attached at the β site and σ_p^+ are preferred for the better correlation.[12] Several papers were published to get the new σ_p^+ values using the correlation of the chemical shifts of C-β of styrene derivatives where strong electron withdrawing cyano and nitro groups are attached.[9,11] In 4-substituted 5-arylmethylenehydantoins,[16] in which an electron-withdrawing carbonyl group and an electron-donating nitrogen atom compete for the C-β site, the overall effects seem to be a little electron-donating at C-β and the linearity of the correlation improves slightly with use of the σ_p^- parameters.

The correlation of chemical shifts of C-α by the DSP method improves the linearity of the correlation over the MSP method. One notable observation of the correlation is its negative substituent effect which was first observed by Brownlee et al.[25] As explained by Brownlee,[26] the direction of localized π polarization of an ethenyl group by the substituent is toward the α carbon and independent of a phenyl group, which is reflected in the negative and positive values of ρ_I of C-α and C-α', respectively. In DSP treatments, no significant preference over the four parameters is observed, every correlation is 99% or greater. In MSP treatments, however, the significant preference of σ_p^- and σ_p°

Table 3. Statistical Data for the Correlations between SCS of Several Carbons of 4-Substituted *trans*-Stilbenes with dual- and mono-Substituent Parameters

Position	Equation	S.D.[a]	f[b]	c[c]
C-α′	SCS = 4.89 σ_I [d] + 8.79 σ_R^{oT} [e] + 0.04	0.30	0.10	0.9925
	SCS = 6.81 σ_I + 9.20 σ_R^{o} + 0.12	0.36	0.12	0.9893
	SCS = 6.22 σ_I + 3.01 σ_R^{+} - 0.04	0.45	0.15	0.9831
	SCS = 4.04 σ_I + 6.35 σ_R^{-} - 0.26	0.70	0.24	0.9586
	SCS = 5.94 σ_P [f] - 0.32	0.30	0.09	0.9949
	SCS = 6.72 σ_P^{o} - 0.79	0.89	0.26	0.9529
	SCS = 3.49 σ_P^{+} + 0.72	0.88	0.25	0.9535
	SCS = 4.78 σ_P^{-} - 0.96	1.06	0.31	0.9313
C-α	SCS = -3.06 σ_I - 1.26 σ_R^{oT} - 0.13	0.09	0.07	0.9941
	SCS = -3.34 σ_I - 1.31 σ_R^{o} - 0.14	0.10	0.08	0.9923
	SCS = -3.25 σ_I - 0.44 σ_R^{+} - 0.12	0.10	0.07	0.9934
	SCS = -2.94 σ_I - 0.91 σ_R^{-} - 0.09	0.13	0.10	0.9876
	SCS = -1.86 σ_P - 0.65	0.48	0.31	0.8775
	SCS = -2.28 σ_P^{o} - 0.48	0.32	0.21	0.9476
	SCS = -0.95 σ_P^{+} - 0.95	0.74	0.48	0.6638
	SCS = -1.63 σ_P^{-} - 0.42	0.35	0.23	0.9366
C-1	SCS = 5.27 σ_I + 20.65 σ_R^{oT} - 0.24	0.78	0.13	0.9867
	SCS = 9.77 σ_I + 21.61 σ_R^{o} - 0.05	0.93	0.15	0.9816
	SCS = 8.39 σ_I + 7.10 σ_R^{+} - 0.40	1.01	0.17	0.9783
	SCS = 3.32 σ_I + 14.85 σ_R^{-} - 0.95	1.75	0.29	0.9339
	SCS = 11.32 σ_P - 2.58	1.97	0.27	0.9405
	SCS = 12.31 σ_P^{o} - 3.40	3.09	0.43	0.8455
	SCS = 7.04 σ_P^{+} - 0.52	1.25	0.17	0.9765
	SCS = 8.72 σ_P^{-} - 3.71	3.32	0.46	0.8189
C-1′	SCS = -1.45 σ_I - 1.79 σ_R^{oT} + 0.00	0.08	0.11	0.9905
	SCS = -1.84 σ_I - 1.86 σ_R^{o} - 0.02	0.10	0.14	0.9859
	SCS = -1.72 σ_I - 0.62 σ_R^{+} + 0.01	0.07	0.10	0.9925
	SCS = -1.29 σ_I - 1.26 σ_R^{-} + 0.07	0.17	0.25	0.9541
	SCS = -1.41 σ_P - 0.04	0.05	0.06	0.9974
	SCS = -1.62 σ_P^{o} + 0.08	0.13	0.16	0.9810
	SCS = -0.80 σ_P^{+} - 0.28	0.27	0.33	0.9195
	SCS = -1.15 σ_P^{-} + 0.12	0.21	0.25	0.9523
C-2′	SCS = 0.50 σ_I [d] + 1.02 σ_R^{oT} [d,e] + 0.01	0.03	0.10	0.9923
	SCS = 0.72 σ_I + 1.07 σ_R^{o} + 0.02	0.04	0.12	0.9891
	SCS = 0.66 σ_I + 0.35 σ_R^{+} + 0.00	0.06	0.17	0.9792
	SCS = 0.40 σ_I + 0.74 σ_R^{-} - 0.02	0.08	0.24	0.9589
	SCS = 0.66 σ_P [d] - 0.05	0.05	0.12	0.9890
	SCS = 0.74 σ_P^{o} - 0.10	0.11	0.29	0.9398
	SCS = 0.39 σ_P^{+} + 0.07	0.09	0.24	0.9587
	SCS = 0.53 σ_P^{-} - 0.12	0.13	0.33	0.9207
C-3′	SCS = 0.24 σ_I + 0.31 σ_R^{oT} - 0.01	0.01	0.12	0.9896
	SCS = 0.31 σ_I + 0.33 σ_R^{o} + 0.00	0.01	0.09	0.9936
	SCS = 0.29 σ_I + 0.10 σ_R^{+} - 0.01	0.03	0.26	0.9526
	SCS = 0.21 σ_I + 0.23 σ_R^{-} - 0.01	0.02	0.14	0.9863
	SCS = 0.23 σ_P + 0.00	0.03	0.18	0.9763
	SCS = 0.27 σ_P^{o} - 0.2	0.02	0.15	0.9831
	SCS = 0.13 σ_P^{+} + 0.04	0.06	0.42	0.8677
	SCS = 0.20 σ_P^{-} - 0.03	0.02	0.17	0.9784
	SCS = 0.33 σ_m - 0.05	0.05	0.35	0.9137
C-4′	SCS = 1.38 σ_I + 2.06 σ_R^{oT} + 0.01	0.07	0.09	0.9944
	SCS = 1.83 σ_I + 2.16 σ_R^{o} + 0.03	0.08	0.11	0.9918
	SCS = 1.69 σ_I + 0.70 σ_R^{+} - 0.01	0.11	0.15	0.9834
	SCS = 1.18 σ_I + 1.49 σ_R^{-} - 0.05	0.16	0.22	0.9661
	SCS = 1.49 σ_P - 0.01	0.04	0.05	0.9982
	SCS = 1.71 σ_P^{o} - 0.13	0.16	0.19	0.9731
	SCS = 0.86 σ_P^{+} + 0.25	0.26	0.30	0.9324
	SCS = 1.22 σ_P^{-} - 0.18	0.22	0.25	0.9536

[a] Standard deviations. [b] Dispersion f = S.D./R.M.S. [c] Correlation coefficient. [d] DSP and MSP parameters are from ref. 20. [e] σ_R^{oT} is an original Taft scale.

over σ_p and σ_p^+ indicates that an induction contribution on the carbon is important and that the phenyl group increases the electron density at this carbon. The ratio λ of ρ_I and ρ_R in the DSP treatment using ρ_R^+ scales is 0.31; thus it indicates that an induction contribution at this carbon is large compared to the resonance contribution; DSP improves linearity of the correlation.[15]

The trend of correlations of C-α and C-1 with four different single parameters is exactly opposite to each other. The correlations of chemical shifts of C-α with α_p^- and αp^o are the best, but the correlations of those of C-1 with σ_p^- and σ_p^o are the worst of all the correlations. The strong preference of σ_p^+ on the correlation of C-1 carbon in the 4-substituted benzene ring,[2] β-nitrostyrenes,[8] and 4-substituted 5-arylmethylenehydantoins[16] were reported previously. Therefore, the tendency of the C-1 carbon over the different parameters is irrelevant to the substituted group attached at the C-1 position and the opposite trends seem to be purely accidental; this conclusion is consistent with the fact that, in stilbenes, the correlation of the chemical shifts of C-α is better with σ_p^- and σ_p^o.

One purpose of this experiment is to study the substituent effect on the benzene ring B, further down the ethenyl group. We found excellent correlations of the chemical shifts of all carbons in the benzene ring B with both MSP and DSP treatments. In the MSP treatment, the correlation with σ_p is generally good. In C-3′ every parameter is equally good for the correlation except σ_p^-. Negative substituent effects are observed on the chemical shifts of C-1′. The phenyl ring is π polarized with respect to the substituent, and C-1′ and C-4′ show negative and positive effects, respectively as in the ethenyl carbons. The values of ρ_I of C-1′ and C-4′ within the same resonance parameter sets are close and opposite in sign. The same trends were observed for the chalcones[27] and explained using the localized π polarization mechanism by Brownlee et al.[26] The correlations of chemical shifts of C-2′ and C-3′ are sound even though the overall chemical shift changes for C-2′ and C-3′ are 1.00 ppm and 0.33 ppm, respectively. In C-3′, the correlation with σ_m is poor compared to σ_p. Originally, the σ_m scales were derived from the same benzene ring in which both substituents and the reaction site exist. Therefore, the parameter may contain several different effects which cannot be applicable to C-3′ of stilbenes. If one considers the resonance of the whole stilbene conjugated system, it is clear that the resonance contribution at C-2′ is larger than that at C-3′ and that this effect is observed in the absolute values of ρ_R of the DSP equations of C-2′ and C-3′. The value of ρ_R of C-2′ is half that of C-4′ within the same sets of parameters used; thus the resonance

contribution at C-2′ is half that at C-4′. The ratio of ρ_I of C-2′ and C-3′ with σ_R^{oT} is 2.08 which indicates that the induction contribution at C-2′ is twice as large as that on C-3′. The large different induction contribution can be attributed to a π inductive effect on C-2′. In 1-substituted biphenyls the ratio is 1.43 (see Table 2 in ref.28) which is smaller than what we observed in *trans*-stilbenes. The reason that the ratio in stilbenes is larger is unclear.

One peculiarity of the correlations of chemical shifts of these two carbons is their positive substituent effect. Several different π polarization mechanisms were presented to interpret the effect of substituents on the carbons of phenyl groups of different molecules.[4,28,29] The probable explanation of the substituent effect at C-2′ and C-3′ is that the nodal point of the extended π polarization mechanism is between C-1′ and C-2′ rather than between C-2′ and C-3′. In contrast, in 1-substituted 4-phenylbicyclo[2.2.2]octanes, the nodal point seems to be between C-2′ and C-3′.[28] The INDO MO method, however, indicated the existence of the nodal point betwoen C-1′ and C-2′ of the molecules.[28] The large resonance contribution at C-2′ together with the π-induction contribution makes the SCS change of C-2′ much larger than that of C-3′.

The results of some attempted correlations of chemical shifts of protons of 4-substituted *trans*-stilbene are listed in Tables 4. Only α'-H and 4′-H show good correlations with dual substituent parameters. 2′-H and 3′-H show only fairly linear relationships c = 0.9099 with σ_R^+ and c = 0.8732 with σ_R^+, respectively. An unexpectedly poor correlation (c = 0.7767) of α-H with σ_R^- was found. The range of chemical shift change of the α-H is 0.08 ppm which is only 24% of that of α'-H. In 5-arylmethylenehydantoins, the range of chemical shift change of the α proton is 0.15 ppm which is 188% what we observed in stilbenes.[16] Among the correlations they reported, the correlation of chemical shifts of α-H with MSP treatment is the poorest among those correlations. Posner et al. reported good correlation of chemical shift of α-proton of benezylidenemalononitriles for which the overall chemical shift change is 0.67 ppm.[9] In the situation of a small change of chemical shift (less than 0.10 ppm), so many effects such as magnetic anisotropy, steric and solvent effects would combine with a concentration effect, thus to make the correlation poor. In contrast to the chemical shifts of carbons, the chemical shifts of protons are much influenced by these effects because of the narrow range of common chemical shifts observed for the protons. However, a good linear correlation of the chemical shifts of 4′-H of stilbenes occurs even though the range of chemical shift change is 188% that of α-H. It strongly indicates that deviation from the linearity of correlation of α-H is a result caused by the environment of α-H which is more susceptible than 4′-H. Thus the substituent parameters cannot be effectively applicable compared to 4′-H of stilbenes.

Calculated charges at position C-4′ were reported by Ulman.[30] The calculated charges and substituent chemical shifts of C-4′ are tabulated in Table 5. We attempted the correlation of SCSs of C-4′ with the calculated charges, and found a good correlation with a correlation coefficient 0.9678; see Fig. 3. There were several reports of correlations of electron densities with SCSs, however, the first known correlation of SCSs with the calculated charges of

Table 4. Statistical Data for the Correlations between SCSs of Several Protons of 4-Substituted *trans*-Stilbenes with dual and mono Substituent Parameters

Position	Equation	S.D.[a]	f[b]	c[c]
α'-H	SCS = 0.122 σ_I[d] + 0.374 σ_R^{oT}[d,e] + 0.003	0.014	0.128	0.9881
	SCS = 0.204 σ_I + 0.391 σ_R^o + 0.007	0.017	0.153	0.9831
	SCS = 0.179 σ_I + 0.128 σ_R^+ - 0.000	0.022	0.196	0.9718
	SCS = 0.086 σ_I + 0.271 σ_R^- - 0.009	0.030	0.269	0.9465
	SCS = 0.216 σ_P - 0.033	0.031	0.237	0.9586
	SCS = 0.238 σ_P^o - 0.049	0.052	0.397	0.8794
	SCS = 0.132 σ_P^+ + 0.006	0.027	0.208	0.9683
	SCS = 0.169 σ_P^- - 0.055	0.056	0.425	0.8598
4′-H	SCS = 0.123 σ_I + 0.116 σ_R^{oT} - 0.005	0.012	0.218	0.9643
	SCS = 0.159 σ_I + 0.120 σ_R^o - 0.005	0.013	0.239	0.9570
	SCS = 0.140 σ_I + 0.043 σ_R^+ - 0.004	0.006	0.103	0.9921
	SCS = 0.116 σ_I + 0.077 σ_R^- - 0.011	0.018	0.327	0.9177
	SCS = 0.105 σ_P + 0.004	0.013	0.204	0.9690
	SCS = 0.122 σ_P^o - 0.005	0.015	0.232	0.9594
	SCS = 0.060 σ_P^+ + 0.022	0.024	0.381	0.8864
	SCS = 0.085 σ_P^- - 0.008	0.021	0.329	0.9166

[a] Standard deviations. [b] Dispersion f = S.D./R.M.S. [c] Correlation coefficient.
[d] DSP and MSP parameters are from ref. 20. [e] σ_R^{oT} is an original Taft scale.

Table 5. Substituent Chemical Shifts of C-4′ and the Calculated Charges of the Position C-4′ of 4-Substituted *trans*-Stilbenes

Compd	SCS	Charge[a]
1	-0.95	-0.1303
2	-0.40	-0.1277
3	-0.21	-0.1274
6	0.23	-0.1220
8	1.23	-0.1165

[a] From ref. 26.

the same position is reported here.

EXPERIRNENTAL SECTION

All 4-substituted trans-stilbenes were prepared from the corresponding 4-substituted benzaldehydes and benzyl chloride by the Wittig reaction.[31] The melting points of 4-substituted *trans*-stilbenes are as follows: **1**: 144.5-146°C; **2**: 132-134°C (lit., 135-136°C);[32] **3**: 118-119°C (lit., 119.5-120°C);[32] **4**: 90.5-91°C; **6**: 126-128°C (lit., 127°C);[33] **7**: 113-114°C (lit., 114°C);[34] **8**: 150-153°C (lit., 157°C).[35] Nonsubstituted *trans*-stilbene (Janssen Chimica) was used without further purification.

NMR measurements of the 4-substituted *trans*-stilbenes (0.2 M, in $CDCl_3$) were carried out at ambient temperature (297 ± 1°K) on a Bruker AM 300 NMR spectrometer equipped with a 5-mm C/H dual probe, operating in the FT mode at 300 MHz and 75.5 MHz for protons and carbons, respectively. Data were collected and processed through an Aspect 3000 computer using the Bruker DISNMR software. ^1H and ^{13}C NMR chemical shifts were determined relative to TMS (δ = 0.000 ppm), and the central peak of triplet of deuterochloroform (δ = 77.0 ppm), respectively. One-dimensional proton spectra were recorded using a sweep width 5000 Hz and 16K data points. Sixteen scans were accumulated and an exponential multiplication was done prior to Fourier transformation. One dimensional carbon-13 spectra were recorded using a sweep width 23809 Hz and 32 K data points, 560 scans were accumulated. Decoupling was done in the composite pulse decoupling mode.[36] ^1H-^1H COSY spectra were acquired with a COSY 45 sequence to reduce the intensities of the diagonal peak. The experimental parameters used for 4-*N,N*-dimethylaminostilbene are summarized as follows: SW2 (420.521 Hz), SW1 (210.261 Hz), Matrix size (before zero filling 128w × 1k, after zero filling 1K × 1K), evolution time (initial value 3 μs, increment 2.38 ms), acquisition time (1.218). relaxation delay (1.00 s), window function (sine bell). ^1H-^{13}C 2D NMR correlation spectra were obtained through XHCORR pulse sequence. The parameters used for 4-*N,N*-dimethylaminostilbene were as follows: f2 (3012.048 Hz), f1 (300.120 Hz), matrix size (before zero filling 128w × 1k, after zero filling 1k × 1k), evolution time (initial 3 μs, increment 0.83 ms), number of scans (48), acquisition time (0.170 s), relaxation delay (1.5 s), window function (sine bell multiplication).

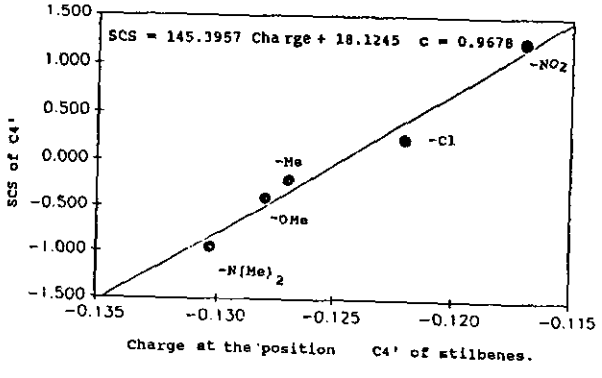


Fig. 3. Correlation between SCS at C-4′ and the calculated charges at the position C-4′ of 4-substituted *trans*-stilbenes.

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Key Words

Substituent effect; Proton and carbon-13 NMR; 4-Substituted *trans*-stilbenes.

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