Unusual Deuterium Isotope Effects in ^{13}C NMR Spectra of *trans*-Stilbene

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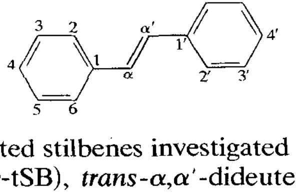
A detailed analysis of the ^{13}C NMR spectra of *trans*-stilbene and ten deuteriated *trans*-stilbenes has been undertaken. Some unusual deuterium isotope effects on carbon–hydrogen spin–spin coupling constants could not be explained by the ordinary primary and secondary isotope effects. The positive and negative changes of ^nJ(CH) were interpreted in terms of a steric effect, the vibrational influence of the C—D bond and the *para*-effect induced by deuterium. In this respect, deuterium behaves as a real substituent with electronic properties different from those of hydrogen. The deuterium isotope effects on ^{13}C NMR chemical shifts and carbon–deuterium coupling constants have also been determined.

INTRODUCTION

Stilbene, selected as a model system for studying photochemical reactions and the transmission of substituent effects in aryl groups linked by double bonds, has been the subject of numerous structural investigations.[1] ^{13}C NMR spectroscopy is frequently used for analysing the physico-chemical properties of the ground state of conjugated molecules. In spite of the expected relative simplicity of the ^{13}C NMR spectrum of *trans*-stilbene, none of the reported analyses[2–6] was complete and each treated only some of the aspects of the NMR spectrum. Moreover, the data for ^{13}C chemical shifts are not congruent and the lack of ^{13}C,^{1}H coupling constants is particularly evident.

In view of these inconsistencies and unknowns, an analysis of the ^{13}C NMR spectra of deuteriated *trans*-stilbenes, including a thorough re-examination of the parent compound, was undertaken as part of an extensive spectroscopic study on stilbenes.[7,8] The use of deuteriated isotopes proved to be extremely useful in assigning very closely spaced or even overlapped peaks in a fully coupled spectrum. In the course of this investigation some unusual isotope effects have been observed, which deserve discussion.

The numbering of the carbon atoms in the *trans*-stilbene (tSB) molecule is shown below:



The deuteriated stilbenes investigated were *trans*-α-deuterio- (α-D-tSB), *trans*-α,α′-dideuterio- (α,α′-D_2-tSB), *trans*-2,2′-dideuterio- (2,2′-D_2-tSB), *trans*-3,3′-dideuterio- (3,3′-D_2-tSB), *trans*-4,4′-dideuterio- (4,4′-D_2-tSB), *trans*-4,α-dideuterio- (4,α-D_2-tSB), *trans*-4,α′-dideuterio- (4,α′-D_2-tSB), *trans*-2,3,4,5,6-pentadeuterio- (D_5-tSB), *trans*-2,2′,3,3′,4,4′,5,5′,6,6′-decadeuterio- (D_{10}-tSB), and *trans*-perdeuterio-stilbene (D_{12}-tSB).

EXPERIMENTAL

Spectroscopy

All NMR spectra were recorded on a JEOL FX-100 spectrometer operating in the pulse FT mode at 25.05 MHz. In case of ambiguous assignment of signals, various solvents and temperatures (−50 to 180 °C) were used. The solvents were $CDCl_3$, DMSO-d_6 and acetone-d_6. The deuterium was used for the internal lock signal. The FIDs were accumulated in 16–4K addresses and the spectral widths were chosen to range from 5000 to 200 Hz, which gave a digital resolution of 0.61–0.09 Hz. The flip angles were 40–60°. The concentration of the samples in 5 mm tubes was 0.5–1.0 mol l^{-1}. All chemical shifts refer to TMS as the internal standard. The operational modes applied were proton noise and gated decoupling.

Substances

trans-Stilbene was purified by zone refining (36 zones on a Desaga zone refining apparatus) and *trans*-perdeuteriostilbene with 99.3% D_{12} (Merck, Sharp and Dohme, Canada) by recrystallization from cyclohexane. *trans*-2,2′,3,3′,4,4′,5,5′,6,6′-D_{10}-Stilbene was synthesized with 93% D_{10} content according to Buu-Hoi.[9] The deuteriated stilbenes α-D-tSB, α,α′-D_2-tSB, 4,α-D_2-tSB, 4,α′-D_2-tSB and D_5-tSB were synthesized via the Wittig synthesis as described by Schlosser.[10] The appropriate deuteriated toluenes were brominated in CCl_4 with *N*-bromosuccinimide

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using dibenzoyl peroxide as catalyst. The resulting benzyl bromides were then converted into the corresponding triphenylbenzylphosphonium bromides.[10] The mixture of the appropriate deuteriated *cis*- and *trans*-stilbenes obtained from the Wittig synthesis was dissolved in 30–50 ml of benzene and, after addition of a few milligrams of iodine, irradiated with a xenon arc lamp (XBO 450 W, Osram) for approximately 30 min. The deuteriated *trans*-stilbenes were isolated and purified by column chromatography on silica gel in benzene and final recrystallization from cyclohexane. The deuterium content of the deuteriated *trans*-stilbenes, determined by mass spectrometry,[11] was 86% D_1 for α-D-tSB, 91% D_2 for α,α'-D_2-tSB, 75% D_2 and 25% D_1 for 4,α-D_2-tSB, 88% D_2 and 12% D_1 for 4,α'-D_2-tSB and 94% D_5 for D_5-tSB.

The *trans*-2,2′-, 3,3′- and 4,4′-dideuteriostilbenes were synthesized according to the following scheme. Deuterium was introduced into 2-, 3- and 4-bromotoluene via the Grignard reaction with D_2O (99.9%). The resulting monodeuteriated toluenes were converted into the corresponding benzal bromides by bromination with bromine in CCl_4 under UV irradiation with a 500-W lamp. After saponification of the benzal bromide, the isolated benzaldehyde was converted into the appropriate deuteriated benzoin, which, on reduction with zinc dust and $HgCl_2$ in D_2O–ethanol, yielded the *trans*-2,2′-D_2-, 3,3′-D_2- and 4,4′-D_2-tSBs, respectively. All compounds were purified by column chromatography and final recrystallization from cyclohexane. The deuterium contents of the compounds synthesized in this way were 81% D_2 and 19% D_1 for 2,2′-D_2-tSB, 67% D_2 and 32% D_1 for 3,3′-D_2-tSB and 75% D_2 and 25% D_1 for 4,4′-D_2-tSB.

All melting points of the deuteriated *trans*-stilbenes were between 122 and 124 °C.

RESULTS AND DISCUSSION

Assignment of *trans*-stilbene (tSB)

Four out of five tSB carbon signals fall within a range of only about 2 ppm, and overlapping can be avoided by applying certain measuring conditions. Only in two cases[5,6] has the C-α resonance been resolved from that belonging to C-3 and -5, although all the authors[2–6] used $CDCl_3$ solutions at room temperature and the same ^{13}C resonances (20–25 MHz). The separation of the two signals by 0.10 ppm could be repeated only at concentrations of approximately 1 mol l^{-1}. By increasing the temperature to 50 °C both signals were shifted downfield (Table 1), but the difference between them increased to 0.19 ppm. At −50 °C the two signals were shifted upfield, their positions were exchanged and a pronounced difference of −0.49 ppm was observed. Thus, overlapping of C-α and C-3,5 multiplets can be partly avoided at an elevated or a lower temperature.

In contrast to the $CDCl_3$ solution, in DMSO-d_6 at 25 °C C-α is more shielded than C-3,5, the separation being −0.29 ppm. When the temperature is increased, C-α is slightly more deshielded and C-3,5 significantly more shielded, giving at 180 °C a difference of 0.44 ppm. A similar behaviour has also been observed in the case of an acetone-d_6 solution. All the chemical shifts and differences between the C-α and C-3,5 signals for the three solutions at selected temperatures are listed in Table 1.

Since the solvent and temperature do not substantially affect spin–spin coupling constants,[12,13] their effects on chemical shifts can be used successfully for assigning coupled ^{13}C NMR spectra of hydrocarbons with closely spaced resonances without the use of high-field spectrometers and shift reagents. Overlapping in the coupled spectrum is probably the main reason for the scarce and imprecise data on $^{13}C,^{1}H$ couplings in tSB. Thus, for example, only ^{1}J (C-α,H-α) was reported in several papers,[2,6,7b] and the values varied between 151.0 and 161.6 Hz.

The difficulty of determining coupling constants on C-α and C-3,5 is illustrated in Fig. 1a, which shows the coupled spectrum of tSB in $CDCl_3$ at room temperature. The C-α first-order (^{1}J) doublet and higher order multiplets cannot be fully recognized. However, at 50 °C the C-α signal occurs 0.19 ppm (i.e. 4.76 Hz) downfield from C-3,5. The separation and intensity relationships of the multiplet peaks are now clearer, especially in the right half of the first-order doublet (Fig. 1b). On the basis of this pattern the multiplets can also be partly deduced from the spectrum at room temperature. It was observed that ^{1}J(CH) values do not vary with the temperature so that, for example, no change occurs in DMSO-d_6 solution up to 180 °C. On the other hand, there are some differences between the two solutions. Thus, ^{1}J(C-α,H-α) is 153.56 Hz in $CDCl_3$ and 154.42 Hz in DMSO-d_6, but both values are smaller than any of the coupling constants in the

Table 1. Solvent effect on ^{13}C chemical shifts[a] of *trans*-stilbene at several temperatures[b]

Carbon atoms	$CDCl_3$			DMSO-d_6			Acetone-d_6		
	−50 °C	25 °C	50 °C	25 °C	100 °C	180 °C	−50 °C	25 °C	50 °C
C-α	127.85	128.64	128.84	128.26	128.31	128.38	128.68	129.05	129.26
C-1	136.46	137.27	137.47	136.88	136.80	136.93	137.73	137.95	138.16
C-2,6	126.06	126.45	126.55	126.36	126.10	125.82	126.96	127.00	127.10
C-3,5	128.34	128.54	128.65	128.55	128.31	127.94	129.26	129.17	129.21
C-4	127.27	127.47	127.58	127.53	127.25	126.84	128.20	128.07	128.12
$\Delta\delta$[c]	−0.49	0.10	0.19	−0.29	0	0.44	−0.58	−0.13	0.05

[a] δ in ppm downfield from internal TMS; accuracy ±0.02 ppm.
[b] Accuracy ±1 °C.
[c] δ(C-α) − δ(C-3) in ppm.

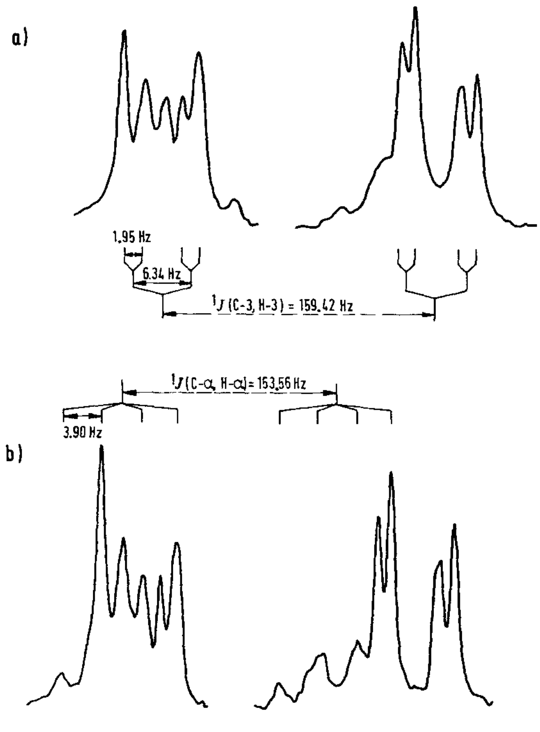

Figure 1. Part of the coupled ^{13}C NMR spectrum of *trans*-stilbene in $CDCl_3$, showing the different overlapping of the C-α and C-3 multiplets at (a) room temperature and (b) 50 °C.

aromatic part of the molecule (Table 2). This is consistent with the olefinic C–H stretching frequencies[7a] which are also lower than the aromatic frequences. It is interesting that the first-order $^{13}C,^1H$ coupling constant in the $CDCl_3$ solution increases from C-α over C-2 and C-3 to C-4 (Table 2). This can be explained in terms of different steric and/or conjugational effects on the corresponding C—H bonds.

Table 2. Carbon–hydrogen coupling constants (Hz) of *trans*-stilbene in two different solvents at room temperature[a]

Carbon Atoms	n	^nJ(CH)		Protons involved	Ref. 6
		$CDCl_3$	DMSO-d_6		
α	1	153.56(d)	154.42(d)	α	160
	2	3.90(q)	3.90(q)	α′	2
	3			2,6	7.5(*H*-2)
	4	Unresolved	0.97(t)	2′,6′	—
1	2	3.90(t)	3.66(t)	2,6	—
	3	7.32(t)	7.32(t)	3,5	—
2,6	1	157.72(d)	157.96(d)	2(6)	156
	3	6.10(t)	5.85(t)	4,6(2)	—
	2	1.95(q)	1.95(q)	3(5)	—
	3			α	—
	4			α′	—
3,5	1	159.42(d)	160.65(d)	3(5)	157
	2	1.95(d)	2.44(d)	4	—
	3	6.34(d)	5.85(d)	5(3)	—
4	1	160.65(d)	160.89(d)	4	157
	2	1.00(t)	Unresolved	3,5	—
	3	7.32(t)	7.32(t)	2,6	—

[a] Spectral width 500 Hz, resolution 0.24 Hz. Abbreviations: d = doublet; t = triplet; q = quartet.

The higher order couplings have been detected by Erb and Bluhm[6] for C-α of tSB. These authors reported second- (^2J) (with H-α′) and third-order (^3J) coupling constants (with H-2) of 2 and 7.5 Hz, respectively. However, one can see from Fig. 1 that a quartet rather than the usual aromatic pattern is present here, with the value of 3.90 Hz for both ^2J(C-α,H-α′) and ^3J(C-α,H-2,6). The C-α quartet splitting is clearly observable in DMSO-d_6 at 180 °C. Moreover, an additional triplet splitting on the C-α multiplet has been observed from this solution, which is indicated in the $CDCl_3$ spectrum (Fig. 1) as a slight signal broadening. This splitting of 0.97 Hz results from the interaction with H-2′ and H-6′, which are as far as four bonds apart.

Particularly remarkable is the splitting pattern of the C-2(6) multiplet (Fig. 2a). In addition to the third-order triplet (^3J = 6.10 Hz in $CDCl_3$) from H-4 and H-6(2), typical of a monosubstituted benzene,[2] there is also a further quartet superimposed, with a splitting of 1.95 Hz. This splitting is due to the simultaneous interaction of C-2(6) with H-α′, H-α and H-3(5) being four, three and two bonds away, respectively. The origin of the quartet was confirmed by the spectra of α,D-, α,α′-D_2- and 3,3′-D_2-tSB, where the number of protons interacting with C-2(6) is reduced (for further proof of the assignment, see the discussion on deuteriated tSBs). Figure 2b shows the splitting of the C-2 multiplet in 3,3′-D_2-tSB, which is a triplet of triplets owing to the lack of interactions with H-3. The change of the third-order coupling constant C-2(6),H-α by nearly one order of magnitude compared with that in styrene (5.02 Hz) is evident.[8] Since tSB is a 'β-phenylstyrene', this change indicates a conformational dependence of an interaction between the aromatic and olefinic parts of the molecule.

The carbon-3(5) signal displays a doublet splitting of 1.95 Hz due to the interaction with H-4 (^2J) and another of 6.34 Hz from H-5(3) (^3J), which is a normal feature for a monosubstituted benzene. However, there is no interaction with H-2,6 here, probably owing to steric interference between the *ortho*-protons and H-α and H-α′.

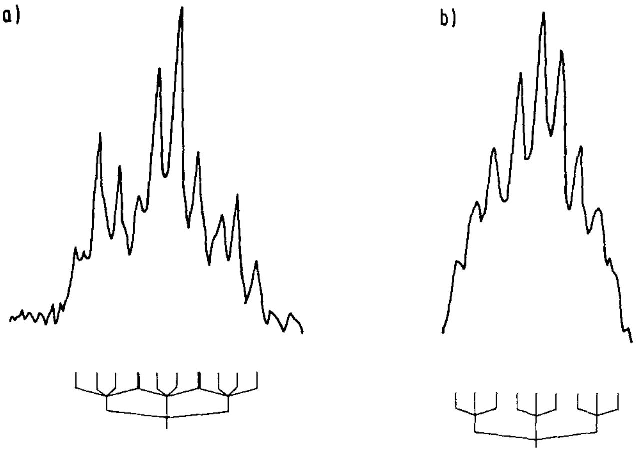

Figure 2. The C-2 multiplet pattern from the coupled ^{13}C NMR spectra of (a) *trans*-stilbene and (b) *trans*-3,3′-D_2-stilbene. This shows the reduction of the higher order quartet into a triplet owing to the lack of interaction between C-2 and H-3 in the latter compound.

The C-4 multiplet pattern is very similar to that for other *para*-carbons in aromatics with ^2J (C-4, H-3,5) = 1.00 Hz, which is the smallest second-order coupling in tSB (Table 2). The third-order coupling constant is the same as for C-1 (7.32 Hz), and both values are higher than the corresponding couplings for C-2,6 and C-3,5 with aromatic protons. All the ^{13}C,^{1}H coupling constants for tSB in $CDCl_3$ and DMSO-d_6 at room temperature are shown in Table 2.

^{13}C, ^{1}H couplings in deuteriated *trans*-stilbenes

In addition to the well known isotope effects on ^{13}C chemical shifts, a regiospecific deuteriation of a molecule simplifies coupled ^{13}C NMR spectra and facilitates the determination of carbon–hydrogen coupling constants. Using the nine partially and the perdeuteriated species of tSB (see Introduction), it was possible to confirm and extend the interpretation of the splitting patterns discussed in the previous section. Much less is known about the deuterium isotope effects on spin–spin coupling constants. These effects on $^1J(^{13}C^1H)$ are small.[13] Although many authors had reported this effect, the observed changes were within the experimental errors.[13,14] Everett[15] recently succeeded in determining precisely the primary deuterium isotope effect (Δ^1J^p) of -0.96 ± 0.13 Hz in chloroform using a high-field spectrometer (62.9 MHz for ^{13}C). For other simple non-hydrocarbon organic solvents, with sp^3 hybridized carbons, he found values between -0.44 ± 0.19 Hz and -0.19 ± 0.70 Hz per deuterium atom. The latter values were interpreted as a combination of both primary and secondary isotope effects. This result confirmed the predictions of Sergeyev and Solkan,[16] who calculated negative primary isotope effects of approximately -1 Hz, and secondary effects of less than -0.1 Hz.

It was therefore surprising that in α-D-tSB a significant change of ^1J(CH) for the neighbouring non-deuteriated C-α′ was observed: 151.81 Hz or a deuterium isotope effect of -1.75 ± 0.20 Hz (Table 3). This result cannot be interpreted in terms of the secondary effect (Δ^1J^s), because it is more than ten times higher than the predicted value,[16] and nearly twice as high as the largest primary effect observed.[15] However, the primary isotope effect in α-D-tSB has not been determined with certainty. It is obvious that another mechanism participates here. A comparison of electron diffraction and spectroscopic data shows a shortening of the C—H bond in ethylene on deuteriation by 0.007 Å (70 ppm).[17] This implies a smaller vibrational amplitude and, hence, a smaller steric requirement of the C—D bond[18] in the olefinic moiety of tSB. It is reasonable to assume that in this way the repulsion between the D-α and *ortho*-protons is reduced, thus slightly changing the molecular geometry. The tSB molecule is non-planar in both the gas[19] and liquid phases.[20] A shorter C—D bond reduces non-planarity, a higher degree of conjugation should then be reached and the π-electron delocalization should become more efficient. The C═C bond becomes weaker, which is partially compensated by a slight drift of s-electron density from the ethylenic C—H bond. This subtle change can explain the decrease of magnitude of $^1J(C-\alpha', H\text{-}\alpha')$. This decrease in ^1J(CH) is also in agreement with the linear relationship between ^1J(CH) and the s character of the C—H bond.[21,22] However, no change in the C-α′-H-α′ stretching frequency has been observed in the vibrational spectra of α-D-tSB,[7a] probably due to insufficient resolution.

Table 3. Carbon–hydrogen coupling constants[a] and carbon–carbon stretching frequencies[b] of the olefinic moiety of *trans*-stilbene and its deuteriated isotopic species

Molecule	^1J(C-α,H-α) (Hz)	^3J(C-2,H-α) (Hz)	ν(C═C)[b] (cm^{-1})	ν_s(C–ϕ)[b] (cm^{-1})	ν_a(C–ϕ)[b] (cm^{-1})
tSB	153.56	1.95	1639	1193	1218
α-D-tSB	151.81	2.00	1618	1192	(1297)
α,α′-D_2-tSB	149.20[c]		1607	1189	(1310)
D_{12}-tSB	145.65[c]		1596	1148	(1321)
2,2′-D_2-tSB	153.56	1.70	1637	1192	1210
3,3′-D_2-tSB	153.56	1.95	1637	1190	1213
4,4′-D_2-tSB	153.70	1.70	1636	1193	1216
D_{10}-tSB	153.70	Unresolved	1635	1148	1235
4,α-D_2-tSB	156.49	6.10	1617	1192	(1290)
4,α′-D_2-tSB	153.70	5.85	1621	1192	(1288)
D_5-tSB	153.80(C-α)		1633	1154	1180
	156.01(C-α′)	1.95			
Styrene	149.85	5.02	1630[d]	1203[d]	

[a] Mean values of several independent measurements from $CDCl_3$ solution at room temperature; accuracy ±0.20 Hz.
[b] Solid-state Raman and IR data taken from Ref. 7a; ν(C═C) is the C-α–C-α′ stretching, ν_s(C–ϕ) is the symmetric and ν_a(C–ϕ) is the antisymmetric C-α–C-1 stretching frequency. Values in parentheses are tentatively assigned.
[c] Calculated from ^1J(CD) values (see text); accuracy ±1.30 Hz.
[d] Raman frequencies of neat liquid styrene taken from D. A. Condirston and J. D. Laposa, *J. Mol. Spectrosc.* **63**, 466 (1976).

For compounds with the fully deuteriated olefinic group only an indirect insight into the magnitude of ^1J(CH) is possible. From the relationship of gyromagnetic ratios for hydrogen and deuterium ($\gamma_H/\gamma_D = 6.514$), the theoretical values for ^1J(CH) have been calculated from ^1J(CD). The values are *ca* 149.20 and *ca* 145.65 Hz for α,α′-D_2- and D_{12}-tSB, respectively (Table 3). In comparison with tSB this is a drastic difference of approximately -4.4 and -7.9 Hz for α,α′-D_2- and D_{12}-tSB, respectively. Although the experimental error for ^1J(CD) was ±0.20 Hz, it involves an uncertainty for the calculated ^1J(CH) of only ±1.30 Hz.

The tendency that the first-order olefinic ^1J(CH) coupling constant decreases with the degree of deuteriation supports the assumption of a higher conjugation and reduced non-coplanarity of the molecular framework in the series of the four deuteriated *trans*-stilbenes discussed above. A comparison with the C-α═C-α′ and C-α–C-1 stretching frequencies[7a] (see Table 3) shows an agreement with this trend. Thus, the first deuterium atom introduced into the ethylenic moiety decreases the ν(C═C) frequency by 21 cm^{-1}, and the second only by a further 11 cm^{-1}. Although the potential energy distribution (PED) for this isotopic series has not yet been calculated, such changes cannot be attributed solely to the mass effect. In fact, in the related series of the three *trans*-1,2-dichloroethylenes, a linear decrease of 4 cm^{-1} has been evaluated by Shimanouchi.[23] The ν(C═C) frequency in D_{12}-tSB is 43 cm^{-1} lower than in tSB, with a contribution of 11 cm^{-1} from the ten deuterium atoms of the two aromatic rings in comparison with α,α'-D_2-tSB. It is interesting that compared with tSB the decrease of this mode in D_{10}-tSB is only 4 cm^{-1} and in D_5-tSB only 6 cm^{-1}, despite the asymmetry.

If the deuteriation in the ethylenic bridge induces a higher degree of conjugation, the C—phenyl bond should be slightly stronger owing to an additional increase in the p-character. An approximate estimate can be made on the basis of symmetric and antisymmetric C–phenyl stretching frequencies,[7a] listed in the last column of Table 3.

There is some correlation between both ν(C=C) and ν(C–phenyl) and the ^1J(CH) values, but vibrations might not be very sensitive to small changes in molecular geometry, especially because of the dominant influence of deuterium on normal modes.

For 2,2′-D_2-tSB three possible rotamers exist.[7a,24] However, on the NMR time scale only one solution spectrum at room temperature has been obtained. Therefore, the average values for all physical constants determined here are very close to those for tSB (Table 3). In the case of 3,3′-D_2-tSB there are also three possible rotamers but, in any case, there would be no steric interference between the *meta*-deuterons and the α-protons. Similarly, such an interaction with *para*-D does not exist in the only isotopomer possible for 4,4′-D_2-tSB. In D_{10}-tSB a change of interaction between α-protons and *ortho*-deuterons is inevitable, but no significant changes in either ^{13}C,^{1}H coupling constants or vibrational frequencies have so far been observed (Table 3). The absence of any changes in ^1J(CH) can be rationalized either through the compensation by another effect from the completely deuteriated aromatic rings, or through a change in the CCD angles in the rings. One should note that the change in mass of both aromatic rings hardly affects the magnitude of ν(C=C), thus indicating a nearly 100% contribution of the corresponding force constant of this normal mode in PED.

An unusual feature has been observed in the spectrum of 4,α-D_2-tSB. The magnitude of ^1J(CH) for the undeuteriated C-α' is now 156.49 Hz (Fig. 3 and Table 3). Although there have been some indications of a positive deuterium isotope effect in the literature,[13] such an effect, amounting to +2.93 Hz, has only here been determined with certainty for the first time. Its real magnitude could be even higher if there were no D-α with its negative effect. A '*para*-effect' has been predicted by Güsten and Klasinc on the basis of HMO calculations for *trans*-4-mono- and *trans*-4,4′-di-substituted stilbenes.[25,26] The more pronounced electronic influence of a *para*-substituent on the olefinic carbon atom at the α'- rather than the α-position has also been experimentally confirmed for other *trans*-4-substituted stilbenes.[8,27] However, it had not been expected here, since deuterium is not a 'usual' substituent and should be electronically equivalent to hydrogen. The effect of D-4 on C-α' extends as far as six bonds, which can be explained by both a different vibrational contribution of the C—D bonds and changes in the electronic distribution in the molecule. Thus, deuterium in the *para*-position of stilbene behaves as a real substituent, with its own electronic properties different from that of hydrogen. It is interesting that in 4,α'-D_2-tSB the non-deuteriated C-α—H-α bond has the same ^1J(CH) as tSB (Fig. 4), although it is 'only' five bonds away from D-4. One can assume that the '*para*-effect' is compensated here by the deuterium effect from the neighbouring D-α', which is −1.75 Hz in α-D-tSB.

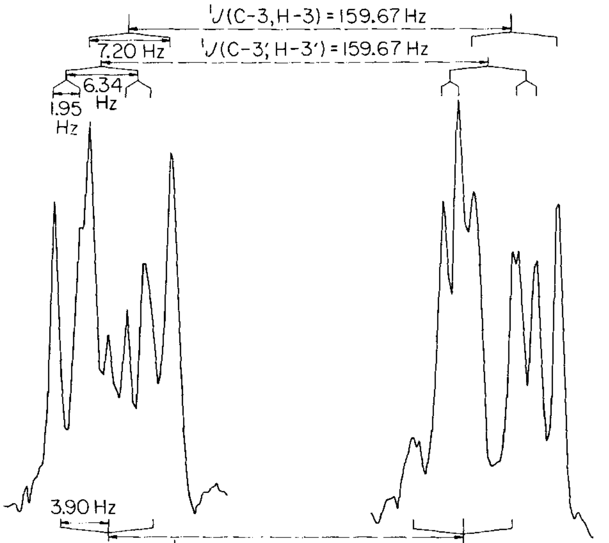

Figure 3. The complex pattern in the ^{13}C NMR spectrum of *trans*-4,α-D_2-stilbene, including the C-3, C-3′ and C-α' multiplets.

Another unusual feature appears in the two latter deuteriated isomers of tSB. The third-order coupling constants due to the interaction between the olefinic hydrogen and the *ortho*-carbons of the adjacent phenyl ring were found to be 6.10 and 5.85 Hz for 4,α-D_2- and 4,α'-D_2-tSB, respectively (Table 3). Such a value has otherwise only been found in styrene,[8] which is believed to be nearly coplanar.[28] It is not clear why such an interaction does not exist in α-D-tSB. Obviously, a deuterium atom at the *para*- or *para′*-position again plays an important role. In the

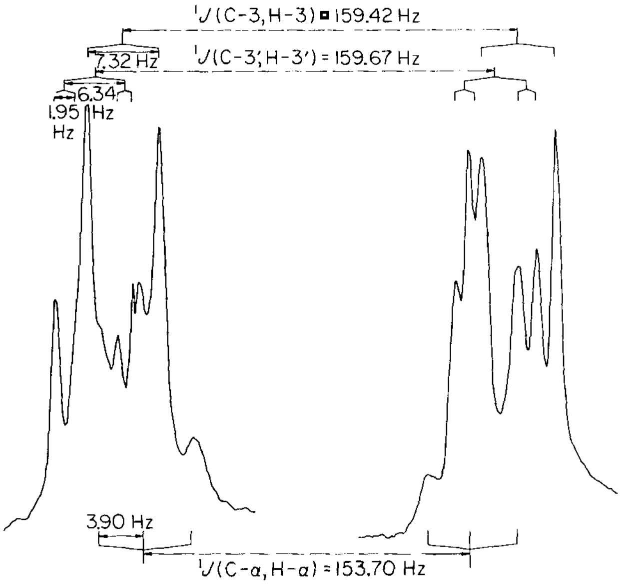

Figure 4. The complex pattern in the ^{13}C NMR spectrum of *trans*-4,α'-D_2-stilbene, including the C-3, C-3′ and C-α multiplets.

other three isotopic stilbenes with deuterium at this position such an effect cannot be seen owing to the molecular symmetry.

In the case of D_5-tSB the simultaneous action of deuterons at all positions in the phenyl ring leads to different values of the first-order ethylenic couplings. The ^1J(CH) value for C-α is 153.80 Hz, a value close to that of tSB, while the ^1J(CH) value for C-α′ is 156.01 Hz, as in 4,α-D_2-tSB. It seems that only D-4 affects the latter value, the *ortho*- and *meta*-deuterons have no influence on ^nJ(CH) in the non-deuteriated part of the molecule. ^3J(C-2′, H-α′) has the usual value of 1.95 Hz (Table 3).

Deuterium at the *para*-position affects the third-order coupling at the adjacent two carbons atoms Thus, ^3J[C-3(5),H-5(3)] is approximately 7.3 Hz in 4,α-D_2-, 4,α′-D_2- and 4,4′-D_2-tSB, but only about 6.1 Hz in the other deuteriated stilbenes (Table 4). All ^nJ(CH) values for partially deuteriated tSBs are compiled in Table 4.

The ν(C=C) frequency in 4,α-D_2-tSB is lower by 22 cm^{-1} than in tSB. In comparison with α-D-tSB this indicates that there is no contribution to this mode when introducing another deuterium atom into the *para*-position. In the case of 4-α′-D_2-tSB a smaller decrease of 18 cm^{-1} was observed, clearly showing an electronic effect in addition to the change in mass. It is important to note that of all three cases where only one deuterium is present in the ethylenic group, the most pronounced decrease of ν(C=C) is in 4-α-D_2-tSB.

It is reasonable to assume that specific solvation effects on ^nJ(CH) can be excluded. There is much evidence in this paper that changes in charge densities and bond polarizations on deuteriation of tSB, as well as different vibrational contributions of C—D bond, affect the magnitudes of ^nJ(CH), causing the variations

Table 4. Carbon–hydrogen coupling constants[a] (Hz) of nine deuteriated *trans*-stilbenes

Molecule	Atom involved	H-α	H-α′	H-2	H-3	H-4	H-5	H-6	H-2′	H-3′	H-4′	H-5′	H-6′
α-D-tSB	C-α′		151.81(d)[b]						3.41(t)				H-2′
	C-1[c]				7.32(t)		H-3						
	C-2		H-3	157.71(d)	2.00(t)	5.77(t)	0.90(d)	H-4					
	C-3				159.91(d)	1.70(d)	6.22(d)						
	C-4			7.32(t)	1.10(t)	160.65(d)	H-3	H-2					
α,α′-D_2-tSB	C-1				7.32(t)		H-3						
	C-2			157.59(d)	1.95(d)	6.71(t)		H-4					
	C-3				159.79(d)	1.95(d)	6.10(d)						
	C-4			7.32(t)	1.10(t)	160.65(d)	H-3	H-2					
2,2′-D_2-tSB	C-α	153.56(d)	3.90(t)					H-α′					
	C-1	3.66(t)			7.32(t)		H-3	H-α					
	C-3				159.17(d)	1.70(d)	6.59(d)						
	C-4					160.89(d)		7.32(d)					
	C-5				7.08(d)	1.95(d)	159.66(d)						
	C-6	H-5	H-5			5.60(d)	1.70(q)	157.96(d)					
3,3′-D_2-tSB	C-α	153.56(d)	H-2	3.90(q)				H-2					
	C-1	H-2		3.90(q)				H-2					
	C-2	1.95(t)	H-α	157.71(d)		6.34(t)		H-4					
	C-4			7.32(t)	1.22(t)	160.40(d)	H-3	H-2					
	C-5					3.90(t)	159.43(d)	H-4					
4,4′-D_2-tSB	C-α	153.70(d)	3.90(q)	H-α				H-α′					
	C-1			3.52(t)	7.42(t)		H-3	H-2					
	C-2	1.70(q)	H-α	157.81(d)	H-α			5.86(d)					
	C-3				159.18(d)		7.42(d)						
4,α-D_2-tSB	C-α′		156.49(d)						3.90(t)				H-2′
	C-1				7.32(t)		H-3						
	C-2[d]		1.22(t)	157.47(d)	H-α			6.10(d)					
	C-3				159.67(d)		7.20(d)						
	C-1′									7.32(t)		H-3′	
	C-2′		6.10(q)						157.47(d)	1.22(t)	H-α′	H-3′	H-α′
	C-3′									159.67(d)	1.95(d)	6.34(d)	
	C-4′								7.32(t)	1.22(t)	160.65(d)	H-3′	H-2′
4-α′-tSB	C-α	153.70(d)		3.90(t)				H-2					
	C-1				6.10(t)		H-3						
	C-2[d]	5.85(t)		157.47(d)				H-α					
	C-3				159.42(d)		7.32(d)						
	C-1′									6.10(t)		H-3′	
	C-2′								157.47(d)		5.85(t)		H-4′
	C-3′									159.67(d)	1.95(d)	6.34(d)	
	C-4′								7.08(t)	1.22(t)	160.89(d)	H-3′	H-2′
D_5-tSB	C-α	153.80(d)	3.90(d)										
	C-α′	3.90(q)	156.01(d)						H-α				H-α
	C-1′									6.71(t)		H-3′	
	C-2′	1.95(q)	H-α						157.96(d)	H-α	5.97(t)		H-4′
	C-3′									159.67(d)	1.95(d)	6.59(d)	
	C-4′								7.32(t)	1.22(t)	160.89(d)	H-3′	H-2′
D_{10}-tSB	C-α	153.70(d)	3.66(d)										

[a] Mean values of several independent measurements from $CDCl_3$ solution at room temperature; accuracy ±0.24 Hz.
[b] Measured at 50 °C.
[c] Additional unresolved fine splitting.
[d] C-2 and C-2′ multiplets completely overlapped.

in either the positive or the negative direction. Of course, an influence of the C=C—H(D) valence angles should also be taken into account. Many authors[29–31] have discussed both experimental and theoretical results of the angular dependence of ^1J(CH). It was observed that in olefins both increasing and decreasing the valence angles gave rise to a decrease in the magnitude of ^1J(CH). The only exception is a slight increase of ^1J(CH) when the angle decreases by 6°.[31] The deuteriation of the olefinic bond in tSB slightly releases the strain with the *ortho* protons in the ring[18] and, hence, a change of the C=C—H(D) bond angle towards the sp^2 configuration is possible. However, the gas electron diffraction,[19] as well as x-ray data,[32] show that the C=C—H angle in tSB is closer to 130° than to 120°. In order to induce a change of ^1J(CH) by the values measured for deuteriated tSBs, an increase by 4° or a decrease by 10° would be necessary.[31] There is no particular reason for such angular variations in the deuteriated tSBs studied here. Substitution of a proton by a deuteron in the olefinic bridge of tSB causes a subtle steric change. A slight rotation of the ring(s) to reach a higher conjugation is obviously more favoured energetically than a variation of the C=C-H(D) valence angle.

Deuterium isotope effects on ^{13}C chemical shifts and ^{13}C,D coupling constants

In proton-noise decoupled spectra of deuteriated tSBs every substituted carbon atom displays a triplet due to the coupling to the nucleus with $I = 1$. The triplets are of a low intensity, so that, for example, the signal of the deuteriated carbon in the —CH=CD— group was not observed, owing to perturbed relaxation times of both carbons, but also possibly because of incomplete deuteriation. Overlapping with undeuteriated C-3 and C-α(α') signals makes an assignment even more difficult. Moreover, long pulse delays, low- and high-temperature measurements and the use of a relaxation agent such as Cr(acac)$_3$ could not effect a gain in the signal intensity of C-α (or C-α') in α-D-, 4,α-D$_2$- and 4,α'-D$_2$-tSB. In compounds with incomplete deuteriation traces of the undeuteriated species were observed (Table 5), which helped in the precise determination of the deuterium isotope shifts.

Most of the α- and β-isotope effects have been determined. A γ-effect was only observed in a few cases. A negative (i.e. upfield) shift always took place, as previously reported in other studies.[14,33–35] The range of the α effect, with values from −0.27 to

Table 5. Carbon-13 chemical shifts[a] (δ/ppm), deuterium isotope effects[b] (Δδ/ppm) and one-bond carbon-deuterium coupling constants[c] [^1J(CD)/Hz] in deuteriated *trans*-stilbenes

Molecule		C-α	C-α′	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′(6′)	C-3′(5′)	C-4′
α-D-tSB	δ	128.66[d]	128.54	137.20	126.45	128.59	127.52			137.27	126.45	128.59	127.52
	Δδ	?	−0.10	0.07									
α,α′-D$_2$-tSB	δ	128.20		137.17[e]	126.40	128.54	127.47						
	Δδ	−0.44		−0.10									
	^1J(CD)	22.90											
2,2′-D$_2$-tSB	δ	128.57[f]		137.17	126.14	128.45	127.47	128.54	126.45	137.24[g]			
	Δδ	−0.07		−0.10	−0.31	−0.09							
	^1J(CD)				24.35								
3,3′-D$_2$-tSB	δ	128.64		137.27	126.35	128.23	127.37	128.52	126.45				127.47[g]
	Δδ				−0.10	−0.31	−0.10						
	^1J(CD)					24.41							
4,4′-D$_2$-tSB	δ	128.64		137.27	126.45	128.45	127.20					128.55[g]	127.47[g]
	Δδ					−0.09	−0.27						
	^1J(CD)						24.41						
4,α-D$_2$-tSB	δ	?	128.54	137.20	126.45	128.47	127.20[h]			137.27[e]	126.45	128.59	127.47
	Δδ	?	−0.10	−0.07		−0.07	−0.27[h]						
	^1J(CD)	?					24.65[h]						
4,α′-D$_2$-tSB	δ	128.57	?	137.27[e]	126.41	128.45	127.20[h]			137.22	126.41	128.54	127.47
	Δδ	−0.07	?			−0.09	−0.27[h]			−0.05			
	^1J(CD)		?				24.29[h]						
D$_5$-tSB	δ	128.60[i]	128.64[i]	137.12[e]	126.02	128.11	127.07			137.27	126.45	128.59	127.47
	Δδ	−0.04[i]		−0.15	0.43	−0.43	−0.40						
	^1J(CD)				24.41	24.77	24.66						
D$_{10}$-tSB	δ	128.64		137.17	126.02	128.11	127.04						
	Δδ			−0.10	−0.43	−0.43	−0.43						
	^1J(CD)				24.41	24.60	24.41						
D$_{12}$-tSB[j]	δ	128.16		137.03	125.99	128.06	126.99						
	Δδ	−0.48		−0.24	−0.46	−0.48	−0.48						
	^1J(CD)	22.36			23.96	24.70	24.60						

[a] In CDCl$_3$ solutions at room temperature; accuracy ±0.02 ppm.

[b] Negative values correspond to shielding effects; isotope shifts relative to tSB values from Table 1.

[c] Accuracy ±0.24 Hz.

[d] Signal belongs to 14% of undeuteriated species.

[e] Signal broadening due to a γ effect.

[f] Overlapped with the C-5 signal; in a narrower spectral range (1000 Hz, digital resolution 0.24 Hz = 0.01 ppm) the C-α signal is a shoulder on the C-5 peak, at a lower field. At 50 °C a further deshielding of C-α by 0.20 ppm was observed.

[g] Signals due to monodeuteriated species: 19% 2-D-tSB, 32% 3-D-tSB and 25% 4-D-tSB for 2,2′-D$_2$-, 3,3′-D$_2$- and 4,4′-D$_2$-tSB, respectively.

[h] Values uncertain.

[i] At 50 °C at a spectral width of 200 Hz (digital resolution 0.10 Hz) the C-α signal is broadened and shifted upfield by 0.04 ppm or 0.98 Hz, showing a negative γ effect.

[j] The signals of undeuteriated species were also detected.

−0.48 ppm (Table 5), is rather broad, as is that for the β effect which, in some cases, approaches the range of the former: −0.07 to −0.24 ppm. However, this proximity is the consequence of the additivity of the two deuterium isotope effects. The γ effect has been detected as an additional broadening of corresponding C signals, such as C-1′ in 4,α-D_2-tSB and C-1 in 4,α'-D_2-tSB and D_5-tSB. A γ effect on the chemical shift of C-α was detected only in the case of 2,2′-D_2- and D_5-tSB (Table 5).

First-order carbon–deuterium coupling constants, ^1J(CD), for aromatic carbons follow the same tendency as the ^1J(CH) values, i.e. an increase is observed from the *ortho*- to the *para*-position. The overall range is from 23.96 Hz (C-2 in D_{12}-tSB) to 24.77 (C-3 in D_5-tSB). As in the case of tSB, the olefinic couplings are smaller, being 22.36 Hz in D_{12}-tSB and 22.90 Hz in α,α'-D_2-tSB. It should be mentioned that a broadening of the C-1 signal in D_5-tSB and a quintet splitting (1.22 Hz) of the C-1,1′ signal in D_{12}-tSB were observed, which are due to the ^3J(CD) with the *meta*-deuterons. The broadening of the C-α signal in D_5-tSB is due to the third-order coupling with D-2 and D-6. Table 5 lists the chemical shifts, deuterium isotope effects and first-order C–D coupling constants for all ten deuteriated *trans*-stilbenes.

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