Evidence That a C–^{2}H Bond Has a Smaller Steric Requirement Than a C–^{1}H Bond

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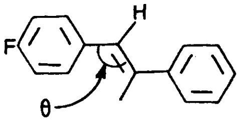
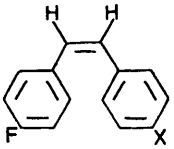
Summary ^{19}F N.m.r. chemical shifts are used to demonstrate that *trans*-stilbenes become more nearly co-planar if a vinylic hydrogen is replaced by deuterium.

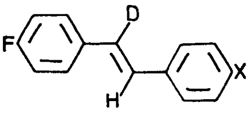
Microwave data indicate that a C–^{2}H bond may be shorter than a C–^{1}H bond by *ca.* 0·007 Å.[1,2] The consequences upon the steric requirements† of a group of changing protium for deuterium must be small, and probably lie within the experimental error of available methods for probing such effects (*e.g.*, conformational analysis, measurement of barriers to internal rotation, *X*-ray analysis). As part of our continuing interest in the origin of ^{19}F n.m.r. chemical shifts[3] and the transmission of substituent effects across bridged binuclear aromatic molecules[4,5] we have compared the ^{19}F n.m.r. chemical shifts in compounds (I)—(IV). Our results indicate that (I) is less co-planar than its



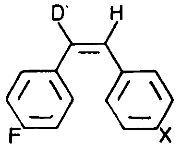
(I)



(III)



(II)



(IV)

Table

	δ[a]		Δ[b]		S.C.S.[c]	
X	(I)	(III)	(II)	(IV)	(I)	(II)
NMe_2	4419·1	4453·8	+0·5	—	−155·9	−156·2
OMe	4503·3	4513·5	+0·6	+1·7	−71·7	−71·8
Me	4537·8	4528·9	+0·7	+1·7	−37·2	−37·3
H	4575·0	4553·8	+0·8	+1·8	0·0	0·0
F	4600·7	4592·5	+0·8	+1·7	+25·7	+25·7
Cl	4637·1	4617·5	+0·9	+1·9	+62·1	+62·2
Br	4644·7	4623·0	+0·8	+1·9	+69·7	+69·7
CN	4771·1	4712·9	+1·1	+1·8	+196·1	+196·4
NO_2	4802·1	4738·3	+1·2	+1·8	+227·1	+227·4

[a] ^{19}F n.m.r. chemical shifts (Hz to low field of C_6F_6 at 94·1 HMz). [b] Δ (Hz) = Change in chemical shift observed when ^{1}H(α) is replaced by ^{2}H; positive shifts are to low field. [c] Substituent Chemical Shifts (Hz) (shifts to low field of X = H are positive)

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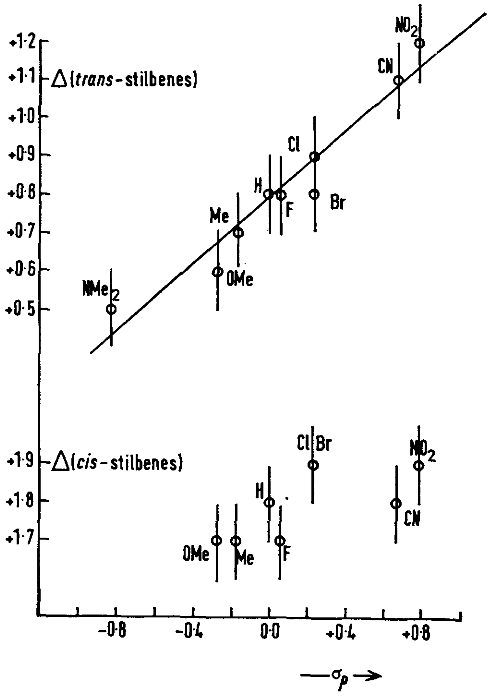
† By 'steric requirement' we imply the effective bulkiness of a group, *i.e.*, how strongly it interacts repulsively (by whatever mechanisms) with neighbouring groups and atoms.

deuteriated analogue (II), while (III) and (IV) do not differ significantly from each other. In (II) the C–^{2}H bond is therefore less bulky than the corresponding C–^{1}H bond in (I), probably because of the smaller vibrational amplitude.



FIGURE

Chemical shifts were measured to an accuracy of ±0·1 Hz at 94·1 MHz, using a Varian XL-100-12 spectrometer operating in Fourier Transform mode with a digitisation rate of 0·09 Hz per point, and noise decoupling of protons. Solutions in n-hexane were examined at a concentration approximating to infinite dilution, using an external perdeuterioacetone lock. Varying compositions of mixtures of deuteriated and non-deuteriated stilbenes were used to identify signals and to provide very accurate relative shifts for the two species. Data are presented in the Table.

Clearly the deuterium isotope effect, Δ, remains constant in the *cis*-series, (III) and (IV), at 1·8 ± 0·1 Hz. In the *trans*-series, however, its magnitude varies with the nature of the substituent X; this is illustrated in the Figure, in which Δ is plotted against Hammett's σ_p for X. The finite positive slope for the *trans*-series indicates that the deuteriated *trans*-olefinic linkage in (II) is more transmissive[4,5] of substituent effects than the fully protiated analogue (I); *i.e.*, the former behaves as if it were more highly conjugated and therefore more nearly co-planar. In the latter molecule the olefinic hydrogens lie at distances of only 2·11 and 2·34 Å from *ortho*- and *ortho'*-protons in the aromatic rings.[6] A less bulky vinylic bond would, to some extent, release this strain and enable the hybridisation of the olefinic carbon to resemble more closely sp^2. Deviation from pure sp^2 hybridisation has been confirmed by *X*-ray analysis[6] of structure (I), which shows θ to be 126·7°.

In the *cis*-series the deciding factor for the overall conformation of the molecule is the minimisation of steric interaction between the aromatic rings, and the small change in size of the bridge upon deuteriation is of little consequence.

A point of interest arises in the spectra of both *cis*- and *trans*-4,4'difluoro-α-deuteriostilbenes, (II) and (IV) (X=F). Each has a fluorine atom in the ring which is β to deuterium and its isotope shift is in the opposite direction to that in the ring α to deuterium. The α-deuterium isotope effect is unusual in that it is to low field, in contrast to the more usually observed high-field heavier isotope shift.[7] The fluorine atoms are non-equivalent by about 2·5 Hz, and the *trans*-compound shows an eleven-bond J_{F-F} of 0·7 Hz, confirming our earlier measurement based upon ^{13}C-satellite ^{19}F n.m.r. spectra.[8] There is no resolvable J_{F-F} in the *cis*-molecule (*i.e.* < 0·1 Hz), suggesting that in this series transmission of substituent effects is caused by a repulsive interaction between the C-H bonds in the bridge, and not by conjugation as in the *trans*-series.[5,8]

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