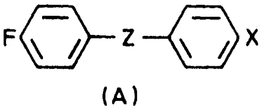
Fluorine-19 Nuclear Magnetic Resonance Studies of Aromatic Compounds. Part 5.[1] Transmission of Substituent Effects across Two Aromatic Rings connected by C–C and –C– Linkages

By **J. Malcolm Gascoyne, Peter J. Mitchell,** and **Lawrence Phillips,*** Organic Chemistry Department, Imperial College of Science and Technology, London SW7 2AY

The ^{19}F n.m.r. spectra of compounds of the type *p*-FC_6H_4·Z·C_6H_4X-*p* [Z = C⋮C, *cis* or *trans* CH:CH, CH_2·CH_2, *threo* or *erythro* CHBr·CHBr, CH_2, CH(OH), CHCl, or CHBr] have been used to examine the transmission of substituent effects of X across the group Z. When Z is unsaturated, the magnitude of the transmitted effect is not solely dependent upon the extent of conjugation between the rings; when Z is a saturated C–C bond the magnitude of the transmitted effect is sensitive to the conformational properties of the system. When Z is a single substituent carbon atom (CHY; Y = H, OH, Cl, or Br) the transmission is greater when Y = OH than for all the other substituents, which all show the same behaviour.

LONG-RANGE substituent effects upon ^{19}F shielding continue to be examined by multi-substituent parameter treatments for systems containing a fluorophenyl group.[2,3] A comprehensive discussion of our interpretation of the dual substituent parameter treatment has been presented elsewhere,[1] and no further mention will be made here. More recently, ^{19}F shielding in some related systems has been examined by the FMMF treatment,[3a] in which the only three effects considered to be significant are field effects (F), the mesomeric effect (M) (which is considered as being indistinguishable from any π-inductive effect), and a mesomeric field effect (MF). This last represents field effects generated by local electron density changes.

In this paper we adopt the same approach as in our previous study,[1] that is, in systems of type (A) we consider that the variation of ^{19}F shielding accompanying the variation of substituent X arises from perturbations to the π-system of the fluorophenyl group, irrespective of whether π-electron density is transferred across the group Z or not.



(A)

Our recent study[1] of the transmission of substituent effects across the N–N bonds of various azobenzene derivatives made it desirable to study compounds with C–C and –C– linkages. When the linking group (Z) is triply bonded (as in diphenylacetylenes) information is obtained concerning the behaviour of a highly unsaturated group, and a comparison of *cis*- and *trans*-stilbenes demonstrates the effect of steric inhibition of conjugation. The consequences of saturating the central CC bond are demonstrated by studying the bibenzyl series, and data for the saturated *threo*- and *erythro*-dibromobibenzyls provide an insight into the importance of the enantiomeric and conformational properties of the system.

Ten series of compounds have been examined in which the substituents F and X are *para* to the linkage (*p*-FC_6H_4·Z·C_6H_4X-*p*); the various connecting groups are illustrated in Table 1.

TABLE 1

Structures of connecting groups in *p*-FC_6H_4·Z·C_6H_4X-*p*

Series no.	Z
1	*trans*-CH:CH
2	*cis*-CH:CH
3	C⋮C
4	CH_2·CH_2
5	*threo*-CHBr·CHBr
6	*erythro*-CHBr·CHBr
7	CH_2
8	CHOH
9	CHCl
10	CHBr

EXPERIMENTAL

Recording of N.m.r. Spectra.—^{19}F Chemical shifts were measured with a Varian XL-100-12 spectrometer operating in Fourier transform mode with proton noise-decoupling and a digitisation rate of 0.09 Hz per point. Solutions of compounds in n-hexane were examined at a concentration

---

[1] Part 4, P. J. Mitchell and L. Phillips, *J.C.S. Perkin II*, 1974, 109.

[2] J. Fukunaga and R. W. Taft, *J. Amer. Chem. Soc.*, 1975, **97**, 1612, and references therein.

[3] (*a*) W. Adcock, M. J. S. Dewar, R. Golden, and M. A. Zeb, *J. Amer. Chem. Soc.*, 1975, **97**, 2198, and references therein; (*b*) W. Adcock, J. Alste, S. Q. A. Rizvi, and M. Aurangzeb, *ibid.*, 1976, **98**, 1701.

approximating to ' infinite dilution '[4a] by using an external perdeuterioacetone lock.

TABLE 2

Physical constants and microanalytical data

Compound	M.p. in °C or (b.p. in °C) or [n_D^{20}]	Found (%)				Required (%)			
		C	H	N	F	C	H	N	F
Series 1	Ref. 4*b*								
2; X = NMe_2	Solid	79.8	6.7	5.65	8.0	79.65	6.7	5.8	7.8
2; X = NH_2	Solid	79.0	6.0	6.6	8.45	78.85	5.65	6.55	8.9
2; X = OMe	[1.599 0]	79.2	5.85		8.5	78.95	5.75		8.3
2; X = Me	[1.590 4]	85.05	5.95		9.35	84.9	6.2		8.95
2; X = H	[1.596 7]	84.55	5.4		9.5	84.8	5.6		9.6
2; X = F	Solid	77.85	4.9		17.6	77.8	4.65		17.55
2; X = Cl	[1.620 8]	72.15	4.55		8.25	72.25	4.35		8.15
2; X = Br	[1.618 4]	60.75	3.7		6.8	60.65	3.65		6.85
2; X = CN	Solid	80.55	4.7	6.2	8.55	80.7	4.5	6.25	8.5
2; X = CF_3		67.4	3.9			67.65	3.8		
2; X = NO_2	Solid	69.35	4.3	5.5	7.55	69.15	4.15	5.75	7.8
3; X = OMe	95—95.5	79.85	4.85			85.7	4.6		
3; X = Me	97.5—98	85.4	5.4		9.1	85.7	5.25		9.05
3; X = H	105.5—106.5	85.45	4.8			85.7	4.6		
3; X = F	94—95	78.4	3.6		17.5	78.5	3.75		17.75
3; X = Cl	113—114	72.8	3.55		8.2	72.9	3.5		8.25
3; X = Br	105.5—107	61.15	2.95			61.1	2.95		
3; X = CN	129—130	81.25	3.45	6.2	8.5	81.45	3.65	6.35	8.6
3; X = NO_2	108—109	69.75	3.35	5.75	7.5	69.7	3.35	5.8	7.9
Series 4	Ref. 18								
5; X = OMe	Prepared as a mixture of 5 and 6; X = OMe								
5; X = Me	84—86	48.65	3.7		5.2	48.4	3.5		5.1
5; X = H	76—77	47.2	3.2		5.55	46.95	3.1		5.3
5; X = F	89—90	44.85	2.8		9.9	44.6	2.95		10.1
5; X = Cl	85—86	42.9	2.75		4.8	42.85	2.55		4.85
5; X = Br	66—68	38.5	2.35		4.5	38.45	2.3		4.35
5; X = CF_3	54.5—56.5	42.3	2.25			42.3	2.35		
5; X = CN	86—88	47.3	2.9	3.65	5.0	47.05	2.65	3.65	4.95
5; X = NO_2	91—93	41.85	2.75	3.45	4.55	41.7	2.5	3.5	4.7
6; X = OMe	Prepared as a mixture of 5 and 6; X = OMe								
6; X = Me	184—185 (decomp.)	48.2	3.65		5.1	48.4	3.5		5.1
6; X = H	199—200 (decomp.)	47.15	3.05		5.4	46.95	3.1		5.3
6; X = F	193.5—195 (decomp.)	44.55	2.9		9.95	44.6	2.95		10.1
6; X = Cl	200.5—202 (decomp.)	43.1	2.85		4.6	42.85	2.55		4.85
6; X = Br	198—199 (decomp.)	38.65	2.5		4.25	38.45	2.3		4.35
6; X = CF_3	190—190.5 (decomp.)	42.4	2.35			42.3	2.35		
6; X = CN	200—201 (decomp.)	47.35	2.85	3.65	5.2	47.05	2.65	3.65	4.95
6; X = NO_2	205—207 (decomp.)	42.0	2.7	3.3	4.75	41.7	2.5	3.5	4.7
Series 7 and 8	Ref. 4*b*								
9; X = OMe	(80 at 0.01 mmHg)	Structure and purity confirmed by ^1H, ^{19}F, and ^{13}C n.m.r. data							
9; X = Me	(80 at 0.01 mmHg)								
9; X = H	(68 at 0.01 mmHg)								
9; X = F	(143 at 4 mmHg)								
9; X = Cl	(87 at 0.01 mmHg)								
9; X = NO_2	(141 at 0.01 mmHg)								
10; X = OMe	(92 at 0.01 mmHg)								
10; X = Me	(90 at 0.01 mmHg)								
10; X = H	(86 at 0.01 mmHg)								
10; X = F	(92 at 0.01 mmHg)								
10; X = Cl	(98 at 0.01 mmHg)								
10; X = NO_2	(155 at 0.01 mmHg)								

The compounds studied were prepared by the methods described below. They were identified by their spectroscopic properties (u.v., i.r., and n.m.r.); microanalytical data were consistent with expected stoicheiometries (Table 2). Table 3 lists the ^{19}F chemical shifts for compounds (1)—(10); Table 4 lists substituent chemical shifts for the same series (*i.e.* referenced to the compounds with X = H).

Syntheses.—trans- *and* cis-4-*Substituted* 4'-*fluorostilbenes* (*series* 1 *and* 2). These were prepared by the Wittig reaction[5] of 4-fluorobenzylphosphonium chloride with

---

[4] (*a*) I. R. Ager and L. Phillips, *J.C.S. Perkin II*, 1972, 1975; (*b*) I. R. Ager, L. Phillips, and S. J. Roberts, *ibid.*, p. 1988.

[5] L. F. Fieser and M. Fieser, ' Reagents for Organic Synthesis,' Wiley, New York, 1967, p. 1238.

various 4-substituted benzaldehydes in ethanolic lithium ethoxide. The isomeric products were separated by chromatography [alumina, grade III; light petroleum (b.p. 40—60 °C)–benzene]. In each case the faster moving component was the *cis*-isomer.

TABLE 3

^{19}F Chemical shifts (p.p.m. to low field of C_6F_6; solvent n-hexane)

Substituent	*trans*-CH:CH	*cis*-CH:CH	C⋮C	CH_2·CH_2	*threo*-CHBr·CHBr	*erythro*-CHBr·CHBr	CH_2	CH(OH)	CHCl	CHBr
NMe_2	46.96	47.33		45.11						
NH_2	47.27	47.55		45.19						
OMe	47.86	47.97	50.73	45.43	50.00	50.33	45.47	47.17	48.48	48.63
Me	48.22	48.13	51.04	45.45	50.09	50.40	45.51	47.29	48.57	48.72
H	48.62	48.39	51.41	45.58	50.35	50.54	45.73	47.60	48.81	48.94
F	48.89	48.80	51.73	45.90	50.80	50.85	46.17	48.15	49.25	49.37
Cl	49.28	49.07	52.05	46.04	50.97	50.96	46.38	48.43	49.45	49.58
Br	49.36	49.13	52.11		51.00	50.98				
CF_3	50.12	49.63		46.33	51.48	51.26				
CN	50.70	50.08	53.36		51.65	51.36				
NO_2	51.03	50.35	53.65		51.82	51.46	47.40	49.78	50.49	50.55

trans- *and* cis-*4-Amino-4′-fluorostilbenes*. These were prepared by reduction of a mixture of *trans*- and *cis*-4-fluoro-4′-nitrostilbene over 5% palladium–charcoal in ethanolic hydrazine hydrate. The isomeric products were separated by chromatography (alumina, grade III; benzene).

Hydrogenation of either the *trans*- or the *cis*-stilbene in ethyl acetate over 5% palladium–charcoal gave the 4-substituted 4′-fluorobibenzyls (series 4).

(±)-threo- *and* (±)-erythro-*Dibromobibenzyls* (*series* 5 *and* 6). These were obtained by the stereospecific *trans*-bromination, by pyridinium hydrobromide perbromide, of *cis*- and *trans*-stilbenes, respectively.[6] Bromination in this way, of *cis*-4-fluoro-4′-methoxystilbene gave exclusively the *erythro*-isomer. The *threo*-isomer of this compound was studied as a component of a 2 : 1 *threo* : *erythro* mixture, obtained by addition of bromine to the *cis*-stilbene, with chloroform as solvent.

TABLE 4

^{19}F S.c.s. for series 1—10 (p.p.m. to high field of X = H are negative)

Substituent	*trans*-CH:CH	*cis*-CH:CH	C⋮C	CH_2·CH_2	*threo*-CHBr·CHBr	*erythro*-CHBr·CHBr	CH_2	CH(OH)	CHCl	CHBr
NMe	−1.66	−1.06		−0.47						
NH_2	−1.35	−0.84		−0.39						
OMe	−0.76	−0.43	−0.68	−0.15	−0.35	−0.21	−0.26	−0.43	−0.33	−0.31
Me	−0.40	−0.26	−0.37	−0.13	−0.26	−0.14	−0.22	−0.31	−0.24	−0.22
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F	0.27	0.41	0.32	0.32	0.45	0.31	0.44	0.55	0.44	0.43
Cl	0.66	0.68	0.64	0.46	0.62	0.42	0.65	0.83	0.64	0.64
Br	0.74	0.74	0.70		0.65	0.44				
CF_3	1.50	1.24		0.75	1.13	0.72				
CN	2.08	1.69	1.95		1.30	0.82				
NO_2	2.41	1.96	2.24		1.47	0.92	1.67	2.18	1.68	1.61

4′-Substituted 4-*fluorodiphenylmethanols* (*series* 8). These were prepared by the reaction between 4-fluorophenylmagnesium bromide and 4-substituted benzaldehydes, in the usual manner. The 4-nitro-compound was obtained by reduction of 4-fluoro-4′-nitrobenzophenone (commercially available) with sodium borohydride.

Chloro- and bromo-diphenylmethanes (*series* 9 *and* 10). These were prepared by the reactions of the diphenylmethanols (series 8) with thionyl chloride and phosphorus tribromide, respectively. The procedures for converting the bromodiphenylmethanes (series 10) into diphenylmethanes (series 7), with either sodium borohydride or lithium aluminium hydride, have been outlined previously.[4b]

4′-Substituted-4-fluorodiphenylacetylenes (*series* 3). These were obtained from reactions between diethyl α-chloro-*p*-fluorobenzylphosphonate with various 4-substituted benzaldehydes, upon treatment with 2 equiv. of sodium hydride (dimethyl sulphoxide as solvent).[7]

RESULTS AND DISCUSSION

In our previous studies,[1,4b] the ability of the linking group Z (Table 1) to transmit electronic effects *via* the π-electron system was discussed in terms of linear correlations of ^{19}F s.c.s. (substituent chemical shifts) in each series with those for *trans*-4′-substituted 4-fluorostilbenes. After correction for solvent effects the slopes of these correlations were given the symbol T (referred to an arbitrary unity for the *trans*-stilbene series) and the values of T were discussed in terms of the electronic structure of group Z and the conformational properties of the molecule. We follow the same procedure in the current investigation; Table 5 lists T values for the series 1—10.

Unsaturated CC *Linkages*.—It is appropriate first to examine the properties of the two series of *trans*- and *cis*-stilbenes because their comparison is analogous to that between *trans*- and *cis*-azobenzenes.[1] The *trans*-stilbene molecule is almost planar[8] and conjugation

---

[6] C. F. Fieser, *J. Chem. Educ.*, 1954, **31**, 291.

[7] H. Zimmer, P. J. Bercz, O. J. Maltenieks, and M. W. Moore, *J. Amer. Chem. Soc.*, 1965, **87**, 2777.

[8] C. F. Finder, M. G. Newton, and A. L. Allinger, *Acta Cryst.*, 1974, **B30**, 411.

between the ethylenic bond and the phenyl rings is nearly at a maximum. In *cis*-stilbene, however, the coplanar arrangement would be extremely crowded and both phenyl rings must be turned through a considerable angle to the planes of the ethylenic bond in order to avoid excessive van der Waals repulsions. The effect of such inhibition of conjugation is analogous to that on going from *trans*- to *cis*-azobenzenes[1] and may be observed in the electronic spectra of the molecules. Table 6 lists wavelengths of absorption maxima (with extinction coefficients) for all members of the two series. A higher energy π–π^* electronic transition, *i.e.* a lower wavelength absorption, for *cis*- ($\lambda_{max.}$ 274—326 nm) as compared with the *trans*-isomer ($\lambda_{max.}$ 286—350 nm) and a concomitant weakening of intensity by *ca.* 65% indicates considerably reduced conjugation in the *cis*-isomer and supports a structure similar to that of *cis*-azobenzene; this is in agreement with the findings of other workers.[9,10] Additional evidence indicating that there is electron delocalisation between the 4- and 4′-positions in *trans*-stilbene but not in *cis*-stilbene is the existence of a long-range coupling of 0.4 Hz between the fluorine nuclei in *trans*-4,4′-difluorostilbene and its absence in *cis*-4,4′-difluorostilbene.[11] The essentially planar conformation of *trans*-stilbene in solution has been further demonstrated[12] by observing the effects upon ^{19}F chemical shifts of replacing a vinylic hydrogen atom in *trans*-stilbene by deuterium; the smaller steric requirement of the C–^{2}H bond relative to the C–^{1}H bond allows the molecule to become even more nearly planar and therefore more highly conjugated. In solution, the *ortho*-phenyl hydrogen atoms are as close to the ethylenic hydrogen atoms as steric interactions will allow, but this situation does not result in a completely planar conformation.

TABLE 5

T Values for series of linked dinuclear aromatic compounds $FC_6H_4{\cdot}Z{\cdot}C_6H_4X$

Z	Slope of correlation with *trans*-stilbene series	Standard deviation (p.p.m.)	Correlation coefficient	*T*
cis-CH:CH	0.75	0.06	0.997 9	0.68
C⋮C	0.93	0.02	0.999 8	0.91
$CH_2{\cdot}CH_2$	0.40	0.07	0.984 0	0.23
threo-CHBr·CHBr	0.60	0.11	0.984 5	0.49
erythro-CHBr·CHBr	0.37	0.08	0.980 1	0.19
CH_2	0.64	0.10	0.988 4	0.54
CHOH	0.86	0.12	0.990 8	0.82
CHCl	0.67	0.10	0.990 2	0.58
CHBr	0.63	0.10	0.988 9	0.53

In the *cis*-stilbenes, the vinylic C–H bonds are in a synperiplanar arrangement, as are the nitrogen lone pairs of *cis*-azobenzene.[1] If the preferred conformation is similar to that of *cis*-azobenzenes, the plane of each aromatic ring is approximately orthogonal to a C–H vinylic bond. It is not possible to define the exact nature of the interaction between the C–H bond and the neighbouring π-system (*i.e.* hyperconjugation, polarisation by charge transfer, or polarisation by a through -space electrostatic interaction) but any such interaction would be expected to depend upon the π-electron density distribution in the ring and also, therefore, upon the nature of substituent X in the *para*-position of that ring. In the light of discussion elsewhere,[1] the variation of such an electronic interaction would be expected to be accompanied by a modification of the repulsive interaction between the vicinal C–H bonds and the ' substituent effects ' of X would be ' relayed '[1] by this mechanism. This is in accord with the observation that the ^{19}F shielding of the *cis*-series parallels exactly the ^{19}F shielding of the *trans*-series (Table 5) (which is common to all series with different groups Z). The *T* value of 0.68 means that the mechanism of transmission across the *cis*-ethylenic bond is only 30% less efficient than that operating in the conjugative system of *trans*-stilbene. π-Conjugation, on the other hand, would be reduced by *ca.* 90% if the conformation was similar to that of *cis*-azobenzene.[1]

TABLE 6

Wavelengths of maximum absorption and molar extinction coefficients for the electronic absorption spectra of *cis*- and *trans*-4′-X-4-fluorostilbenes and 4′-X-4-fluorodiphenylacetylenes[a]

X	$\lambda_{max.}$/nm ($\varepsilon_{max.}$)			
trans-Stilbenes				
OMe	228 (13 200)		302 (28 300)	318 (26 100)
Me	228 (14 100)		297 (28 000)	311 (25 200)
H	226 (16 900)		293 (29 600)	307 (25 800)
F	226 (16 400)		286 (29 200)	307 (22 900)
Cl	228 (14 100)		298 (29 600)	312 (26 700)
Br	228 (14 500)		298 (32 700)	313 (29 700)
CN	229 (17 200)		321 (36 400)	
NO_2	236 (12 400)	264 (8 200)	350 (26 900)	
cis-Stilbenes				
OMe	229 (16 900)		285 (13 100)	
Me	226 (15 800)		279 (9 700)	
H	223 (18 100)		275 (10 700)	
F	222 (17 700)		274 (11 200)	
Cl	227 (18 300)		279 (11 000)	
Br	228 (18 500)		281 (11 700)	
CN	232 (21 500)		295 (13 000)	
NO_2	228 (12 700)		326 (9 600)	
Diphenylacetylenes				
OMe		284 (32 300)		301 (26 400)
Me	264 (24 600)	278 (34 000)	287 (24 600)	296 (28 100)
H	261 (23 500)	275 (33 100)	284 (23 100)	293 (26 800)
F	260 (25 000)	275 (34 200)	284 (24 000)	292 (26 500)
Cl	266 (24 000)	280 (33 700)	289 (24 700)	298 (28 600)
Br	267 (23 400)	282 (32 400)	290 (24 500)	299 (28 000)
CN		293 (30 300)		310 (29 200)
NO_2		324 (30 600)		

[a] Spectra of *trans*- and *cis*-stilbenes for solutions in ethanol and of diphenylacetylenes for solutions in methanol.

The proportionality constant relating observed ^{19}F shielding changes to π-electron density variation depends

---

[9] K. W. Blake and B. Jacques, *J.C.S. Perkin II*, 1973, 1660.

[10] F. Heatley, M. K. Cox, and A. Jones, *J.C.S. Perkin II*, 1976, 510.

[11] P. J. Mitchell, L. Phillips, S. J. Roberts, and V. Wray, *Org. Magnetic Resonance*, 1974, **6**, 126.

[12] P. J. Mitchell and L. Phillips, *J.C.S. Chem. Comm.*, 1975, 908.

upon an average excitation energy[13] and, as has been pointed out before,[1] it is possible that this term may vary from series to series, accounting, at least in part, for the apparent variation of transmission amongst different series.

Another class of compounds which possess an unsaturated linking group Z is the series of diphenylacetylenes. *X*-Ray analysis of diphenylacetylene[14] indicates that the phenyl rings are coplanar and that the central acetylenic bond is strictly linear with a C≡C–C angle within 2° of 180°. Evidence which supports the same preferred conformation in solution is provided by the u.v. spectra of these compounds. Comparison of the spectrum of a diphenylacetylene with that of the analogous *trans*-stilbene (Table 6) shows that the absorption maximum in the former is of slightly greater energy (*i.e.* smaller $\lambda_{max.}$). Generally the values of $\epsilon_{max.}$ are larger for the diphenylacetylenes, probably reflecting the slightly greater effective length of the chromophore. Although the extent of positive overlap between neighbouring *p* orbitals in diphenylacetylene would be expected to be no less than that in *trans*-stilbene, the u.v. data imply that the diphenylacetylenes are slightly less conjugated. That there is delocalisation of π-electrons between the 4- and 4′-positions of diphenylacetylene is supported by the observation of a 0.4 Hz eleven-bond F · · · F coupling in the 4,4′-difluoro-compound. Further evidence which supports the preferred planar conformation of diphenylacetylene in solution has been provided by the dipole moment of the 3,3′-dichloro-derivative;[15] the value indicates that the observed dipole corresponds approximately to an average between the possible anti- and syn-periplanar arrangements and rules out previous doubt[16] that diphenylacetylene is freely rotating or that it exists in a preferred conformation in which the phenyl rings are perpendicular to one another.

The value of *T* of the diphenylacetylene series (0.91) (Table 5) demonstrates that the acetylenic bond is slightly less efficient at transmitting an electronic effect than the *trans*-ethylenic bond in *trans*-stilbene. In view of the implication from u.v. data that the diphenylacetylene is slightly less conjugated, it is reasonable to interpret this result as showing that substituent effects are transmitted entirely *via* the π-system.

Saturated CC *Linkages*.—A suitable study of the transmission of substituent effects across a saturated linkage is afforded by the dibenzyl molecule. *X*-Ray diffraction[17] indicates that in the crystalline state the phenyl rings are *anti* to one another and the central CC bond is inclined at 70° to the planes of the rings, which are parallel but not coplanar. In this conformation steric repulsions between the phenyl rings are minimised and because this interaction must be the most destabilising aspect of the structure, it is likely that this conformation will pertain in solution. Although the C–H bonds in the connecting group are not as close to orthogonality with the phenyl rings as those in *cis*-stilbene, they are still favourably oriented to engage in some interaction with the π-system. Such an interaction will be influenced by the nature of the substituent in the *para*-position of the neighbouring ring and its effect will be transmitted to the vicinal bond by the modification of the repulsive interaction between them. In this case, however, the C–H bonds are not *syn*, as in the *cis*-stilbene molecule, but *gauche* to one another, so the repulsive interaction between them cannot be as large and is reduced further by the increased C–C bond length (1.48 Å) as compared with that in *cis*-stilbene. The absence of a long-range F · · · F coupling in 4,4′-difluorobibenzyl confirms that there is no delocalisation between the two phenyl rings.[11] The intramolecular interactions which are described above result in the bibenzyl molecule having a *T* value of 0.23, which is small as expected, but large enough to confirm that the $CH_2\cdot CH_2$ group is capable of relaying a substituent effect. This is in contradiction to an assumption made by Pews *et al.*,[18] who considered bibenzyl and *trans*-stilbene as being two extremes of transmission, *i.e.* of 0 and 100%, respectively.

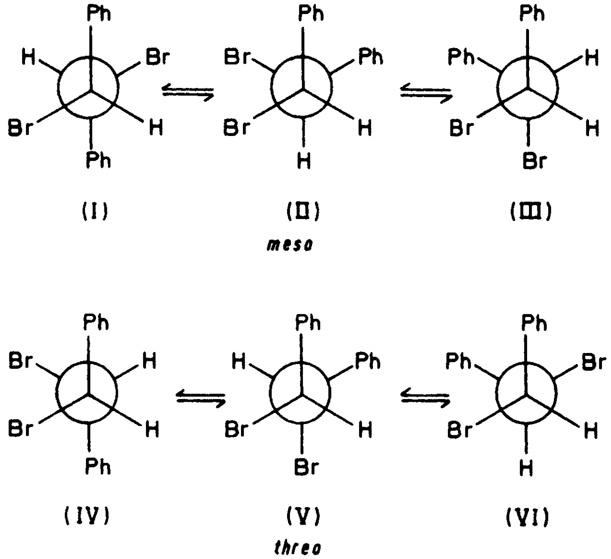


FIGURE 1 Conformations of *meso*- and *threo*-dibromobibenzyl

In order to assess further the effect of conformation upon transmission of substituent effects, we compared the properties of two series of enantiomeric compounds, namely *threo*- and *erythro*-dibromobibenzyls. Each sample is a racemic mixture, except for the *erythro*-4,4′-difluoro-compound which is *meso*. The preferred conformations of representative molecules in the crystalline state have been determined by *X*-ray analysis,[19] the

---

[13] F. P. Prosser and L. Goodman, *J. Chem. Phys.*, 1963, **38**, 374.

[14] J. M. Robertson, *Proc. Roy. Soc.*, 1938, **164**, 436.

[15] A. Liberles and B. Matlosz, *J. Org. Chem.*, 1971, **36**, 2710.

[16] S. Castellano and J. Lorenc, *J. Phys. Chem.*, 1965, **69**, 3552.

[17] G. A. Jeffrey, *Proc. Roy. Soc.*, 1947, **188**, 222.

[18] R. G. Pews and N. D. Ojha, *J. Amer. Chem. Soc.*, 1969, **91**, 5769.

[19] J. D. McCullough, *J. Amer. Chem. Soc.*, 1940, **62**, 480.

possible conformations being illustrated in Figure 1. The *meso*-form, which corresponds to the *erythro*-series, crystallises in conformation (I) where both the phenyl groups and the bromines are *anti* (bromine–bromine distance 4.50 Å) so that both steric and dipolar repulsions are at a minimum; the *threo*-form, however, crystallises in conformation (IV) in which the bromines are approximately *gauche* (bromine–bromine distance 3.85 Å, equal to the sum of the combined van der Waals radii) and in which the steric repulsion of the bulky phenyl groups is at a minimum, even though the steric and dipolar repulsions of the C–Br bonds are not.

The different intramolecular interactions in the two isomers lead to an observable difference in properties. The *T* values of the *threo*- and *erythro*-series, 0.49 and 0.19, respectively (Table 5), demonstrate that the *threo*-CHBr·CHBr group can transmit an electronic effect much more efficiently than the *erythro*-group. The points in the plots of ^{19}F s.c.s. of these series against those of *trans*-stilbene are slightly scattered (correlation coefficients 0.984 5 and 0.980 1) as is also true of the analogous correlation of bibenzyl itself (correlation coefficient 0.984 0). A more precise comparative study of these systems is to discuss chemical shift data of *threo*- and *erythro*-dibromobibenzyl by means of linear correlations with those of bibenzyls. Results of this treatment are illustrated in Table 7, which shows very high correlation coefficients (0.997 6 and 0.998 3) and shows that the *erythro*-CHBr·CHBr link is as effective as $CH_2 \cdot CH_2$ in bibenzyl but that the *threo*-CHBr·CHBr link is *ca.* 60% more so.

TABLE 7

Slopes of plots of ^{19}F s.c.s. of *threo*- and *erythro*-dibromobibenzyls *vs.* bibenzyls

Isomer	Slope	Standard deviation (p.p.m.)	Correlation coefficient
threo	1.59	0.04	0.997 6
erythro	1.60	0.02	0.998 3

In view of the close structural similarity between the *threo*- and *erythro*-dibromobibenzyls, and the probably very similar orientation of the C–H and C–Br bonds with respect to the phenyl rings, a difference between the ΔE terms of the two systems seems unlikely. It seems reasonable, therefore, that the different *T* values reflect a real difference between the abilities of the two linkages to relay an electronic effect *via* the π-systems of the two phenyl rings. This interpretation may be rationalised from consideration of the preferred conformations. In the *threo*-CHBr·CHBr link, the repulsive interaction between vicinal bonds is presumably larger than in the *erythro*- because the bromine atoms are as close as possible to one another and the relay mechanism operates more efficiently. It is still surprising, however, that the *erythro*-CHBr·CHBr group should behave identically with the $CH_2 \cdot CH_2$ group.

Single-carbon Linkages.—In our previous study,[4b] we observed that the linking group CH(OH) (*T* 0.82) is more effective at relaying substituent effects than CH_2 (*T* 0.54). We now present data for CHCl and CHBr (Figure 2; Y = Cl or Br) in order to examine the dependence of relay upon the nature of the substituent *Y* and to examine the validity of our previous interpretations.

The most stable conformation of a diphenylmethane molecule (Figure 2; Y = H) is probably that in which the ring *ortho*-hydrogen atoms are least mutually hindered,[4b] and recent evidence[20] comprising Raman line-shape analysis shows the existence of some mutual interaction between the phenyl rings. An *X*-ray study of a related compound, 3,3′-dichloro-4,4′-dihydroxydiphenylmethane[21] shows that in the crystalline state each ring prefers to orient itself so that its plane is approximately orthogonal to one of the C–H bonds and parallel to the other. Our results show that for the single atom groups (Y = H, Cl, or Br), the *T* value is constant at 0.55 ± 0.03 (Table 5), but for Y = OH, it is much higher (0.82). We interpret this as suggesting that the relative conformation of the rings is the same when Y = H, Cl, or Br and the magnitude of the relayed effect does not depend significantly upon the nature of Y. When Y = OH, however, there is the possibility of conformational motion about the C–Y bond, which is absent in the other cases which have axial symmetry. A preferred conformation about this bond may well affect the relative disposition of the two rings and lead to a different value of *T*. These observations should be contrasted with our earlier suggestions concerning this phenomenon[4b] in which we attribute the increased value of *T* for Y = OH to the presence of *p* electrons on Y.

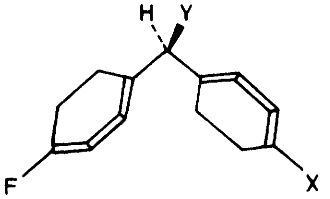


FIGURE 2 Preferred conformation of various diphenylmethanes

TABLE 8

Slopes of plots of ^{19}F s.c.s. of substituted diphenylmethanes *vs.* diphenylmethanes

Z	Slope	Standard deviation (p.p.m.)	Correlation coefficient
CH(OH)	1.33	0.03	0.999 6
CHCl	1.03	0.02	0.999 6
CHBr	0.99	0.02	0.999 4

The plots of ^{19}F s.c.s. of the various diphenylmethanes against the ^{19}F s.c.s. of *trans*-stilbenes show scatter, and a better comparative study is that of the substituted diphenylmethanes (Y = OH, Cl, or Br) against diphenylmethane itself (Y = H). Results of this treatment are illustrated in Table 8, which shows that, within experimental error, the groups CH_2, CHCl, and CHBr are

---

[20] H. Nomura, Y. Miyahara, and S. Koda, *Bull. Chem. Soc. Japan*, 1976, **49**, 811.

[21] E. J. W. Whittaker, *Acta Cryst.*, 1953, **6**, 714.

indeed equally transmissive but that CH(OH) is *ca.* 30% more so.

The electronic natures of the linking groups in the various diphenylmethanes are certainly different enough for different electron distributions in the system to be expected. This is evidenced to some extent by the dissimilar ^{19}F s.c.s. of the various PhCHY groups which are −4.35 (Y = H), −2.48 (Y = OH), −1.27 (Y = Cl) and −1.14 p.p.m. (Y = Br), respectively. There is on evidence, however, to suggest how electronic effects are transmitted across these groups.

We thank Wilkinson Match (Research Division) for financial support and maintenance grants (to P. J. M. and J. M. G.).

[6/1537 *Received, 5th August,* 1976]