^{19}F Nuclear Magnetic Resonance Studies of Aromatic Compounds. Part III.† The Transmission of Substituent Effects across Bridged Ring Systems

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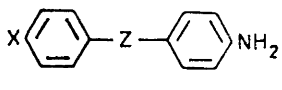
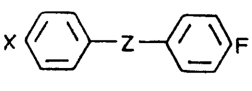
The synthesis of several series of bridged dinuclear aromatic compounds of the type p-F·C$_6$H$_4$·Z·C$_6$H$_4$·X-p [Z = all-*trans*-·CH=CH–CH=CH·, C=CH$_2$, CH$_2$, CH(OH), CMe(OH), –O–, or –S–; X = NH$_2$, OMe, H, F, Cl, or NO$_2$] is described. The ^{19}F n.m.r. spectra of these compounds are used to examine the 'transmission' of electronic effects, due to the group X, across the bridge Z. A distinction is drawn between 'transmission effects' in which electron density may be considered to be transferred from one ring to the other and 'relay effects' in which there is probably no net transfer of electron density.

WHEN aromatic rings are bonded together *via* an intervening bridge of atoms, there exists the possibility that substituent changes in one of the rings will affect the chemical or physical properties of functional groups in the other. This phenomenon has received attention and the long-range substituent effects upon ^{1}H n.m.r. spectra,[1,2] ^{19}F n.m.r. spectra,[3-5] and chemical properties [6] have been studied in a variety of bridged dinuclear systems.

Based upon studies of acylation of NH$_2$ groups in compounds of the type (A), Litvinenko *et al.*[6] have evolved an 'order of transmissivity' of the groups Z


(A)


(B)

which has been extended by Hyne;[1] the order in decreasing power to transmit electronic interactions is: Z = –NH– > –S– > –Se– > –O– > –SO– > –SO$_2$– > –CH$_2$–. ^{19}F N.m.r. shielding is particularly sensitive to substituent effects, and our recent work on 3- and 4-substituted 4′-fluoro-*trans*-stilbenes [3] encouraged us to extend the studies to a variety of systems of the type (B). Data are available [4,5,7] for some structures Z, and we have now studied others. A list of these bridges is given in the Chart; the series numbers quoted are used for identification in text and Tables.

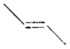
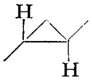
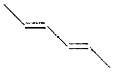
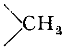
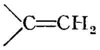
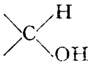
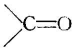
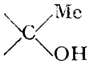
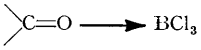
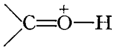
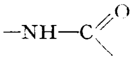
EXPERIMENTAL

^{19}F N.m.r. spectra were recorded for dilute solutions of the compounds in hexane as solvent, with C$_6$F$_6$ as internal reference; spectra were recorded for a variety of concentrations and the results extrapolated to infinite dilution.

A modified Varian HA100 n.m.r. spectrometer was used, operating in extended field-frequency locked mode with fully automatic phase correction.[8] Chemical shifts were measured, by use of the frequency difference technique, with a Beckman frequency counter.

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.) and by microanalysis; physical constants and microanalytical data are in Table 1.

CHART

Series no.	Z	Ref.	Series no.	Z	Ref.
1		*a*	9		7
2		*a*	10		*a*
3	——	*a*	11	—CH$_2$·CH$_2$—	7
4		*a*	12		*a*
5		4	13		*a*
6		4	14a	—O—	*a*
7		4	14b	—O—	*a*
8		5	15	—S—	*a*

[a] This work.

4-*Fluorodiphenyl Ether* (I).—Phenol (3 g, 26·8 mmol) was warmed with potassium hydroxide (1·3 g, 23·2 mmol), and dried by heating under vacuum at 150 °C for 3 h. p-Bromofluorobenzene (5 g, 28·7 mmol) and dry activated copper (0·3 g) were added together with a few crystals of dry phenol, and the mixture refluxed at 170—180 °C for 18 h. The product was cooled, poured into water, and extracted with ether. The extract was washed with base, twice with water, and dried (MgSO$_4$), and the solvent removed to yield a yellow oil. The oil was distilled under reduced pressure (70—71 °C at 0·1 mmHg) (lit.,[9] 247—248 °C at 744 mmHg) to give *product*; yield 1·99 g (53%). 3-*Fluorodiphenyl ether* (II), 4-*fluoro*-4′-*methoxydiphenyl ether* (III), 3-*fluoro*-3′-*methoxydiphenyl ether* (IV), 4-*chloro*-4′-*fluorodiphenyl ether*

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† Part II, ref. 3.

[1] J. B. Hyne, *Reaktsionnaya Sposobnost' Organicheskikh Soedineii*, 1968, **5**, 886.

[2] J. B. Hyne and J. W. Greidanus, *Canad. J. Chem.*, 1969, **47**, 803.

[3] I. R. Ager, L. Phillips, T. J. Tewson, and V. Wray, preceding paper.

[4] R. G. Pews, Y. Tsuno, and R. W. Taft, *J. Amer. Chem. Soc.*, 1967, **89**, 2391.

[5] R. G. Pews, *Chem. Comm.*, 1971, 458.

[6] L. M. Litvinenko, A. F. Popov, R. S. Popova, and L. P. Snagoschenko, *Reaktsionnaya Sposobnost' Organicheskikh Soedineii*, 1968, **5**, 744, and references therein.

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

[8] P. N. Jenkins and L. Phillips, *J. Phys.* (*E*), 1971, **4**, 530.

[9] E. C. Britton and A. J. Dietzler, U.S.P. 2,950,325/1960 (*Chem. Abs.*, 1960, **55**, 7359c).

(V), and 3-*chloro*-3′-*fluorodiphenyl ether* (VI) were prepared by the method described for (I), by use of the corresponding 3- or 4-substituted phenols.

4-*Fluoro*-4′-*nitrodiphenyl Ether* (VII).—Potassium hydroxide (2·0 g, 35·7 mmol) was dissolved in *p*-fluorophenol (4·75 g, 42·4 mmol) by heating to 130 °C. *p*-Chloronitrobenzene (4·0 g, 25·5 mmol) was then added and the mixture heated to 170 °C with stirring for 2 h. The product was cooled, dissolved in ether, and washed with water, base (twice), and water. The solution was dried ($MgSO_4$) and the solvent removed to give an orange solid which was recrystallised from benzene–hexane to give pale yellow *crystals*; yield 4·4 g (75%). 4-*Amino*-4′-*fluorodiphenyl ether hydrochloride* (VIII) was prepared by dissolving compound (VII) (2·0 g, 8·6 mmol) in ethanol (25 ml) and adding 100% hydrazine hydrate (2 ml, 2·06 g, 4·12 mmol) and 5% palladised charcoal (25 mg); the mixture was refluxed for 30 min. The catalyst was filtered off and ethanol removed under vacuum to leave a pale yellow oil which was dissolved in ether and dried ($MgSO_4$). Concentrated hydrochloric acid was added dropwise, and the precipitated amine hydrochloride † was filtered off. The product was recrystallised from water, dried, and vacuum sublimed to give a crystalline solid; yield 0·99 g, sublimes at *ca.* 190 °C with some decomposition at *ca.* 175 °C.

TABLE 1

Physical constants and microanalytical data

	B.p./°C at *p*/mmHg or m.p. in parentheses		n_D^{23}	Found						Calculated					
				C	H	N	F	Cl	I	C	H	N	F	Cl	I
(I)	70—71	0·1	1·5562	76·5	4·7		10·55			76·59	4·78		10·10		
	[247—248	744] *													
(II)	80—81	1·0		76·4	4·8		10·0			76·59	4·78		10·10		
(III)	102	0·3	1·5559	71·4	5·2		9·0			71·55	5·04		8·71		
(IV)	134	3·0		71·8	5·2		8·6			71·55	5·04		8·71		
(V)	94—95	0·5	1·5661	65·1	3·7		8·6	16·5		64·70	3·59		8·53	15·95	
(VI)	100	1·0		64·7	3·6			15·9		64·70	3·59			15·95	
(VII)	(73—74)			62·0	3·6	5·9	7·9			61·80	3·43	6·00	8·15		
	[(71)]														
(VIII)	(190 sublimed)			60·4	4·7	5·9	7·95	14·8		60·10	4·59	5·84	7·93	14·82	
(IX)	(56—57)			72·9	6·1	5·9	8·2			72·72	6·06	6·06	8·22		
(X)	(180—181)			47·9	4·5	4·0	5·2		33·85	48·25	4·55	3·75	5·09		34·04
(XI)	130	7	1·6043	70·2	4·3		9·5			70·58	4·41		9·31		
(XII)	(34—35)			59·4	3·3		8·9	14·0		60·38	3·35		7·97	14·88	
(XIII)	166—170	6	1·5983	66·3	4·7		8·6			66·67	4·70		8·11		
(XIV)	(94—95)	95		58·0	3·35	5·7	8·2			57·80	3·21	5·62	7·63		
(XV)	Sublimes			58·1	4·4	5·5	8·6	12·0		56·36	4·31	5·48	7·44	13·89	
(XVI)	138—139	3·0	1·5659	77·8	6·1		8·6			77·80	6·01		8·79		
(XVIII)	136—138	1·0	1·5728	66·65	4·9		7·2	14·5		67·06	4·79		7·58	14·17	
(XIX)				72·7	6·1		7·55			73·17	6·09		7·72		
(XX)			1·5746	85·3	5·4		9·7			84·84	5·55		9·59		
(XXI)				71·7	4·3		7·8	15·0		72·76	4·30		8·17	15·27	
(XXII)	(100—101)			79·6	6·7	5·7	7·8			79·66	6·63	5·80	7·88		
(XXIII)	(71—72)			78·7	5·65		8·2			78·94	5·70		8·34		
(XXIV)	(140—143 decomp.)			53·0	5·4	3·6	4·3		32·6	53·26	4·96	3·65	4·96		33·15
(XXV)	(65—66)			70·0	4·1	5·7	8·0			69·13	4·11	5·76	7·81		
(XXVI)	115	0·4	1·5684	76·9	5·5		9·35			77·22	5·44		9·40		
	[118—120 *	10·0]													
(XXVII)	143—146	1·0		65·9	4·2		7·8	15·1		65·96	4·22		8·03	15·01	
	(53—54)														
(XXVIII)	(77—78)			63·55	4·0	5·5	7·65			63·15	4·04	5·66	7·69		
(XXIX)				72·4	5·6		8·25			72·41	5·60		8·18		
(XXX)				84·2	6·3		9·3			83·87	5·91		10·21		
(XXXI)				70·8	4·6		8·5	15·8		70·74	4·53		8·61	16·09	
(XXXII)	(55—56)			67·8	4·7	6·1	8·1			67·53	4·32	6·06	8·22		
(XXXIII)	(40—41)			78·3	7·3	5·9	8·3			78·60	6·98	6·11	8·29		
(XXXIV)	(130—131)			51·9	4·9	4·0	5·5		34·65	51·75	5·12	3·77	5·12		34·23
(XXXV)				78·0	6·1		8·8			77·77	6·01		8·79		
(XXXVI)				85·5	5·8		8·3			85·68	5·84		8·47		
(XXXVII)				80·5	6·0					80·29	5·94				
(XXXVIIIa)				No satisfactory analysis. Structure confirmed by mass spectrometry.											
(XXXVIIIb)															
(XXXIX)				74·15	4·7		6·6			74·20	4·67		7·34		

* Square brackets enclose literature values, where known. Parentheses enclose m.p.s.

4-*Dimethylamino*-4′-*fluorodiphenyl Ether* (IX).—Compound (VII) (2·3 g, 9·9 mmol) was added to 40% aqueous formaldehyde (1·5 g, 20 mmol) dissolved in methanol (50 ml), together with 5% palladised charcoal (1 g). The mixture was shaken under hydrogen at atmospheric pressure and room temperature for 3 h, after which time 1190 ml of hydrogen had been used. The catalyst was filtered off and solvent evaporated to yield an off-white solid which was recrystallised from methanol to give colourless *flakes*; yield 1·42 g (61%).

4-*Trimethylammonio*-4′-*fluorodiphenyl Ether Iodide* (X).—Compound (IX) (1·0 g, 4·3 mmol) was dissolved in methanol (20 ml), methyl iodide (5 ml, 11·3 g, 80 mmol) added, and the mixture refluxed for 90 min. The solvent was removed

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† N.m.r. spectra were recorded for the free base, obtained by basification of the hydrochloride and extracting into hexane solvent.

under vacuum and the yellow solid was recrystallised from methanol to give pale cream *flakes*; yield 0·92 g (57%).

4-*Fluorodiphenyl Sulphide* (XI).—Potassium (0·5 g, 12·8 mmol) was dissolved in methanol (5 ml), thiophenol (2·0 g, 18·2 mmol) was added, and the solvent was removed by heating to 130 °C under vacuum for 1 h. The resulting solid was dissolved in dry dimethylformamide (5 ml) and dry activated copper (0·5 g), thiophenol (1 drop), and *p*-fluorobromobenzene (5 g, 28·7 mmol) added; the mixture was refluxed at 160 °C for 60 h. After cooling, the product was extracted with ether and the catalyst was filtered off; the ethereal solution was washed twice with dilute potassium hydroxide solution, twice with water, and dried ($MgSO_4$), and the solvent removed by distillation to give a red oil. The *sulphide* was isolated by column chromatography (grade III alumina, 10% benzene in light petroleum) and purified by distillation under reduced pressure (130 °C at 7 mmHg) to give an oil; yield 0·88 g (34%). 4-*Chloro*-4′-*fluorodiphenyl sulphide* (XII) and 4-*methoxy*-4′-*fluorodiphenyl sulphide* (XIII) were prepared from the corresponding *para*-substituted thiophenol by the method described for (XI). 4-*Nitro*-4′-*fluorodiphenyl sulphide* (XIV) was prepared from *p*-fluorothiophenol by the method described for (VII). 4-*Amino*-4′-*fluorodiphenyl sulphide* (XV) was prepared from (XIV) by the method described for (VIII).

p-*Fluoro*-1,1-*diphenylethanol* (XVI).—The Grignard reagent of *p*-bromofluorobenzene was prepared by dissolving the compound (5 g, 28·7 mmol) in diethyl ether (25 ml) and adding magnesium turnings (0·7 g, 29·2 mmol). Acetophenone (3·5 g, 29·2 mmol) in dry ether (10 ml) was added slowly with stirring, and the mixture was refluxed for 10 min. The product was triturated with saturated aqueous ammonium chloride, the ether layer separated, and washed twice with water; after drying (Na_2SO_4) the solvent was evaporated to yield a yellow oil. The oil was distilled under reduced pressure (138—139 °C at 3 mmHg) to give unchanged acetophenone (0·44 g) and an *oil*; yield 3·17 g (59% based upon used acetophenone). p-*Dimethylamino*-p′-*fluoro*-1,1-*diphenylethanol* (XVII), p-*chloro*-p′-*fluoro*-1,1-*diphenylethanol* (XVIII), and p-*methoxy*-p′-*fluoro*-1,1-*diphenylethanol* (XIX) were prepared from the corresponding *para*-substituted acetophenones by the method described for (XVI). Distillation of (XVII) and (XIX) was avoided to minimise dehydration; it was not possible to obtain (XVII) pure, and its spectral properties were recorded in the presence of olefin.

p-*Fluoro*-1,1-*diphenylethylene* (XX).—Compound (XVI) (0·8 g, 3·7 mmol) was refluxed with acetic anhydride (8 ml, 8·6 g, 85 mmol) and glacial acetic acid (2 ml, 2·1 g, 35 mmol) for 5 h. The mixture was neutralised with concentrated aqueous sodium hydroxide, and the product extracted with ether; the ethereal solution was washed twice with water, and dried ($MgSO_4$) and the solvent evaporated to leave a yellow oil. The product was purified by column chromatography (grade III alumina, light petroleum) to give an *oil*; yield 710 mg (89%). p-*Chloro*-p′-*fluoro*-1,1-*diphenylethylene* (XXI) was prepared by dehydration of (XVIII) in the manner described for (XX). p-*Dimethylamino*-p′-*fluoro*-1,1-*diphenylethylene* (XXII) and p-*methoxy*-p′-*fluoro*-1,1-*diphenylethylene* (XXIII) were prepared by dehydration of the corresponding diphenylethanols [(XVII) and (XIX) respectively] by distillation. p-*Trimethylammonio*-p′-*fluoro*-1,1-*diphenylethylene iodide* (XXIV) was prepared by refluxing (XXII) (1 g, 4·1 mmol) with methyl iodide (5 ml, 11·3 g, 80 mmol) in methanol (20 ml) for 2 h. The solvent was removed under vacuum and the product recrystallised from ether–acetone and washed with ethyl acetate to give a light brown *solid*; yield 560 mg (35%).

p-*Nitro*-p′-*fluoro*-1,1-*diphenylethylene* (XXV).—Triphenylmethylphosphonium bromide (5 g, 14 mmol) was suspended in dry ether (20 ml), sodium t-pentyloxide (1·8 g, 16·4 mmol) in dry benzene (15 ml) was added, and the reaction container was flushed out with dry nitrogen. 4-Nitro-4′-fluorobenzophenone (2·45 g, 10 mmol) in solution in dry benzene (20 ml) was added and the mixture refluxed under nitrogen for 18 h. The product was allowed to cool, filtered, washed twice with water, and dried (Na_2SO_4), and the solvent evaporated to leave a very dark red oil. The oil was triturated with ether to precipitate triphenylphosphine oxide which was filtered off; the ether was removed under vacuum and the product purified by chromatography (grade III alumina, benzene, followed by grade III alumina, 10% ether in light petroleum) to give a yellow oil which solidified. The product was recrystallised from benzene–light petroleum to give pale yellow *crystals*; yield 1·52 g (63%).

4-*Fluorodiphenylmethanol* (XXVI).—Benzaldehyde (2·0 g, 18·9 mmol) in ether (20 ml) was added to an ethereal solution of *p*-fluorophenylmagnesium bromide [prepared from *p*-fluorobromobenzene (4 g, 22·9 mmol) and magnesium (0·55 g, 22·9 mmol)], and the mixture refluxed for 30 min. The product was worked up with saturated aqueous ammonium chloride; the ethereal layer was separated, washed twice with water and dried ($MgSO_4$). The solvent was evaporated to yield a yellow oil. The product was distilled under reduced pressure to give a pale green fluorescent oil which turned colourless on standing; yield 2·34 g (61%). 4-*Chloro*-4′-*fluorodiphenylmethanol* (XXVII) was prepared from *p*-chlorobenzaldehyde by the method described for (XXVI).

4-*Nitro*-4′-*fluorodiphenylmethanol* (XXVIII).—4-Nitro-4′-fluorobenzophenone (12·25 g, 50 mmol) was dissolved in ethanol (10 ml); sodium borohydride (1·0 g, 36 mmol) was added while stirring, and the mixture refluxed for 30 min. The resulting complex was decomposed with water, the solution filtered, and the solvent removed under vacuum to leave a red oil. This was dissolved in ether, washed twice with water, dilute hydrochloric acid, sodium carbonate solution, and water (twice). The solution was dried ($MgSO_4$) and ether removed to give an orange crystalline *solid*; yield 12·0 g (97%). The product was recrystallised from benzene to give off-white crystals.

4-*Methoxy*-4′-*fluorodiphenylmethanol* (XXIX).—4-Methoxy-4′-fluorobenzophenone (1·15 g, 5 mmol) was dissolved in ether (25 ml), and slowly added to lithium aluminium hydride (0·25 g, 6·6 mmol) with stirring; the mixture was refluxed for 2 h. The complex was decomposed with saturated aqueous ammonium chloride solution and the ether layer separated; this was washed twice with water, dried ($MgSO_4$), and the ether removed to give an oil. The oil was purified by chromatography (grade III alumina, 50% chloroform in light petroleum) and the *product* stabilised with one added drop of 2,6-lutidine; yield 0·83 g (72%).

4-*Fluorodiphenylmethane* (XXX).—Compound (XXVI) (0·9 g, 4·5 mmol) was stirred with phosphorus tribromide (1 ml, 2·85 g, 10·5 mmol) for 1 h; the excess of PBr_3 was decomposed with water, neutralised with sodium hydrogen carbonate solution and the product extracted with ether and dried ($MgSO_4$). The ethereal solution was slowly added to lithium aluminium hydride (0·5 g, 13·2 mmol) with stirring and the mixture was refluxed for 25 h. The solution was cooled in ice, worked up with saturated aqueous ammonium chloride solution, and the ether layer separated. This was washed twice with water, dried ($MgSO_4$), and the solvent removed to leave an oil. The *oil* was purified by chromatography (grade III alumina, light petroleum); yield 0·53 g (64%).

4-*Chloro*-4′-*fluorodiphenylmethane* (XXXI).—Compound (XXVII) (1·3 g, 5·5 mmol) was brominated and reduced as described for (XXX).

4-*Nitro*-4′-*fluorodiphenylmethane* (XXXII).—Compound (XVIII) (12 g, 4·9 mmol) was converted into the bromide as described for (XXX). This was added to a mixture of sodium borohydride (1·51 g, 40 mmol), diglyme (6·5 ml), water (3·5 ml), and sodium hydroxide (0·4 g, 10 mmol) at 50 °C and stirred for 30 min. The mixture was poured into water and the product extracted with ether; after washing twice with water, the ethereal solution was dried ($MgSO_4$) and the solvent removed to give an orange oil. This was purified by chromatography (grade III alumina, 25% ether–light petroleum) and the product recrystallised from ethanol to give off-white *crystals*; yield 330 mg (29%).

4-*Dimethylamino*-4′-*fluorodiphenylmethane* (XXXIII).—Compound (XXXII) (8·6 g, 34·8 mmol) was dissolved in methanol (50 ml); 5% palladised charcoal (1 g) and 40% aqueous formaldehyde (5·5 g, 73 mmol) were added, and the mixture shaken under hydrogen at room temperature and pressure. 3870 ml of hydrogen were absorbed. The catalyst was filtered off and the solvent removed under reduced pressure; the product was redissolved in ether and dried ($MgSO_4$) and the ether removed to give a yellow oil. The oil was distilled under reduced pressure (140—160 °C at 0·8 mmHg) to give a pale yellow oil which was further purified by chromatography (grade III alumina, 50% benzene–light petroleum). The *product* was recrystallised from ethanol to give white flakes; yield 1·96 g (25%).

4-*Trimethylammonio*-4′-*fluorodiphenylmethane Iodide* (XXXIV).—This was prepared by refluxing compound (XXXIII) (0·9 g, 3·9 mmol) with methyl iodide (5 ml, 11·3 g, 80 mmol) in methanol (5 ml) for 30 min. After removing the solvent under vacuum, the product was recrystallised twice from acetone to give colourless *flakes*; yield 890 mg (61%).

4-*Methoxy*-4′-*fluorodiphenylmethane* (XXXV).—Compound (XXIX) was brominated and then reduced in the manner described for (XXX).

p-*Fluoro*-1,4-*diphenylbuta*-1,3-*diene* (XXXVI).—Cinnamaldehyde (4·09 g, 31 mmol) and *p*-fluorobenzyltriphenylphosphonium chloride (12·6 g, 31 mmol) were dissolved in ethanol (21 ml); ethanolic lithium ethoxide (0·2N, 155 ml) was added with stirring and a precipitate began to form almost immediately. The mixture was stirred for 16 h, after which time water (112 ml) was added. The product was filtered off, washed with 60% ethanol, and recrystallised from glacial acetic acid; yield 1·74 g (25%). p-*Methoxy*-p′-*fluoro*-1,4-*diphenylbuta*-1,3-*diene* (XXXVII) and p-*nitro*-p′-*fluoro*-1,4-*diphenylbuta*-1,3-*diene* (XXXVIII) were prepared from the corresponding *para*-substituted benzyltriphenylphosphonium chlorides by the method described for compound (XXXVI). In the case of (XXXVIII) the ^{19}F n.m.r. spectrum indicated the presence of two isomers, which were separated by chromatography to yield (XXXVIIIa) (the *cis–trans*-isomer) and (XXXVIIIb) (the *trans–trans*-isomer). These were identified by their u.v. spectra, and by the fact that the more highly conjugated molecule (*trans–trans*) would be expected to have its ^{19}F resonance to higher field.

p-*Chloro*-p′-*fluoro*-1,4-*diphenylbuta*-1,3-*diene* (XXXIX).—*p*-Fluorophenylacetic acid (2·31 g, 15 mmol) and *p*-chlorocinnamaldehyde (2·50 g, 15 mmol) were dissolved in acetic anhydride (4 ml, 4·33 g, 43 mmol) and lead monoxide (1·6 g, 7·5 mmol) added. The mixture was refluxed for 5 h at 140 °C and poured into boiling 50% aqueous acetic acid. The boiling was continued for 5 min. The mixture was cooled to 0 °C, and the product filtered off and recrystallised from glacial acetic acid, followed by benzene–ethanol; yield 300 mg (7·8%).

RESULTS AND DISCUSSION

Pews[5,7] has used ^{19}F n.m.r. studies to examine the transmission of electronic effects across the bridge in compounds of the type B, in which Z is $-CH_2{\cdot}CH_2-$, *cyclo*-C_3H_4, $-CONH-$, and $-CH{=}CH-$. The results are discussed in terms of linear correlations of the ^{19}F shielding parameters with Taft's σ^0 constants, and the conclusion has been reached that transmission across the bridge in *trans*-stilbenes ($Z = -CH{=}CH-$) is 100% while that across the linkage in bibenzyls ($Z = -CH_2{\cdot}CH_2-$) is essentially zero, with the other groups lying in between these extremes. In earlier work, Pews *et al.*[4] studied a series of 4-substituted 4′-fluorobenzophenones, together with adducts formed between these molecules and BCl_3 and H_2SO_4; in the benzophenones (series 5) the transmission is of the same order as in the stilbene series, but the acid adducts (series 6 and 7) have greatly enhanced transmission. This phenomenon was not commented upon, but in the present work we have studied series (diphenyl ethers and sulphides) in which the transmission is also apparently much greater than in *trans*-stilbenes and the phenomenon is worthy of further consideration.

We have recently made an extensive study of substituent effects upon ^{19}F shielding in 3- and 4-substituted 3′- or 4′-*trans*-stilbenes, and observed a very good linear correlation with unmodified Hammett σ parameters (a correlation which is significantly better than that with σ^0 in spite of the inclusion of so-called anomalous substituents such as OMe which Pews excludes from his correlations[5,7]). It is reasonable that the substituent effects transmitted across such distances occur by perturbation of the π-electronic system, and that Hammett σ values are a good measure of this perturbation alone;[3] the results of the present work, together with those of Pews, will be discussed in this light.

In his study of 3- and 4-substituted 4′-fluorobenzanilides,[5] Pews makes some reference to solvent effects, and concludes that transmissive effects in this series decrease with an increase in solvent polarity. This is attributed to an ' increase in neutralisation of the amide dipole with an increase in solvent polarity ' but it is not made clear how this would affect electronic transmission between two rings. We have recently made a detailed study of solvent effects upon fluoroaromatic compounds in general and upon fluorostilbenes in particular[10,11] and it seems clear that the solvent variation in the shielding parameters of the fluorobenzanilides probably arises from the effects of reaction fields rather than from an inherent variation in the transmissive power of the bridge. An important point does arise from this observation however, for even in relatively non-polar solvents a variation of ^{19}F shielding with substituent nature will be observed as the molecular dipole moment, and hence solvent reaction field, changes; even in the absence of transmission through bonds there will still be an observed substituent effect upon shielding, and it is important to separate this contribution from the observed trends.

The magnitude of the effect of reaction field upon the shielding of a ^{19}F nucleus in a C–F bond will be greatest when the field is collinear with the bond; in the molecules studied in the present work, which are of similar overall size, this will occur with the 4-fluorostilbenes. The shielding of ^{19}F in these molecules relative to the unsaturated case (substituent chemical shift, s.c.s.) arising from the reaction field can be calculated by the method described elsewhere[10] and for solutions in n-hexane (the solvent for the present studies) the relevant data are in Table 2 (column 16). It should be considered that these values represent the probable maximum contribution of the reaction field effect in hexane; in other solvents, such as those used by Pews, the effects may be somewhat larger.

TABLE 2

^{19}F S.c.s. of the ^{19}F nucleus in various series of the type (B) (p.p.m. to high field of X = H)

Series	1	2	3	4	5	6	7	8	9	10	11	12	13	14a	14b *	15	Reaction field in hexane
NMe_2	1·60			0·77	2·19					0·72			1·00	2·20			0·25
NH_2	1·31		2·34 [a]											2·00		3·30	0·25
OMe	0·71	0·47		0·24	0·91	5·05	6·10	0·46 [c]	0·19 [b]	0·25	0·10	0·42	0·35	1·28	0·66	2·19	0·17
H	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
F	−0·24		−0·14 [b]		−0·19		0·83										−0·18
Cl	−0·62	−0·35		−0·64	−0·52	−1·05	−0·45	−0·37 [c]	−0·37 [b]	−0·65	−0·20	−0·77	−0·76	−0·95	−0·06	−0·97	− 0·21
Br	−0·69		−0·78 [b]														−0·22
I	−0·76		−0·90 [b]														−0·22
Me_3N^+	−1·49			−1·39						−1·29				−2·44			
NO_2	−2·38	−1·66	−2·74 [b]	−1·66	−2·01	−6·31	−6·78	−1·04 [c]	−0·99 [b]	−1·68	−0·50	−2·05		−3·50		−4·21	−0·56

[a] Dimethylformamide. [b] Benzene. [c] Tetrahydrofuran.

* *m*-X·C_6H_4·Z·C_6H_4·F-*m*. All others *para*.

Since our most extensive study has been of the series of fluorostilbenes[3,10] it will be convenient to discuss the chemical shift data of the other series by means of linear correlations with the ^{19}F s.c.s. for the stilbenes. Table 2 lists the s.c.s. observed in the present work, together with those of the series studied elsewhere[3,4,5,7,12] and Table 3 shows the slopes given by a least-squares analysis of the linear correlation between these values and the corresponding stilbene data. It is interesting that the reaction field contributions to the s.c.s. (Table 2) correlate linearly with the observed s.c.s. for the 4-fluorostilbenes to a satisfactory degree of precision (*r* 0·986); the slopes in Table 3 may therefore be corrected for solvent effects by subtracting from them the slope of this correlation, to yield the transmissive factors, *T* (also quoted in Table 3) which are based upon an arbitrary unity for the stilbenes.

This analysis confirms the suggestion of Pews that in the bibenzyls (series 11) there is no transmission of electronic effects through the bridge ($T = 0$) but that in *trans*-1,2-diphenylcyclopropanes (series 9) there is significantly more transmission ($T = 0·21$). In order to provide a further basis for discussion we have studied 4-fluoro-4′-X-diphenyl-*trans*,*trans*-butadienes (series 2). Increasing the extent of formal π conjugation by one C=C unit decreases *T* from unity to 0·60; the cyclopropyl group is therefore a relatively inefficient bridge even when compared with this more extended system and probably is not very much better than a normal saturated linkage such as $-CH_2·CH_2-$.

It is interesting to compare the data for series in which the group Z is a single carbon atom; this occurs for diphenylmethanes (series 10), diphenylmethanols (series 12), 1,1-diphenylethanols (series 13), and 1,1-diphenylethylenes (series 4). The first thing to observe is that *T* does not depend significantly upon the state of hybridisation of the carbon atom, for series 4 and 10 the values

TABLE 3

Correlation of ^{19}F s.c.s. in series (B) with the corresponding data for 4-X-4′-fluorostilbenes, and calculated *T* values

Series		Slope of correlation with stilbene series	Corrected *T* value
1		1·00	1·00
2		0·69 ± 0·04	0·60
3		1·36 ± 0·20	1·46
4		0·65 ± 0·13	0·55
5		1·03 ± 0·19	1·03
6		3·32 ± 0·91	3·97
7		3·70 ± 1·0	4·46
8		0·47 ± 0·08	0·32
9		0·39 ± 0·05	0·21
10		0·64 ± 0·11	0·53
11		0·20 ± 0·03	0·00
12		0·82 ± 0·09	0·76
13		0·76 ± 0·11	0·69
14a		1·50 ± 0·14	1·64
14b *		0·55 ± 0·13	0·42
15		2·06 ± 0·28	2·35
16	Reaction field contribution	0·22 ± 0·04	0·00

* *m*-X·C_6H_4·Z·C_6H_4·F-*m*. All others *para*.

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[10] I. R. Ager and L. Phillips, *J.C.S. Perkin II*, 1972, 1975.

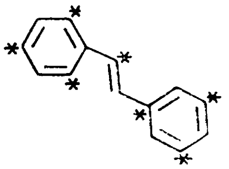
[11] J. W. Emsley and L. Phillips, *Mol. Phys.*, 1966, **11**, 437.

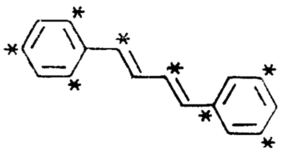
[12] M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, 1966, **88** 3318.

are essentially the same (0·55 and 0·64 respectively). When Z is a substituted sp^3 carbon however (*e.g.* series 12 and 13) T increases (to 0·76 and 0·69), and the transmission is as effective as in the butadienes. If the carbon is replaced by oxygen or sulphur (B, Z = O or S, series 14a or 15), T increases substantially to 1·64 and 2·35 respectively; thus, sulphur and oxygen are better ' transmitters ' than a single carbon atom or, perhaps more surprisingly, than the formally conjugated linkage in the *trans*-stilbenes (series 1). In order to understand these observations, it is useful to examine the π electronic structure of these molecules in qualitative terms.

trans-Stilbene and *trans*,*trans*-1,4-diphenylbutadiene are examples of even-alternant hydrocarbons [13] in which it is useful to divide the carbon atoms which contribute a p electron to the π system into two sets, starred and unstarred, such that no atom is formally bonded to a member of the same set, as in (C) and (D). In such a molecule, a change of substituent on a starred atom may be considered to cause π electron density changes throughout the system which are considerably greater at unstarred positions than at starred (the converse, of course, is also true); this results, for example, in *ortho*- and *para*-substituent effects being much larger than *meta*. It is not surprising, therefore, that 4,4′-substituent effects in (C) and (D) are appreciable, since 4 is starred and 4′ is unstarred. 1,1-Diphenylethylene may also be considered as an even-alternant hydrocarbon (E), although the bond integrals involving the bridging sp^2 carbon may be reduced from their normal values because of steric interaction between the two rings. In this case the 4- and 4′-positions are both starred, and conjugated substituent effects between the two will be minimal; this is probably the main reason for the reduction in substituent effects between these positions compared with the stilbenes and diphenylbutadienes, although the inter-ring conjugation will also be reduced by steric interactions.

In the series of 1,1-diphenylmethanes it is possible to envisage that some inter-ring π conjugation could result from overlap of the ring carbon p_z orbitals with the central CH bonds combined together to give an orbital of p_z symmetry (' hyperconjugation '); the result could be described as an odd-alternant hydrocarbon (F), but again the 4- and 4′-positions are both starred. A model indicates that steric interactions between the two rings is even more severe than in 1,1-diphenylethylenes and that the rings will be even less coplanar; it is therefore very surprising that substituent effects between the 4- and 4′-positions should be larger than in the case of the 1,1-diphenylethylenes, the more so in view of the fact that hyperconjugative overlap will be inherently smaller than pure p_π–p_π interactions. Perhaps even more puzzling is the fact that when the bridging carbon atom is bonded to OH (series 12) or to OH and Me (series 13) the substituent effects between the 4- and 4′-positions are even larger; it is difficult to visualise significant hyperconjugative interaction between carbon $2p_z$ orbitals and C–C or C–OH bonds, and it would usually be assumed that such an interaction was negligible. An alternative explanation must therefore be sought to explain the facts.


(C)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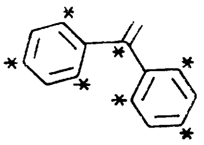
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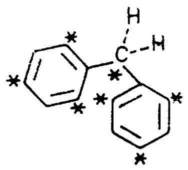
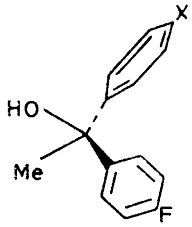


(F)



(G)

The most probable preferred conformation for molecules such as these is one in which the steric interactions between the ring *ortho*-positions are minimised, and this will probably occur when the plane of each ring is approximately orthogonal to a C–X (X = Me, H, or OH) bond on the bridge; each ring will be orthogonal to a different bond, as shown in (G) for 1,1-diphenylethanol. In this conformation, each aromatic π system (considered separately) will undergo a maximum ' orbital penetration interaction ' with the lone pairs on the C–OH oxygen, or the H atoms of the C–$\mathrm{Me_3}$ group.[14,15] Murrell has suggested that the magnitude of such repulsive interactions should be proportional to the π electron density on the ring α-carbon atom; [15] the effect will be mutual, and will result not only in an increase of the energy of the α carbon $2p_z$ orbital but also in the energy of the orbitals of the interacting group (the C–OH or C–Me bond). We suggest that the interaction felt by each bond separately is transmitted to the other because of geminal delocalisation between them; [16] this, in turn, modifies the orbital penetration perturbation of the other ring and the substituent effect is transmitted *without*

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[13] A. Streitwieser ' Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, p. 45.

[14] M. G. Belsham, A. R. Muir, L. Phillips, and L. M. Twanmoh, unpublished results.

[15] J. N. Murrell, ' The Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963, p. 206.

[16] J. N. Pople and D. A. Santry, *Mol. Phys.*, 1963, **7**, 269.

transfer of electron density between the rings. ' Orbital penetration ' or ' π inductive ' effects cause alternation of charge density in a fashion exactly analogous to that of the mesomeric effect;[17] because of this, the maximum inter-ring interaction will occur when the substituents are *ortho* or *para* to the bridge, and the large effect between 4- and 4'-positions is explained. If the bridging atom was involved in a molecular orbital of π symmetry, 4,4'-interaction would be minimal.

The work of Murrell *et al.*[15,16] indicates that orbital penetration interaction between an aromatic π system and a substituent will be greater if that substituent has a non-bonding lone pair of electrons and will be proportional to the energy of the lone pair. The interaction with an oxygen atom should be greater than with the lone-pairs on the oxygen of the C–OH group or the H atoms of the C–Me group, and interaction with a sulphur atom (which has $3p$ orbitals) should be even greater; for this reason, 4,4'-substituent effects in diphenyl ethers are larger than in the other series ($T = 1{\cdot}64$), and they are larger still in diphenyl sulphides ($T = 2{\cdot}35$).

X-Ray studies on diphenyl sulphides[18] provide some support for the hypothesis, in that the geometry required for such interaction is indicated, at least in the crystal state. Thus, the C–S–C bond angle is 109°, indicating that the sulphur is probably sp^3 hybridised; the two benzene rings are twisted so that the angle between the two normals is 56°, and if the lone pairs on sulphur are assumed to be in sp^3 hybrid orbitals then the plane of each ring is at an angle of *ca.* 90° to a different lone pair. Some evidence is also available for the suggested interaction mechanism from e.s.r. studies on diphenyl ether radicals; spin density is not transferred from one ring to the other[19] as would be expected if the oxygen was involved in a π molecular orbital delocalised over the whole system, and this is in accord with our suggestion that there is no transfer of electron density between the rings. Additionally, the u.v. spectra of 4-substituted 4'-nitrodiphenyl ethers are best understood in terms of π-electronic levels localised within each ring separately.[20]

The substituent effects upon fluorine in 3-substituted 3'-fluorodiphenyl ethers (series 14b, $T = 0{\cdot}42$) are much smaller than in the 4,4'-case (series 14a, $T = 1{\cdot}64$). This is in accord with our view that the important factor in deciding the magnitude is the relative disposition of the substituent with respect to the bridge (in this case both are *meta*). In a fully delocalised π system involving the bridge both the 3- and 3'-positions would be ' unstarred ' and hence conjugative interactions between the two positions would be minimal as would the similar interaction between the 4- and 4'-positions.

The present work confirms the suggestions of Hyne[1] that sulphur and oxygen are better transmitters than a saturated carbon atom; further it demonstrates that they are even better than sp^2 carbon or a vinyl linkage. It is probable however that the bridge acts as a relay rather than a transmitter for such electronic interactions, and there is no net charge transfer between rings. When the bridge is an sp^2 carbon atom (*e.g.*, series 4) or a vinyl linkage (*e.g.* series 1), both the orbital penetration and a normal conjugative mechanism will apply, and there is no virtue in trying to separate the two.

It is necessary to consider what may be understood from the variations in the transmissive power T of the various bridges. If the bridge consists of conjugated sp^2 carbon atoms, the substituent effects between the 4- and 4'-positions would be expected to attenuate uniformly with increase in chain length; thus the transmission in biphenyls ($T = 1{\cdot}46$), stilbenes ($T = 1{\cdot}00$), and diphenylbutadienes ($T = 0{\cdot}60$) decreases in the expected order and a fall-off factor of about 0·4 per C=C bond is indicated. In utilising variations in the ^{19}F s.c.s. to assess the phenomenon, however, it is assumed that there is a proportionality between this parameter and π-electron density changes,[3,21] and that the proportionality constant remains the same for each series.

The meaning of this proportionality constant is not really clear[21,22] but it probably depends in part upon the reciprocal of a rather ill-defined ' average excitation energy, ΔE '[23] concerned with wavefunctions describing the total molecular electronic properties. If the constant is the same for all series, then the factor T is a measure of the variation in π electron density at a 4'-position caused by changes in a 4-substituent. For those series in which it is suggested that the bridge relays the substituent effects by an orbital penetration mechanism (series 12, 13, 14b, and 15) the proportionality would be expected to be similar to that for benzenes and hence directly comparable with the fully conjugated series.

When the bridge is a single sp^2 carbon atom however (*e.g.*, series 4, 5, 6, and 7) the comparison is not so obvious. The overlap between the central carbon p_z orbital with the corresponding orbitals on the α ring carbons will be reduced (compared with the stilbenes) by steric interactions between the rings but should remain more or less constant for all these series. As indicated earlier, the 4- and 4'-positions are not in direct conjugation, and in this light the value of T for 1,1-diphenylethylenes (series 4) of 0·55 is reasonable. However, when the bridge Z is C=O the value of T increases to 1·03, and forming the BCl_3 and H^+ adducts of this causes a great increase to 3·3 and 3·7 respectively; probably in all these series the variations in the π electron density at the 4-position caused by 4'-substituent changes are of the same order of magnitude, and the reason for the large T

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[17] D. T. Clark, J. N. Murrell, and J. M. Tedder, *J. Chem. Soc.*, 1963, 1250.

[18] W. R. Blackmore and S. C. Abrahams, *Acta Cryst.*, 1955, **8**, 329.

[19] L. H. Sutcliffe, personal communication.

[20] J. J. K. Boulton, personal communication.

[21] J. W. Emsley, *J. Chem. Soc.* (*A*), 1968, 2532.

[22] J. W. Emsley and L. Phillips, *Progr. N.M.R. Spectroscopy*, 1971, **7**, 47 *et seq.*

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

values is an increase in the proportionality constant relating these changes to ^{19}F s.c.s. (*i.e.*, a lowering in the average excitation energy). At present there is no evidence to suggest that in these series long-range substituent effects upon chemical properties of a 4-substituent are unusually large; clearly such a possibility exists and merits further investigation.

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