Nuclear Magnetic Resonance Study of Charge-transfer Complexes of 1,3,5-Trinitrobenzene, Picric Acid, and Fluoranil with Methoxy- and Methyl-substituted Benzenes and Biphenyls. Indication of the Structure of the Complexes in Solution

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Association constants for the charge-transfer complexes formed between 1,3,5-trinitrobenzene, fluoranil, or picric acid and methoxy- and methyl-substituted benzenes and biphenyls have been determined from n.m.r. chemical shift measurements. With some exceptions the log K values of these complexes vary linearly with the energy of the charge-transfer transition.

For complexes of non-hindered biphenyl donors a larger shift of the acceptor protons in pure complex (Δ_0) is found than for the complexes of the corresponding substituted benzenes. It is shown that this increase in Δ_0 is only due to a ring-current effect of the second ring of the biphenyl donor. For several model structures of the complex this effect has been calculated. The agreement for the model with a coaxial arrangement of donor and acceptor is very satisfactory. The conclusion is that Mulliken's principle of maximum overlap does indeed apply for these complexes.

CHARGE-TRANSFER complexes have been of interest recently.[1] Since Mulliken founded a theoretical basis for the quantum-mechanical description of charge-transfer interaction [2] and formulated his ' overlap and orientation ' principle [3] there has been considerable discussion about the structure of charge-transfer complexes in solution.[4-9]

The crystal structures of a number of complexes between π-donors and π-acceptors are known.[10-13] The planes of donor and acceptor molecules are parallel but a relative orientation according to the maximum-overlap principle is not generally observed. Care should be taken to extrapolate properties of charge-transfer complexes from the solid phase to solution. It has been reported that the molecular centres of the components of the chloranil–hexamethylbenzene complex in solution might not be superimposed.[4] There is still considerable uncertainty about the structure of charge-transfer complexes in solution.

In certain cases, n.m.r. spectroscopy can be used to

[1] See *e.g.*, R. Foster, ' Organic Charge-Transfer Complexes,' Academic Press, London and New York, 1969.
[2] R. S. Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.
[3] R. S. Mulliken, *Rec. Trav. chim.*, 1956, **75**, 845.
[4] A. H. Ewald, *Trans. Faraday Soc.*, 1968, **64**, 733.
[5] E. Shilton and C. H. J. Wells, *J. Chem. Soc.* (*B*), 1970, 1613.
[6] H. Kuroda, I. Kemoto, and H. Akamatu, *Bull. Chem. Soc. Japan*, 1960, **39**, 1842.

[7] G. K. Vemulapalli, *J. Amer. Chem. Soc.*, 1970, **92**, 7589.
[8] J. L. Lippert, M. W. Hanna, and P. J. Trotter, *J. Amer. Chem. Soc.*, 1970, **91**, 4035.
[9] E. M. Voigt, *J. Amer. Chem. Soc.*, 1964, **86**, 3930.
[10] N. D. Jones and R. E. Marsh, *Acta Cryst.*, 1962, **15**, 809.
[11] A. Hanson, *Acta Cryst.*, 1963, **16**, 1147.
[12] D. S. Brown, S. C. Wallwork, and A. Wilson, *Acta Cryst.*, 1964, **17**, 168.
[13] S. C. Wallwork, *J. Chem. Soc.*, 1961, 494.

study charge-transfer complexes in solution.[14,15] *A priori* it must be possible to obtain information about the structure of a complex from chemical-shift measurements. However, the origin of the changes in position of n.m.r. signals by complexation is not fully understood.[16,17]

Generally the shift in position of the acceptor signal is recorded in solutions in which the donor is in large excess.[15] The acceptor signal moves to higher field on complexation. By analogy with the contributions to the solvent shift for solute molecules,[18] the shift of the acceptor protons in pure complex δ^A_{AD} relative to the shift of the pure acceptor in solution δ^A_0 can be expressed by equation (1). Here $-\delta^c_w$ is the difference between

$$\delta^A_0 - \delta^A_{AD} = \Delta_0 = \delta^c_w + \delta^c_e + \delta^c_a \qquad (1)$$

the contribution of dispersion forces to the chemical shift of the acceptor in the complex and the acceptor in solution.

$-\delta^c_e$ Is the difference between the contribution of an electric field (the 'reaction field' generated by a permanent dipole, *e.g.*, the dipole of the complex) to the chemical shift of the acceptor in complex and the acceptor in solution.

It has been reported[19] that, in addition to charge-transfer forces, a considerable part of the stabilisation energy and dipole moment of the complex may be due to polarisation of the donor by local dipoles of the acceptor.

$-\delta^c_a$ Arises from the anisotropy in the molecular susceptibility of the donor molecule in the complex. A comprehensive list of calculated shielding contributions, based on the Johnson–Bovey equations,[20] for protons at various orientations relative to a benzene ring provides the possibility for an estimation of δ^c_a in complexes with aromatic donor molecules and varying conformations.[21]

With normal intermolecular distances for the trinitrobenzene–benzene complex an upfield shift of approximately 0·4 p.p.m. is calculated (see below) for various positions of the components in the complex. For complexes of several methylbenzenes an approximately constant value of Δ_0 (1·1 p.p.m.) is observed.[15] So a substantial part of the shift should arise from the contributions δ^c_e and δ^c_w. That ring currents are important, however, is apparent from the large Δ_0 value (1·7 p.p.m.) for the complex of trinitrobenzene and α-methylnaphthalene.[22]

If in a set of similar complexes in the same solvent dispersion interactions, polarisation forces, and charge-transfer interactions remain constant, then the contributions of δ^c_e and δ^c_w to Δ_0 remain constant, and we can write equation (2). Here Δ_i is the constant contribution

$$\Delta_0 = \Delta_i + \Delta_a \qquad (2)$$

of the interactions mentioned above and Δ_a is the contribution to Δ_0 of ring-current effects.

Based on this assumption the following approximation was used in a study of the structure of charge-transfer complexes. In several series of complexes with simple aromatic and comparable biphenyl donors, those biphenyl complexes were selected by analysis of equilibrium constants in which the presence of an extra aromatic ring does not vary the structure of the complex. In those cases differences in Δ_0 found for biphenyl and comparable ' half ' molecules (simple aromatic molecules) can be wholly ascribed to the ring-current influence of the added ring, and can be compared with values calculated for various structural models.

Our investigations concern complexes with trinitrobenzene, picric acid, or fluoroanil as acceptor. As donor molecules were used methylbenzenes, biphenyl or methylbiphenyls, and the corresponding methoxy-derivatives, anisole, methylanisoles, or methyl-4,4'-dimethoxybiphenyls.

EXPERIMENTAL

The methylbenzenes were commercial samples generally of high purity and were used as such or freshly distilled. The anisoles were prepared from their corresponding phenols by methylation with dimethyl sulphate. The biphenyls were prepared from the corresponding bromobenzenes or -anisoles by the procedure described;[23] their purity was checked by m.p., refractive index, and n.m.r.

Trinitrobenzene was recrystallized twice from ethanol and once from carbon tetrachloride and had m.p. 124—124·5 °C. Picric acid, recrystallized twice from water, had m.p. 123—124 °C. Fluoranil, twice sublimed *in vacuo*, had m.p. 178 °C.

All n.m.r. spectra were measured at 20 °C with a Varian HA 100 spectrometer. [1]H N.m.r. spectra were measured at 100 MHz with 5% tetramethylsilane as internal reference. The estimated accuracy of the line positions is 0·2 Hz. [19]F N.m.r. spectra were measured at 94·102 MHz. In this case a concentrated solution of fluoranil in dichloroethane was used as external reference. Changes in the line position of the acceptor were measured with the sideband technique. The estimated accuracy is 1 Hz.

Initial association constants (K^{AD}) and values of Δ_0 were calculated by the method described[15] from relation (3)

$$\Delta/[D_0] = -K^{AD}\Delta + K^{AD}\Delta_0 \qquad (3)$$

[14] M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, 1964, **68**, 811.
[15] R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, 1965, **61**, 1626.
[16] A. A. Sandoval and M. W. Hanna, *J. Phys. Chem.*, 1966, **70**, 1202.
[17] R. Foster and C. A. Fyfe, in ' Progress in Nuclear Magnetic Resonance Spectroscopy,' vol. IV, eds. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon, London, 1969.
[18] A. D. Buckingham, T. Schaeffer, and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.

[19] R. J. W. Le Fèvre, D. V. Radford, and P. J. Stiles, *J. Chem. Soc. (B)*, 1968, 1297.
[20] C. E. Johnson and E. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.
[21] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, vol. I, p. 595.
[22] M. D. Johnston, F. P. Gasparro, and F. D. Kuntz, *J. Amer. Chem. Soc.*, 1969, **91**, 5715.
[23] C. E. Castro, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, 1958, **80**, 2332.

in which Δ is the measured value. For the estimation of 95% confidence limits of K^{AD} and Δ_0 equation (4) was used.[14] It was assumed that the error in $1/[D_0]$ is much

$$1/\Delta = (1/K^{AD}\Delta)(1/[D_0]) + 1/\Delta_0 \qquad (4)$$

smaller than that in $1/\Delta_0$, and that the errors are independent.[24]

The concentrations of the acceptors trinitrobenzene, picric acid, and fluoranil were 4×10^{-3}, 6×10^{-3}, and 6×10^{-3}M respectively.

For strong complexes ($K^{AD} > 5$) the concentrations of the donors were in the range 0·02—0·6M. For the complexes with $K^{AD} < 5$ the concentrations of the donors varied between 0·16 and 1·4M.

In all cases the data plotted according to equation (3) provided straight lines, indicating the absence of termolecular complexes.[25] Carbon tetrachloride, distilled before use, was used as solvent. U.v. and visible spectra were recorded with a Beckman DK2A spectrophotometer.

RESULTS AND DISCUSSION

The results are compiled in Tables 1—5.

Association Constants.—For the complexes of all three acceptors with the anisoles and benzenes, an

TABLE 1

Values of K^{AD}_r for donor–trinitrobenzene complexes in carbon tetrachloride at 20 °C, together with the chemical shift of the measured nucleus in solutions of the pure complex relative to the chemical shift in solution of the pure acceptor (Δ_0)

Donor	$K^{AD}_r/$ kg mol^{-1}	Δ_0/Hz	$10^{-4}\nu_{CT}/$ cm^{-1}
(1) Anisole	1·56 ± 0·12	91 ± 5	2·80
(2) 2-Methylanisole	1·99 ± 0·17	101 ± 6	2·71
(3) 3-Methylanisole	2·01 ± 0·09	95 ± 3	2·70
(4) 4-Methylanisole	2·94 ± 0·34	82 ± 6	2·62
(5) 2,3-Dimethylanisole	2·42 ± 0·15	100 ± 4	2·64
(6) 2,4-Dimethylanisole	2·94 ± 0·18	93 ± 3	2·54
(7) 2,5-Dimethylanisole	3·06 ± 0·19	91 ± 4	2·58
(8) 2,6-Dimethylanisole	2·54 ± 0·17	81 ± 2	2·82
(9) 3,4-Dimethylanisole	3·45 ± 0·12	89 ± 2	2·56
(10) 3,5-Dimethylanisole	3·17 ± 0·36	85 ± 5	2·63 [a]
(11) 2,4,6-Trimethylanisole	3·20 ± 0·18	80 ± 2	2·75
(12) 4,4'-Dimethoxybiphenyl [b]			2·32
(13) 2,2'-Dimethyl-4,4'-dimethoxybiphenyl	3·17 ± 0·17	56 ± 2	2·52
(14) 3,3'-Dimethyl-4,4'-dimethoxybiphenyl	9·32 ± 0·70	111 ± 4	2·22
(15) 2,2',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl	2·11 ± 0·37	65 ± 5	2·43
(16) 2,2',6,6'-Tetramethyl-4,4'-dimethoxybiphenyl	2·30 ± 0·23	41 ± 3	2·55
(17) 3,3',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl	8·49 ± 0·19	99 ± 1	2·43

[a] Shoulder, value inaccurate. [b] Too insoluble to measure.

increase in K^{AD} with increasing methylation of the donor component is observed. Methyl substitution

lowers the ionisation potential of a donor and hence increases its electron-donating ability.[26,27] The values of the association constants for the complexes of donor 8 are lower than those of its isomers; also with (11) as a donor low K^{AD} values are found. In addition the

TABLE 2

Values of K^{AD}_r and Δ_0 for the complexes of picric acid with some of the donors of Table 1, measured in CCl$_4$ at 20 °C

Donor	$K^{AD}_r/$ kg mol^{-1}	Δ_0/Hz
(1) Anisole	1·82 ± 0·15	88 ± 3
(2) 2-Methylanisole	2·08 ± 0·18	98 ± 4
(3) 3-Methylanisole	2·13 ± 0·15	89 ± 3
(5) 2,3-Dimethylanisole	3·13 ± 0·15	95 ± 3
(8) 2,6-Dimethylanisole	2·29 ± 0·15	77 ± 2
(9) 3,4-Dimethylanisole	3·52 ± 0·20	89 ± 2
(10) 3,5-Dimethylanisole	4·04 ± 0·32	77 ± 3
(11) 2,4,6-Trimethylanisole	3·19 ± 0·14	72 ± 1
(13) 2,2'-Dimethyl-4,4'-dimethoxybiphenyl	2·49 ± 0·11	54 ± 1
(14) 3,3'-Dimethyl-4,4'-dimethoxybiphenyl	9·48 ± 0·78	102 ± 4
(15) 2,2',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl	1·80 ± 0·22	65 ± 4
(16) 2,2',6,6'-Tetramethyl-4,4'-dimethoxybiphenyl	2·37 ± 0·22	35 ± 2
(17) 3,3',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl	7·17 ± 0·45	97 ± 3

values of ν_{CT} are relatively large in these complexes. In these donors the methoxy-group is forced out of the plane of the benzene ring.[28-31] The conjugation of the methoxy-group with the benzene ring is reduced by this effect, so the ionisation potential is increased.

The values of K^{AD} of the complexes of the non-hindered biphenyl donors [(14), (17), (31), (32), and (33)] are 3—4 times as large as the values of K^{AD} for the complexes of the corresponding 'half' molecules [(2), (8), (19), and (20)]. These donors have a much lower ionisation potential owing to a substantial increase in the π-system. In addition there might be a statistical factor involved,[26,32] because of the presence of two donor sites in the biphenyl moiety. In the present case, however, the two phenyl rings are conjugated and in close proximity. Hence the statistical factor will be close to unity. For the o-methylbiphenyls [(13), (15), (16), (34), (35), and (36)] a coplanar conformation is no longer possible. The conjugation between the two benzene rings is considerably reduced. The ionisation potential of these donors is higher and hence the association constant smaller.

A second effect on the association constant in the hindered biphenyls is due to a restriction of close approach between donor and acceptor in the conformation most suitable for charge-transfer. This may be called

[24] W. H. Laarhoven and R. J. F. Nivard, *Rec. Trav. chim.*, 1965, **84**, 1478.

[25] B. Dodson, R. Foster, A. A. S. Bright, M. I. Foreman, and J. Gorton, *J. Chem. Soc. (B)*, 1971, 1283.

[26] P. H. Emslie, R. Foster, J. W. Morris, and D. E. Twiselton, *J. Chem. Soc. (B)*, 1969, 1161.

[27] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.

[28] J. P. Schaefer and T. J. Miraglia, *J. Amer. Chem. Soc.*, 1964, **86**, 64.

[29] A. Balasubramanian, J. C. Pearden, W. F. Forbes, and N. F. Cheetham, *Canad. J. Chem.*, 1965, **43**, 2603.

[30] M. J. Aroney, M. G. Cortfield, and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1964, 2954.

[31] A. Zweig, *J. Phys. Chem.*, 1963, **67**, 506.

[32] R. Foster and H. A. S. Payne, *Rec. Trav. chim.*, 1971, **90**, 630.

TABLE 3

Values of K^{AD}_r, Δ_0, and ν_{CT} for the complexes of trinitrobenzene with various donors, measured in CCl$_4$ at 20 °C

Donor	K^{AD}_r/kg mol^{-1}	Δ_0/Hz	$10^{-4}\nu_{CT}$/cm^{-1}	K^{AD}_r/kg mol^{-1}	Δ_0/Hz
(19) Benzene	0.59 ± 0.03	126 ± 4	3.54	0.58 [a]	126 [b]
(20) Toluene	0.95 ± 0.04	111 ± 3	3.27	0.80 [a]	120 [b]
(21) o-Xylene	1.28 ± 0.18	109 ± 8	3.18	1.34 [a]	112 [b]
(22) m-Xylene	1.36 ± 0.06	101 ± 2	3.18	1.26 [a]	108 [b]
(23) p-Xylene	1.22 ± 0.08	104 ± 3	3.19	1.13 [a]	113 [b]
(24) Mesitylene	1.72 ± 0.18	97 ± 5	3.00	1.60 [a]	102 [b]
(25) 1,2,4-Trimethylbenzene	2.03 ± 0.29	104 ± 6	3.07	1.98 [a]	102 [b]
(26) 1,2,3-Trimethylbenzene	2.11 ± 0.11	107 ± 4	3.09	1.88 [a]	108 [b]
(27) 1,2,4,5-Tetramethylbenzene	2.84 ± 0.28	102 ± 5	2.94	2.74 [a]	103 [b]
(28) 1,2,3,5-Tetramethylbenzene	3.27 ± 0.06	98 ± 2	2.87	2.85 [a]	112 [b]
(29) Pentamethylbenzene	5.11 ± 0.22	104 ± 2	2.67	4.07 [a]	110 [b]
(30) Hexamethylbenzene	7.51 ± 0.66	109 ± 5	2.53	6.90 [a]	108 [b]
(31) Biphenyl	1.75 ± 0.14	130 ± 5	3.03 [d]	1.7 [c]	
(32) 3,3'-Dimethylbiphenyl	3.80 ± 0.18	119 ± 3	2.74	3.4 [c]	
(33) 4,4'-Dimethylbiphenyl	4.41 ± 0.23	117 ± 3	2.63	4.1 [c]	
(34) 2,2'-Dimethylbiphenyl	1.03 ± 0.07	87 ± 4	3.17	0.7 [c]	
(35) 2,2',4,4',6,6'-Hexamethylbiphenyl	0.37 ± 0.02	80 ± 4	2.94	<0.2 [c]	
(36) 2,2',6,6'-Tetramethylbiphenyl	0.43 ± 0.02	76 ± 4	3.12	<0.2 [c]	

[a] Data from ref. 26, converted to 20 °C with published values of ΔH from ref. 36. Values of ΔH for isomers were taken equal. [b] Calculated from data of ref. 26 at 100 MHz. [c] Calculated from data of ref. 26, expressed in kg mol^{-1} at 20 °C. [d] Determined from a plot of the values of ν_{CT} against the photoionisation potentials of the methylbenzenes (R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc.*, 1960, *A*, **528**, 459). The photoionisation potential of biphenyl is 8.27 eV (K. Watanabe, T. Nakayama, and J. Matte, *J. Quantum Spectroscopy Radiation Transfer*, 1962, **2**, 369).

TABLE 4

Values of K^{AD}_r and Δ_0 for the complexes of picric acid with some of the donors of Table 3, measured in CCl$_4$ at 20 °C

| Donor	K^{AD}_r/kg mol^{-1}	Δ_0/Hz
(19) Benzene	0.63 ± 0.04	131 ± 6
(22) m-Xylene	1.29 ± 0.12	112 ± 4
(23) p-Xylene	1.20 ± 0.09	119 ± 4
(24) Mesitylene	1.86 ± 0.15	101 ± 4
(25) 1,2,4-Trimethylbenzene	1.68 ± 0.12	113 ± 3
(27) 1,2,4,5-Tetramethylbenzene	2.68 ± 0.14	106 ± 3
(30) Hexamethylbenzene	6.34 ± 0.27	101 ± 2
(31) Biphenyl	1.94 ± 0.09	130 ± 2
(32) 3,3'-Dimethylbiphenyl	3.02 ± 0.21	126 ± 4
(33) 4,4'-Dimethylbiphenyl	3.88 ± 0.38	122 ± 6
(34) 2,2'-Dimethylbiphenyl	0.97 ± 0.15	92 ± 9
(36) 2,2',6,6'-Tetramethylbiphenyl	0.37 ± 0.06	88 ± 6

TABLE 5

Values of K^{AD}_r, Δ_0 (for ^{19}F resonance), and ν_{CT} for complexes formed between fluoranil and some donors in carbon tetrachloride at 20 °C

Donor	K^{AD}_r/kg mol^{-1}	Δ_0/Hz	$10^{-4}\nu_{CT}$/cm^{-1}
(1) Anisole	1.41 ± 0.10	277 ± 11	2.34
(2) 2-Methylanisole	2.21 ± 0.15	242 ± 8	2.24
(3) 3-Methylanisole	2.82 ± 0.24	337 ± 17	2.23
(4) 4-Methylanisole	3.19 ± 0.37	305 ± 25	2.12
(5) 2,3-Dimethylanisole	4.96 ± 0.46	300 ± 16	a
(6) 2,4-Dimethylanisole	3.75 ± 0.26	327 ± 15	1.98
(7) 2,5-Dimethylanisole	3.95 ± 0.33	330 ± 19	2.06
(8) 2,6-Dimethylanisole	1.79 ± 0.12	297 ± 15	2.53
(9) 3,4-Dimethylanisole	3.83 ± 0.32	352 ± 16	2.01
(10) 3,5-Dimethylanisole	4.62 ± 0.39	350 ± 20	a
(11) 2,4,6-Trimethylanisole	2.92 ± 0.50	316 ± 28	2.37
(12) 4,4'-Dimethoxybiphenyl [b]			1.82
(13) 2,2'-Dimethyl-4,4'-dimethoxybiphenyl	3.13 ± 0.28	278 ± 18	2.12
(14) 3,3'-Dimethyl-4,4'-dimethoxybiphenyl	10.5 ± 3.0	195 ± 40	1.69
(15) 2,2',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl	1.91 ± 0.16	283 ± 20	1.94
(16) 2,2',6,6'-Tetramethyl-4,4'-dimethoxybiphenyl	2.36 ± 0.24	323 ± 26	2.14
(17) 3,3',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl	6.39 ± 0.45	289 ± 15	1.91

[a] The position of the lowest-energy charge-transfer band could not be determined owing to strong overlap with the high energy charge-transfer band. [b] Too insoluble to measure.

the primary steric effect.[23,26] Similar reductions in the value of the association constant have been observed in complexes of tetracyanoethylene with a series of alkylated 4,4'-dimethoxystilbenes having increasing lack of coplanarity.[24]
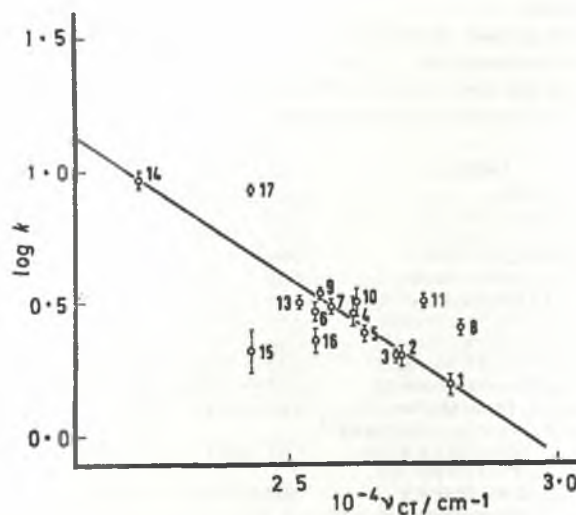
FIGURE 1 Plots of log K for a series of trinitrobenzene complexes against the energy (ν_{CT}) of the charge-transfer transition; data from Table 1

Figures 1—3 show plots of log K against the energy ν_{CT} of the charge-transfer transition (generally proportional to the ionisation potential) for several series of complexes (data from Tables 1—3). The straight lines drawn in the Figures are calculated, the results for the non-planar donors [(8) and (11) in the anisole, (13), (15), (16), (17), (34), (35), and (36) in the biphenyl series] being neglected. Correlation coefficients are 0.984, 0.981, and 0.971, respectively.

Flurry introduced a semi-empirical molecular orbital

theory for charge-transfer complexes.[33,34] The charge-transfer interaction between donor and acceptor was assumed to arise primarily from the interaction of the highest occupied MO of the donor $(HOMO)_D$ with the lowest empty MO of the acceptor $(LEMO)_A$. The resulting complex orbital ψ_{DA} is assumed to be a linear
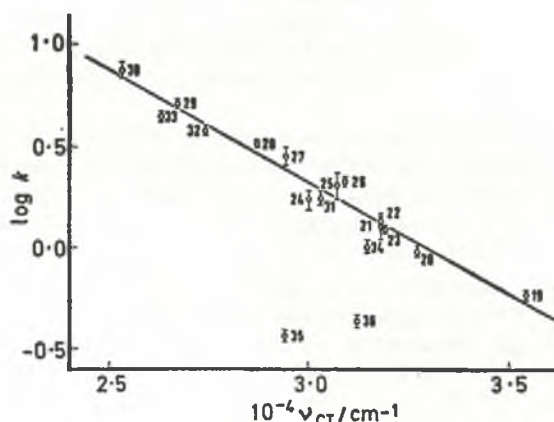

FIGURE 2 Plots of log K for a series of trinitrobenzene complexes against the energy (ν_{CT}) of the charge-transfer transition; data from Table 3
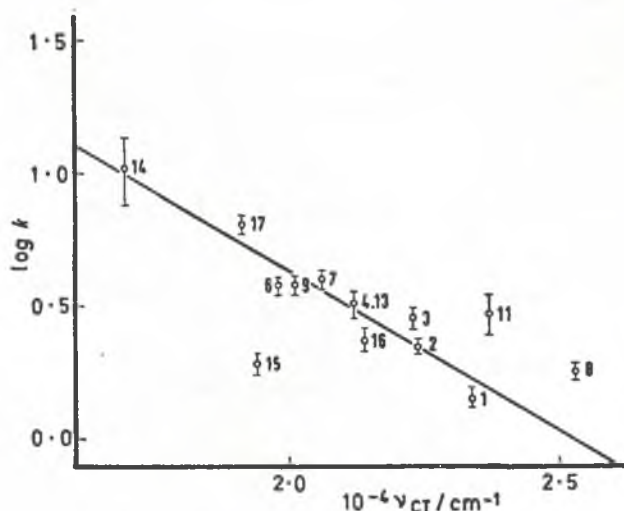

FIGURE 3 Plots of log K for a series of fluoranil complexes against the energy (ν_{CT}) of the charge-transfer transition; data from Table 5

combination (5) of these MO's. The stabilisation

$$\psi_{DA} = a\phi_D + b\phi_A \qquad (5)$$

energy of a complex may be expressed [33] as in (6).

$$E_{stab} = b^2 D - b^2 A - 2ab\beta_{DA} + b^2 Ves \qquad (6)$$

D Is the energy of the $(HOMO)_D$ and A is the energy of the $(LEMO)_A$. β_{DA} Is an energy term containing the resonance interaction between donor and acceptor. $-Ves$ Is the contribution of the Coulomb energy.

[33] R. L. Flurry, *J. Phys. Chem.*, 1965, **69**, 1927.
[34] R. L. Flurry, *J. Phys. Chem.*, 1969, **73**, 2111.
[35] G. Briegleb, ' Electronen–Donator–Acceptor–Komplexe,' chap. IX, Springer-Verlag, Berlin–Göttingen–Heidelberg, 1961.

Flurry did not take into consideration the stabilisation by polarisation and dispersion forces, which can be accounted for by an extra no-bond energy term G_0 as in equation (7).

$$E_{stab} = b^2 D - b^2 A - 2ab\beta_{DA} + b^2 Ves + G_0 \qquad (7)$$

Several authors [35] found that for many series of complexes containing similar donors with the same acceptor the stability (equilibrium constants) of the complexes are linearly related to the ionisation potential or the energy of the charge-transfer transition, but are on the whole rather independent of other factors. Therefore, it seems justified to assume that in such series the degree of charge-transfer, β_{DA}, Ves, and G_0 remain nearly constant. Thus we obtain equation (8),

$$E_{stab} = b^2 D + C_1 \qquad (8)$$

where C_1 is constant. If in such series of complexes variations in the equilibrium constant K^{AD} are mainly due to changes in energy rather than in entropy or the entropy changes linearly with the enthalpy,[36] ΔG is proportional to ΔH for the whole series and we may write equation (9). According to Koopmans'

$$RT \ln K \approx b^2 D + C_1 \qquad (9)$$

theorem $-D$ is equal to the ionisation potential I_P of the donor.[37] Thus we obtain equation (10). Because

$$RT \ln K \approx b^2 I_p + C_1 \qquad (10)$$

the linear relationships, found for most complexes with anisoles or methylbenzenes as donors, also include complexes with corresponding biphenyl derivatives, it seems justified to assume that charge-transfer and no-bond interactions in biphenyl complexes are similar to those in complexes with corresponding half-molecules. In that case, the assumption that Δ_i [in equation (2)] does not vary by introduction of a phenyl residue in a donor will be correct. Changes in Δ_0 will then only be due to differences in Δ_a, caused by the anisotropy of the phenyl residue introduced.

It is clear that within a series of complexes with the same acceptor and only anisoles or methylbenzenes as donors Δ_a ought to be almost constant, as found.

Finally, the deviations from the linear relationship found in Figures 1—3 for the hindered biphenyls (13), (15), (16), and (34), (35), and (36) can be ascribed to the primary steric effect. Obviously the steric requirements of fluoranil are smaller than those of trinitrobenzene; the deviations are smaller in Figure 3 than in Figure 1. According to expectation, (35) and (36) deviate more than (34), and (16) more than (13). However, the deviation of (15) both with fluoranil and trinitrobenzene is surprisingly large.

[36] For complexes of trinitrobenzene with the methylbenzenes ΔS is approximately constant, while for the complexes of fluoranil ΔS varies considerably but almost linearly with ΔH; M. I. Foreman, R. Foster, and C. A. Fyfe, *J. Chem. Soc. (B)*, 1970, 528.
[37] T. Koopmans, *Physica*, 1933, **1**, 104.

All other deviations [(8), (11), (17)], remarkably enough in the opposite direction, concern donors in which a methoxy-group is enclosed between two methyl substituents. Foster et al.[26] reported a non-linear relation
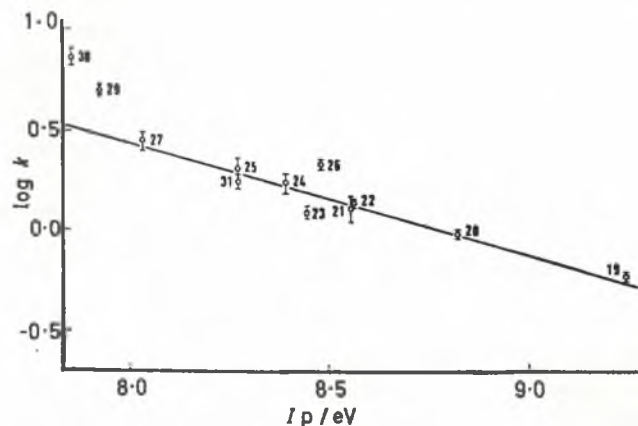

FIGURE 4 Plots of log K for a series of trinitrobenzene complexes against the ionisation potentials (I_p) of the donors. The numbering corresponds to the donors listed in Table 3

between log K values and ionisation potentials for complexes between trinitrobenzene and methylbenzenes. A similar plot (Figure 4) reveals that the deviations concern just those donors in which at least three vicinal methyl substituents are present (1,2,3-trimethyl- and especially pentamethyl- and hexamethyl-benzene) whereas, e.g., biphenyl falls on the straight line. (I_p values are determined by photoionisation.)

Crowding of substituents in the donor may cause changes in Coulomb and resonance interaction within a series of otherwise similar complexes.* For complexes of such donors, the supposition that the contribution of Δ_i to Δ_0 [equation (2)] is constant will not be fully justified.

A second argument can be derived from a comparison between K^{AD} values for complexes with varying acceptors. Generally the trinitrobenzene complexes with methoxy-substituted donors have smaller K^{AD} values than those of picric acid, but with methylated donors (benzenes or biphenyls) the difference is very small or even in the opposite direction. This may be explained by hydrogen bonding between the acidic proton of picric acid and the ether oxygen of the methoxy-group. With donors (8), (11), and (17) this trend is not found; clearly the acidic proton cannot approach the methoxy-group sufficiently.

Proton Δ_0 Values.—For reasons mentioned above it is expected that within a series of complexes with the same acceptor and similar donors, an almost constant value of Δ_0 will be observed, so long as the variation in the donors causes no primary steric effect or accumulation

of vicinal substituents in the donors. Tables 1—4 show that this expectation is justified.

For the complexes of trinitrobenzene with the anisoles (1)—(10), excluding (8), an average value of Δ_0 (Δ_0^{av}) of 92 Hz is found. Corresponding results are observed for the other series: for picric acid complexes of anisoles Δ_0^{av} is 89 Hz (almost equal to the value for trinitrobenzene complexes), and for trinitrobenzene and picric acid complexes of the methylbenzenes Δ_0^{av} is 105 and 112 Hz respectively.

Because in these series Δ_i and Δ_a remain constant no information about the structure of the complexes can be obtained from these data. With the help of tables [21] values of Δ_a can be calculated for several models (Figure 5). The results show that, so long as a parallel orientation is maintained, Δ_a is almost insensitive to displacements of the acceptor relative to the donor.

For the calculations a distance between donor and acceptor of 3·3 Å is taken, as found in solid complexes; [12,13] the C–H bond-length is 1·09 Å and the radius of the benzene ring 1·39 Å. In structure (II) the displacement relative to (I) is 1·09 Å (a C–H bond-length) and in (III) 2·13 Å. Apparently the influence of ring currents (Δ_a) is less than half the total effect Δ_0.

Because the complexes of the non-hindered biphenyl derivatives are similar to those of the corresponding 'half' molecules, the increase in the Δ_0 values for the
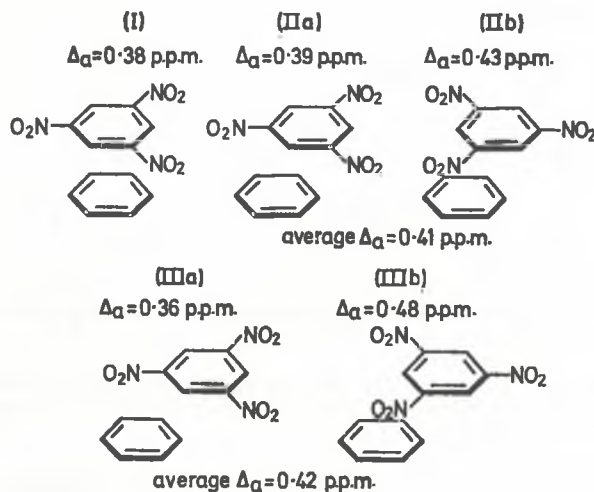

FIGURE 5 Various model structures for a trinitrobenzene–benzene complex

biphenyl complexes can be ascribed to an extra ring-current effect (Δ_a^e) of the second ring (11).

$$\Delta_0 = \Delta_i + \Delta_a + \Delta_a^e \qquad (11)$$

Table 6 compares the Δ_0 values of the various biphenyl complexes and the Δ_0^{av} of the corresponding 'half' molecules. For the non-hindered biphenyl donors (14), (31), (32), and (33) $\Delta_0 - \Delta_0^{av} = \Delta_a^e$ is 18 ± 1 Hz in the trinitrobenzene series and 14 ± 1 in the picric acid series. From calculations of Δ_a^e for

* In a plot of ν_{CT} values of the trinitrobenzene complexes with the methylbenzenes against I_p of the donors, (29) and (30) are found to deviate substantially. This corroborates the argument that the deviations are due to variations in the energy terms mentioned.

three models [Figure 6; formulae (IV), (V), and (VI), corresponding with (I), (II), and (III), respectively] it appears that the experimental values of Δ_a^e agree quite well with the one calculated for (IV) (16 Hz, Table 7). The deviations for (V) and (VI) are appreciable. For the calculations the same parameters were used as above. The angle of twist of the non-hindered biphenyl is taken[38] as 20° and the central C–C bondlength[39] as 1·48 Å.

Because of the similarity between the complexes of the non-hindered biphenyls and their corresponding 'half' molecules it seems very probable that in both cases an aromatic ring of the donor and the aromatic

TABLE 6

Comparison of the Δ_0 values of the biphenyl complexes of trinitrobenzene and picric acid with the average values of Δ_0 (Δ_0^{av}) of their corresponding 'half' molecules

Acceptor, trinitrobenzene

	$\Delta_0/$ Hz	$\Delta_0^{av}/$ Hz	$\Delta_0 - \Delta_0^{av}/$ Hz
(13) 2,2'-Dimethyl-4,4'-dimethoxy-biphenyl	56	92	−36
(14) 3,3'-Dimethyl-4,4'-dimethoxy-biphenyl	111	92	+19
(15) 2,2',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl	65	92	−27
(16) 2,2',6,6'-Tetramethyl-4,4'-dimethoxybiphenyl	41	92	−51
(17) 3,3',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl	99	81[b]	+18
(31) Biphenyl (32) 3,3'-Dimethylbiphenyl (33) 4,4'-Dimethylbiphenyl	122[a]	105	+17
(34) 2,2'-Dimethylbiphenyl	87	105	−18
(35) 2,2',4,4',6,6'-Hexamethyl-biphenyl	80	105	−25
(36) 2,2',6,6'-Tetramethylbiphenyl	76	105	−29

Acceptor, picric acid

(13) 2,2'-Dimethyl-4,4'-dimethoxy-biphenyl	54	89	−35
(14) 3,3'-Dimethyl-4,4'-dimethoxy-biphenyl	102	89	+13
(15) 2,2',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl	65	89	−24
(16) 2,2',6,6'-Tetramethyl-4,4'-dimethoxybiphenyl	35	89	−54
(17) 3,3',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl	97	77[b]	20
(31) Biphenyl (32) 3,3'-Dimethylbiphenyl (33) 4,4'-Dimethylbiphenyl	126[a]	112	14
(34) 2,2'-Dimethylbiphenyl	92	112	−20
(36) 2,2',6,6'-Tetramethylbiphenyl	88	112	−24

[a] Average value of (31), (32), (33). [b] Δ_0 Of the corresponding 2,6-dimethylanisole complex.

ring of the acceptor have a coaxial conformation, in agreement with Mulliken's principle of maximum overlap.

On account of the discussion of K values a completely analogous structure for the complexes of donor (17) (in which the methoxy-group is flanked by two methyl substituents) is not certain. However, a comparison with the complexes of 2,6-dimethylanisole reveals a difference in Δ_0 values (19 ± 1) similar to those of the complexes discussed above. Consequently, also in

this case the structure can probably be described by model (IV), possibly with a preference for conformation (IVa).

In the complexes of the hindered biphenyls the structure is influenced by a primary steric effect, so less

TABLE 7

Calculated values of $\Delta_a^e/$Hz at 100 MHz for various conformations and angles of twist of the biphenyl donors

Angle of twist	0°	20°	70°	90°
Structure (IVa)		20	−13	−17
Structure (IVb)		12	−3	−7
Average Δ_a^e in (IV)		16	−5	−12
Structure (Va)		+6	−9	−11
Structure (Vb)		+3	−1	−7
Average Δ_a^e in (V)		+4·5	−5	−9
Structure (VI)	+42			

straightforward conclusions about the structure can be drawn.

Table 6 shows that Δ_0 values are substantially smaller than Δ_0^{av} of the corresponding 'half' molecules. The
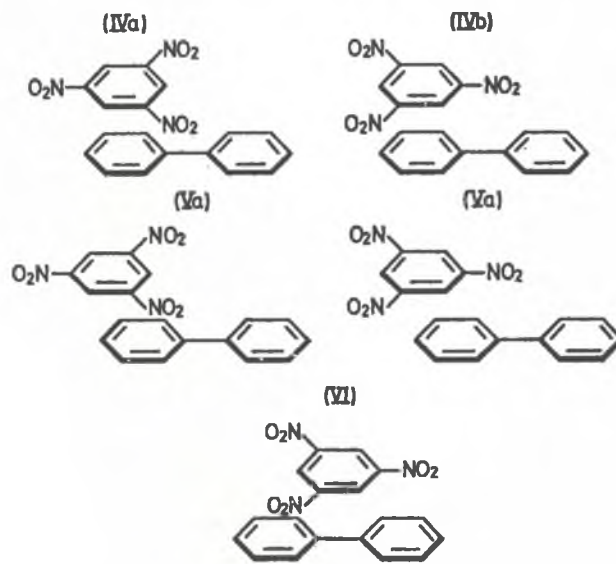

FIGURE 6   Various model structures for a trinitrobenzene-biphenyl complex

experimental values of $|\Delta_0 - \Delta_0^{av}|$ are much larger than is calculated for models (IV) and (V), even if a much larger angle of twist (70 or 90°) is taken[38] (Table 7).

Owing to these large angles of twist in the biphenyl donors the acceptor position will be approximately as in (V) [possibly with a preference for (Va)]. Such a change in conformation of the complex causes undoubtedly changes in Δ_i, which would also contribute to the relatively low Δ_0 values.

Remarkably, the values of Δ_0 of the hindered biphenyls decrease more if the donor possesses a 4-methoxy-group [compare (13) with (34), and (16) with (35) and (36)].

[38] H. Suzuki, *Bull. Chem. Soc. Japan*, 1959, **32**, 1350.
[39] O. Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408.

On the contrary the primary steric effect is smaller for (13) and (16) (Figures 1—3).

In conformation (V) the acceptor interacts primarily with the 3-, 4-, and 5-positions of the biphenyl donor. When a methoxy-group is substituted in the 4-position, there may be a strong local interaction of the acceptor with the methoxy-group. Moreover, there is a high electron density at the 3- and 5-positions owing to the mesomeric effect of the methoxy-group. Both effects enhance charge-transfer interactions in the complexes of the hindered methoxy-substituted biphenyls. The local interaction of the acceptor with the methoxy-group might result in an extra decrease in Δ_i in addition to the decrease caused by the change in structure of the complex.

Fluorine Δ_0 *Values.*—The Δ_0 values of fluoranil complexes (^{19}F resonance) are about three times sa large as the corresponding values (^{1}H resonance) of trinitrobenzene or picric acid complexes. ^{19}F Chemical shifts are, however, much more dependent on changes in charge density than proton shifts [40] and rather insensitive to variations in ring-current effects.

Therefore, the differences in Δ_0 for various complexes are due to differences in Δ_i rather than in Δ_a and less apt for a study as in this paper.

[40] A. Saika and C. P. Slichter, *J. Chem. Phys.*, 1954, **22**, 26.