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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

By H. J. M. Andriessen,* W. H. Laarhoven, and R. J. F. Nivard, Department of Organic Chemistry, Catholic University, Toernooiveld, Nijmegen, The Netherlands
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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 (A₀) is found than for the complexes of the corresponding substituted benzenes. It is shown that this increase in $\Delta_A$ 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. Since Mulliken founded a theoretical basis for the quantum-mechanical description of charge-transfer interaction and formulated his 'overlap and orientation' principle there has been considerable discussion about the structure of charge-transfer complexes in solution.

The crystal structures of a number of complexes between $\pi$-donors and $\pi$-acceptors are known. 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 chloranil-hexamethylbenzene complex in solution might not be superimposed. 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

study charge-transfer complexes in solution.\textsuperscript{14,15} A \textit{priorty} 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.\textsuperscript{16,17}

Generally the shift in position of the acceptor signal is recorded in solutions in which the donor is in large excess.\textsuperscript{16} The acceptor signal moves to higher field on complexation. By analogy with the contributions to the solvent shift for solute molecules,\textsuperscript{18} the shift of the acceptor protons in pure complex $\delta^{\text{AD}}$ relative to the shift of the pure acceptor in solution $\delta^{\text{a}}$ can be expressed by equation (1). Here $-\delta_w$ is the difference between

$$\delta^{\text{AD}} - \delta^a = \lambda = \delta_w + \delta_w + \delta_a$$

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

$-\delta_w$ is the difference between the contribution of an electric field (the 'reaction field' generated by a permanent dipole, \textit{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\textsuperscript{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.

$-\delta_e$ 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,\textsuperscript{20} for protons at various orientations relative to a benzene ring provides the possibility for an estimation of $\delta_e$ in complexes with aromatic donor molecules and varying conformations.\textsuperscript{21}

With normal intermolecular distances for the trinitrobenzene-benzenzene 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 $\lambda_0$ (1-1 p.p.m.) is observed.\textsuperscript{15} So a substantial part of the shift should arise from the contributions $\delta_e$ and $\delta_w$. That ring currents are important, however, is apparent from the large $\lambda_0$ value (1-7 p.p.m.) for the complex of trinitrobenzene and $\alpha$-methylnaphthalene.\textsuperscript{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 $\delta_e$ and $\delta_w$ to $\lambda_0$ remain constant, and we can write equation (2). Here $\lambda_0$ is the constant contribution

$$\lambda_0 = \lambda + \lambda_0$$

of the interactions mentioned above and $\lambda_0$ is the contribution to $\lambda_0$ 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 $\lambda_0$ 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 fluoranil 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 bromo-derivatives, anisole, methylanisoles, or methyl-4,4'-dimethoxybiphenyls.

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 bromo-derivatives, anisole, methylanisoles, or methyl-4,4'-dimethoxybiphenyls.

Initial association constants ($K^{\text{AD}}$) and values of $\lambda_0$ were calculated by the method described\textsuperscript{18} from relation (3)

$$\Delta [D] = -K^{\text{AD}} + K^{\text{AD}} \lambda_0$$

\textsuperscript{20} C. E. Johnson and E. A. Bovey, J. Chem. Phys., 1958, \textbf{29}, 1012.
in which \( \Delta \) is the measured value. For the estimation of 95% confidence limits of \( K_{AD} \) and \( \Delta \), equation (4) was used.\(^{14}\) It was assumed that the error in \( 1/|D| \) is much smaller than that in \( 1/\Delta \), and that the errors are independent.\(^{24}\)

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

For strong complexes \( (K_{AD} > 5) \) the concentrations of the donors were in the range \( 0.02-0.6\)M. For the complexes with \( K_{AD} < 5 \) the concentrations of the donors varied between \( 0.16-1.4\)M.

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 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 values of \( \omega_{CT} \) 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 \( n \)-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 \( \sigma \)-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

### Table 1

Values of \( K_{AD} \), for donor-trinitrobenzene complexes in carbon tetrachloride at 20 °C, together with the chemical shift of the measured nucleus in solutions of the pure compound relative to the chemical shift in solution of the pure acceptor (\( \Delta \)).

<table>
<thead>
<tr>
<th>Donor</th>
<th>( K_{AD} ) kg mol(^{-1}) ( 10^{4} \omega_{CT} ) cm(^{-1})</th>
<th>( \Delta ) Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Anisole</td>
<td>( 1.56 \pm 0.12 )</td>
<td>( 91 \pm 5 )</td>
</tr>
<tr>
<td>(2) 2-Methylanisole</td>
<td>( 1.99 \pm 0.17 )</td>
<td>( 101 \pm 6 )</td>
</tr>
<tr>
<td>(3) 3-Methylanisole</td>
<td>( 2.01 \pm 0.09 )</td>
<td>( 95 \pm 3 )</td>
</tr>
<tr>
<td>(4) 4-Methylanisole</td>
<td>( 2.94 \pm 0.34 )</td>
<td>( 82 \pm 6 )</td>
</tr>
<tr>
<td>(5) 2,3-Dimethylanisole</td>
<td>( 2.24 \pm 0.18 )</td>
<td>( 93 \pm 3 )</td>
</tr>
<tr>
<td>(6) 2,4-Dimethylanisole</td>
<td>( 2.94 \pm 0.19 )</td>
<td>( 90 \pm 4 )</td>
</tr>
<tr>
<td>(7) 6,5-Dimethylanisole</td>
<td>( 2.04 \pm 0.17 )</td>
<td>( 81 \pm 2 )</td>
</tr>
<tr>
<td>(8) 3,4-Dimethylanisole</td>
<td>( 3.45 \pm 0.12 )</td>
<td>( 89 \pm 2 )</td>
</tr>
<tr>
<td>(9) 3,5-Dimethylanisole</td>
<td>( 3.17 \pm 0.36 )</td>
<td>( 92 \pm 2 )</td>
</tr>
<tr>
<td>(10) 2,4,6-Trimethylanisole</td>
<td>( 3.20 \pm 0.18 )</td>
<td>( 80 \pm 2 )</td>
</tr>
<tr>
<td>(11) 1,3-Dimethoxybiphenyl</td>
<td>( 3.17 \pm 0.17 )</td>
<td>( 56 \pm 2 )</td>
</tr>
<tr>
<td>(12) 2,5-Dimethoxybiphenyl</td>
<td>( 3.32 \pm 0.37 )</td>
<td>( 111 \pm 4 )</td>
</tr>
<tr>
<td>(13) 3,4-Dimethoxybiphenyl</td>
<td>( 2.11 \pm 0.37 )</td>
<td>( 65 \pm 5 )</td>
</tr>
<tr>
<td>(14) 2,2',5,5'-Tetramethoxybiphenyl</td>
<td>( 2.30 \pm 0.43 )</td>
<td>( 41 \pm 1 )</td>
</tr>
<tr>
<td>(15) 2,2',6,6'-Tetramethoxybiphenyl</td>
<td>( 2.49 \pm 0.19 )</td>
<td>( 99 \pm 1 )</td>
</tr>
</tbody>
</table>

* Shoulder, value inaccurate. \(^{b}\) Too insoluble to measure.
Values of $K_{ADr}$, $A_0$ and $\nu_{CT}$ for the complexes of picric acid with some of the donors of Table 3, measured in CCl$_4$ at 20 °C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$K_{ADr}$/kg mol$^{-1}$</th>
<th>$A_0$/Hz</th>
<th>$10^4 \nu_{CT}$/cm$^{-1}$</th>
<th>$K_{APr}$/kg mol$^{-1}$</th>
<th>$A_0$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>(19) Benzene</td>
<td>0.37 ± 0.04</td>
<td>114 ± 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(20) α-Xylene</td>
<td>1.38 ± 0.07</td>
<td>101 ± 2</td>
<td>3.18</td>
<td>1.37 ± 0.04</td>
<td>112 ± 3</td>
</tr>
<tr>
<td>(21) β-Xylene</td>
<td>1.32 ± 0.08</td>
<td>103 ± 4</td>
<td>3.19</td>
<td>1.15 ± 0.03</td>
<td>113 ± 3</td>
</tr>
<tr>
<td>(22) Mesitylene</td>
<td>1.22 ± 0.08</td>
<td>97 ± 5</td>
<td>3.00</td>
<td>1.07 ± 0.04</td>
<td>110 ± 2</td>
</tr>
<tr>
<td>(23) 1,2,4-Trimethylbenzene</td>
<td>2.03 ± 0.29</td>
<td>104 ± 6</td>
<td>3.07</td>
<td>1.89 ± 0.04</td>
<td>102 ± 2</td>
</tr>
<tr>
<td>(24) 1,2,4,5-Tetramethylbenzene</td>
<td>2.84 ± 0.28</td>
<td>102 ± 5</td>
<td>2.94</td>
<td>2.74 ± 0.04</td>
<td>103 ± 2</td>
</tr>
<tr>
<td>(25) 1,2,3,5-Tetramethylbenzene</td>
<td>3.97 ± 0.06</td>
<td>98 ± 1</td>
<td>2.87</td>
<td>2.85 ± 0.04</td>
<td>112 ± 2</td>
</tr>
<tr>
<td>(26) Pentamethylbenzene</td>
<td>5.11 ± 0.22</td>
<td>104 ± 2</td>
<td>2.67</td>
<td>4.07 ± 0.04</td>
<td>110 ± 0</td>
</tr>
<tr>
<td>(27) Hexamethylbenzene</td>
<td>7.51 ± 0.66</td>
<td>109 ± 5</td>
<td>2.53</td>
<td>0.90 ± 0.04</td>
<td>108 ± 0</td>
</tr>
<tr>
<td>(28) Biphenyl</td>
<td>1.75 ± 0.14</td>
<td>130 ± 5</td>
<td>3.03 ± 0.2</td>
<td>1.7 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>(29) 3,3'-Dimethylbiphenyl</td>
<td>3.90 ± 0.18</td>
<td>119 ± 3</td>
<td>2.74</td>
<td>3.4 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>(30) 4,4'-Dimethylbiphenyl</td>
<td>4.41 ± 0.23</td>
<td>117 ± 3</td>
<td>2.63</td>
<td>4.1 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>(31) 2,2'-Dimethylbiphenyl</td>
<td>1.03 ± 0.07</td>
<td>87 ± 4</td>
<td>3.17</td>
<td>0.7 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>(32) 2,2',4,4',6,6'-Hexamethylbiphenyl</td>
<td>0.97 ± 0.02</td>
<td>80 ± 4</td>
<td>2.84</td>
<td>&lt;0.2 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>(33) 3,3'-Dimethylbiphenyl</td>
<td>3.80 ± 0.18</td>
<td>119 ± 3</td>
<td>2.74</td>
<td>3.4 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>(34) 3,3'-Dimethylbiphenyl</td>
<td>3.02 ± 0.21</td>
<td>120 ± 4</td>
<td>3.12</td>
<td>&lt;0.2 ± 0.04</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated from data of ref. 36. Values of $\Delta H$ for isomers were taken equal. $^a$ Data from ref. 26, converted to 20 °C with published values of $\Delta H$ from ref. 36. $^b$ Calculated from data of ref. 26, expressed in kg mol$^{-1}$ at 20 °C. $^c$ Determined from a plot of the values of $\nu_{CT}$ against the photoionisation potentials of the methylbenzenes (R. Brelsford, P. V. Harris, and W. C. Price, Proc. Roy. Soc., 1960, A, 228, 489). The photoionisation potential of biphenyl is 8.27 eV (K. Watanabe, T. Nakayama, J. Quantum Spectroscopy Radiation Transfer, 1962, 2, 369).

Figures 1—3 show plots of log $K$ against the energy $\nu_{CT}$ of the charge-transfer transition; data from Table 1.

Flurry introduced a semi-empirical molecular orbital...
theory for charge-transfer complexes.\textsuperscript{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)\textsubscript{D} with the lowest empty MO of the acceptor (LEMO)\textsubscript{A}. The resulting complex orbital \( \psi_{DA} \) is assumed to be a linear combination (5) of these MO’s. The stabilisation energy of a complex may be expressed\textsuperscript{33} as in (6).

\[
E_{\text{stab}} = b^2D - b^2A - 2ab\beta_{DA} + b^2\Delta v_{es} + G_0 \quad (6)
\]

\( D \) is the energy of the (HOMO)\textsubscript{D} and \( A \) is the energy of the (LEMO)\textsubscript{A}. \( \beta_{DA} \) is an energy term containing the resonance interaction between donor and acceptor. \( -\Delta v_{es} \) is the contribution of the Coulomb energy.

Several authors\textsuperscript{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, \( \beta_{DA}, \Delta v_{es} \), and \( G_0 \) remain nearly constant. Thus we obtain equation (8),

\[
E_{\text{stab}} = b^2D + C_1 \quad (8)
\]

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,\textsuperscript{36} \( \Delta G \) is proportional to \( \Delta H \) for the whole series and we may write equation (9). According to Koopmans’ theorem 

\[
RT \ln K \approx b^2D + C_1 \quad (9)
\]

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 \( \Delta_{\alpha} \) [in equation (2)] does not vary by introduction of a phenyl residue in a donor will be correct. Changes in \( \Delta_{\alpha} \) will then only be due to differences in \( \Delta_{\alpha} \) 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 \( \Delta_{\alpha} \) 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.

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).

\[
E_{\text{stab}} = b^2D - b^2A - 2ab\beta_{DA} + b^2\Delta v_{es} + G_0 \quad (7)
\]

\textsuperscript{36} For complexes of trinitrobenzene with the methylbenzenes \( \Delta S \) is approximately constant, while for the complexes of fluoranil \( \Delta S \) varies considerably but almost linearly with \( \Delta H \); M. I. Foreman, R. Foster, and C. A. Fyfe, \textit{J. Chem. Soc. (B)}, 1970, 528.

\textsuperscript{37} T. Koopmans, \textit{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. reported a non-linear relation between log \( K \) values and ionisation potentials \( (I_p) \) of the donors. The numbering corresponds to the donors listed in Table 3.

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 \( A_i \) to \( A_0 \) [equation (2)] 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 \( \Delta_0 \) 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 \( \Delta_0 \) 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 \( \Delta_0 \) \( (\Delta_0^{av}) \) of 92 Hz is found. Corresponding results are observed for the other series: for picric acid complexes of anisoles \( \Delta_0^{av} \) is 80 Hz (almost equal to the value for trinitrobenzene complexes), and for trinitrobenzene and picric acid complexes of the methylbenzenes \( \Delta_0^{av} \) is 105 and 112 Hz respectively.

Because in these series \( \Delta_i \) and \( \Delta_a \) remain constant no information about the structure of the complexes can be obtained from these data. With the help of tables \( \Delta_0 \) values can be calculated for several models (Figure 5). The results show that, so long as a parallel orientation is maintained, \( \Delta_a \) 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; the C–H bond-length is 1-09 Å and the radius of the benzene ring 1-30 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 \( (\Delta_a) \) is less than half the total effect \( \Delta_0 \).

Because the complexes of the non-hindered biphenyl derivatives are similar to those of the corresponding ‘half’ molecules, the increase in the \( \Delta_0 \) values for the biphenyl complexes can be ascribed to an extra ring-current effect \( (\Delta_a) \) of the second ring (11).

\[
\Delta_0 = \Delta_i + \Delta_a + \Delta_a^{(2)} \quad \text{(11)}
\]

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

* In a plot of \( v_{GP} \) 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 $\Delta_\text{ae}$ 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 \(^{29}\) 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 ring of the acceptor have a coaxial conformation, in agreement with Mulliken's principle of maximum overlap.

### Table 6

Comparison of the $\Delta_\text{a}$ values of the biphenyl complexes of trinitrobenzene and picric acid with the average values of $\Delta_\text{a}$ ($\Delta_\text{av}$) of their corresponding 'half' molecules

<table>
<thead>
<tr>
<th>Acceptor, trinitrobenzene</th>
<th>$\Delta_\text{a}$/Hz</th>
<th>$\Delta_\text{av}$/Hz</th>
<th>$\Delta_\text{a} - \Delta_\text{av}$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>(13) 2,2'-Dimethyl-4,4'-dimethoxy-biphenyl</td>
<td>56</td>
<td>92</td>
<td>-36</td>
</tr>
<tr>
<td>(14) 3,3'-Dimethyl-4,4'-dimethoxy-biphenyl</td>
<td>111</td>
<td>92</td>
<td>+19</td>
</tr>
<tr>
<td>(15) 2,2',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl</td>
<td>65</td>
<td>92</td>
<td>-27</td>
</tr>
<tr>
<td>(16) 2,2',6,6'-Tetramethyl-4,4'-dimethoxybiphenyl</td>
<td>41</td>
<td>92</td>
<td>-51</td>
</tr>
<tr>
<td>(17) 3,3',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl</td>
<td>99</td>
<td>81</td>
<td>+18</td>
</tr>
<tr>
<td>(31) Biphenyl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(32) 3,3'-Dimethylbiphenyl</td>
<td>122</td>
<td>105</td>
<td>+17</td>
</tr>
<tr>
<td>(33) 4,4'-Dimethylbiphenyl</td>
<td>87</td>
<td>105</td>
<td>-18</td>
</tr>
<tr>
<td>(34) 2,2'-Dimethylbiphenyl</td>
<td>80</td>
<td>105</td>
<td>-25</td>
</tr>
<tr>
<td>(35) 2,2',4,4',6,6'-Hexamethylbiphenyl</td>
<td>76</td>
<td>105</td>
<td>-29</td>
</tr>
<tr>
<td>(36) 2,2',5,5'-Tetramethylbiphenyl</td>
<td>54</td>
<td>89</td>
<td>-35</td>
</tr>
<tr>
<td>(14) 3,3'-Dimethyl-4,4'-dimethoxy-biphenyl</td>
<td>102</td>
<td>89</td>
<td>+13</td>
</tr>
<tr>
<td>(15) 2,2',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl</td>
<td>65</td>
<td>89</td>
<td>-24</td>
</tr>
<tr>
<td>(16) 2,2',6,6'-Tetramethyl-4,4'-dimethoxybiphenyl</td>
<td>35</td>
<td>89</td>
<td>-54</td>
</tr>
<tr>
<td>(17) 3,3',5,5'-Tetramethyl-4,4'-dimethoxybiphenyl</td>
<td>97</td>
<td>77</td>
<td>20</td>
</tr>
<tr>
<td>(31) Biphenyl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(32) 3,3'-Dimethylbiphenyl</td>
<td>128</td>
<td>112</td>
<td>14</td>
</tr>
<tr>
<td>(33) 4,4'-Dimethylbiphenyl</td>
<td>92</td>
<td>112</td>
<td>-20</td>
</tr>
<tr>
<td>(34) 2,2'-Dimethylbiphenyl</td>
<td>88</td>
<td>112</td>
<td>-24</td>
</tr>
</tbody>
</table>

* Average value of (31), (32), (33).

### Table 7

Calculated values of $\Delta_\text{a}$/Hz at 100 MHz for various conformations and angles of twist of the biphenyl donors

<table>
<thead>
<tr>
<th>Angle of twist</th>
<th>Structure (IVa)</th>
<th>Structure (IVb)</th>
<th>Average $\Delta_\text{a}$ in (IV)</th>
<th>Average $\Delta_\text{av}$ in (V)</th>
<th>Average $\Delta_\text{av}$ in (VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>+13</td>
<td>-3</td>
<td>16</td>
<td>+5</td>
<td>-12</td>
</tr>
<tr>
<td>20°</td>
<td>-3</td>
<td>+19</td>
<td>-5</td>
<td>-9</td>
<td>+7</td>
</tr>
<tr>
<td>70°</td>
<td>+9</td>
<td>-5</td>
<td>-12</td>
<td>-11</td>
<td>-9</td>
</tr>
<tr>
<td>90°</td>
<td>-3</td>
<td>+17</td>
<td>+45</td>
<td>-5</td>
<td>-9</td>
</tr>
</tbody>
</table>

### Figure 6

Various model structures for a trinitrobenzene-biphenyl complex

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 $\Delta_\text{a}$, which would also contribute to the relatively low $\Delta_\text{a}$ values.

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


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 \( \Delta_i \) in addition to the
decrease caused by the change in structure of the
complex.

**Fluorine \( \Delta_0 \) Values.**—The \( \Delta_0 \) values of fluoranil
complexes (\( ^{19} \text{F} \) resonance) are about three times as
large as the corresponding values (\( ^{1} \text{H} \) resonance) of
trinitrobenzene or picric acid complexes. \( ^{19} \text{F} \) 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 \( \Delta_0 \) for various complexes
are due to differences in \( \Delta_i \) rather than in \( \Delta_a \) and less
apt for a study as in this paper.

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for help in statistical analysis.
