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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

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Nuclear Magnetic Resonance Study of Charge-transfer Complexes of
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By H. J. M. Andriessen,* W. H. Laarhoven, and R. J. F. Nivard,
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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 ($A_0$) is
found than for the complexes of the corresponding substituted benzenes. It is shown that this increase in $A_0$ 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 interaction2 and formulated his ‘overlap and orientation’ principle3 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 $\pi$-donors and $\pi$-acceptors are known.10-13
The planes of donor and acceptor molecules are parallel

1 See e.g., R. Foster, ‘Organic Charge-Transfer Complexes,’
Japan, 1960, 35, 1842.
11 A. Hanson, Acta Cryst., 1963, 18, 1147.
12 D. S. Brown, S. C. Wallwork, and A. Wilson, Acta Cryst.,
1964, 17, 168.
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.16 The acceptor signal moves to higher field on complexation. By analogy with the contributions to the solvent shift for solute molecules,19 the shift of the acceptor protons in pure complex \( \delta^A_{AD} \) relative to the shift of the pure acceptor in solution \( \delta^A_0 \) can be expressed by equation (1). Here \( -\delta^a_w \) is the difference between the contribution of dispersion forces to the chemical shift of the acceptor in the complex and the acceptor in solution.

\[
\delta^A_0 - \delta^A_{AD} = \Delta_0 = \delta^a_w + \delta^e_w + \delta^a_e
\]

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

\(-\delta^a_e\) 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 reported19 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.

\(-\delta^a_e\) 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,20 for protons at various orientations relative to a benzene ring provides the possibility for an estimation of \( \delta^a_e \) in complexes with aromatic donor molecules and varying conformations.

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 \( \Delta_0 \) (1-1 p.p.m.) is observed.15 So a large \( \Delta_0 \) value calculated for various structural models.

In those cases differences in \( \Delta_0 \) 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 the corresponding phenols by methylation with dimethyl sulphate. The biphenyls were prepared from the corresponding bromobenzenes or -anisoles by the procedure described;21 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. 1H 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. 19F 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 \( \Delta_0 \) were calculated by the method described13 from relation (3)

\[
\Delta/[D_A] = -K_{AD} + K_{AD} \Delta_0
\]
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 \( 1/[D_0] \) is much 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 \( 4 \times 10^{-3}, 6 \times 10^{-3}, \) and \( 6 \times 10^{-3} \) M respectively.

For strong complexes (\( K^{AD} > 5 \)) the concentrations of the donors were in the range 0-02-0-6M. 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.\(^{33} \) 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 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 \( \pi \)-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 methyl rings are conjugated and in close proximity. Hence the statistical factor will be close to unity. For the \( \sigma \)-methylnaphthyls [(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>
<thead>
<tr>
<th>Donor</th>
<th>( K^{AD}/ ) kg mol(^{-1} )</th>
<th>( \Delta_0/ ) Hz</th>
<th>( \omega^{CT}/ ) cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anisole</td>
<td>1-56 ± 0-12</td>
<td>91 ± 5</td>
<td>2-80</td>
</tr>
<tr>
<td>2-Methylanisole</td>
<td>1-99 ± 0-17</td>
<td>101 ± 6</td>
<td>2-71</td>
</tr>
<tr>
<td>3-Methylanisole</td>
<td>2-01 ± 0-09</td>
<td>95 ± 3</td>
<td>2-70</td>
</tr>
<tr>
<td>4-Methylanisole</td>
<td>2-94 ± 0-54</td>
<td>82 ± 6</td>
<td>2-62</td>
</tr>
<tr>
<td>2,3-Dimethylanisole</td>
<td>2-42 ± 0-15</td>
<td>100 ± 4</td>
<td>2-84</td>
</tr>
<tr>
<td>2,4-Dimethylanisole</td>
<td>2-04 ± 0-18</td>
<td>93 ± 3</td>
<td>2-54</td>
</tr>
<tr>
<td>2,5-Dimethylanisole</td>
<td>3-06 ± 0-19</td>
<td>91 ± 4</td>
<td>2-58</td>
</tr>
<tr>
<td>2,6-Dimethylanisole</td>
<td>2-04 ± 0-17</td>
<td>81 ± 2</td>
<td>2-82</td>
</tr>
<tr>
<td>3,4-Dimethylanisole</td>
<td>3-45 ± 0-12</td>
<td>89 ± 2</td>
<td>2-96</td>
</tr>
<tr>
<td>3,5-Dimethylanisole</td>
<td>3-17 ± 0-36</td>
<td>85 ± 5</td>
<td>2-63</td>
</tr>
<tr>
<td>2,4,6-Trimethylanisole</td>
<td>3-20 ± 0-18</td>
<td>80 ± 2</td>
<td>2-75</td>
</tr>
<tr>
<td>4,4'-Dimethoxybiphenyl</td>
<td>3-17 ± 0-17</td>
<td>56 ± 2</td>
<td>2-62</td>
</tr>
<tr>
<td>2,2'-Dimethyl-4,4'-di- methoxybiphenyl</td>
<td>9-32 ± 0-70</td>
<td>111 ± 4</td>
<td>2-22</td>
</tr>
<tr>
<td>3,3'-Dimethyl-4,4'-di- methoxybiphenyl</td>
<td>2-11 ± 0-37</td>
<td>65 ± 5</td>
<td>2-43</td>
</tr>
<tr>
<td>2,5,5'-Tetramethyl-4,4'- di methoxybiphenyl</td>
<td>2-30 ± 0-23</td>
<td>41 ± 3</td>
<td>2-55</td>
</tr>
<tr>
<td>2,2',6,6'-Tetramethyl-4,4'- di methoxybiphenyl</td>
<td>8-49 ± 0-19</td>
<td>99 ± 1</td>
<td>2-43</td>
</tr>
</tbody>
</table>

* Shoulder, value inaccurate. \(^{15} \) Too insoluble to measure.
Values of $K_{AD}$, $\Delta_0$, and $v_{CT}$ for the complexes of trinitrobenzene with various donors, measured in CCl$_4$ at 20 °C

<table>
<thead>
<tr>
<th>Donor</th>
<th>$K_{AD}$/kg mol$^{-1}$</th>
<th>$\Delta_0$/Hz</th>
<th>$10^4 v_{CT}$/cm$^{-1}$</th>
<th>$K_{AD}$/kg mol$^{-1}$</th>
<th>$\Delta_0$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>(19) Benzene</td>
<td>0.65 ± 0.04</td>
<td>120 ± 4</td>
<td>3.54 ± 0.08</td>
<td>129 ± 1</td>
<td></td>
</tr>
<tr>
<td>(20) Toluene</td>
<td>0.95 ± 0.04</td>
<td>111 ± 3</td>
<td>3.27 ± 0.08</td>
<td>129 ± 1</td>
<td></td>
</tr>
<tr>
<td>(21) o-Xylene</td>
<td>1.28 ± 0.08</td>
<td>109 ± 8</td>
<td>3.18 ± 0.12</td>
<td>128 ± 1</td>
<td></td>
</tr>
<tr>
<td>(22) m-Xylene</td>
<td>1.32 ± 0.05</td>
<td>101 ± 2</td>
<td>3.18 ± 0.12</td>
<td>128 ± 1</td>
<td></td>
</tr>
<tr>
<td>(23) p-Xylene</td>
<td>1.92 ± 0.08</td>
<td>104 ± 3</td>
<td>3.19 ± 0.16</td>
<td>129 ± 1</td>
<td></td>
</tr>
<tr>
<td>(24) Mesitylene</td>
<td>1.72 ± 0.18</td>
<td>97 ± 5</td>
<td>3.00 ± 0.16</td>
<td>128 ± 1</td>
<td></td>
</tr>
<tr>
<td>(25) 1,2,4-Trimethylbenzene</td>
<td>2.03 ± 0.29</td>
<td>104 ± 6</td>
<td>3.07 ± 0.18</td>
<td>129 ± 1</td>
<td></td>
</tr>
<tr>
<td>(26) 1,2,4-Trimethylbenzene</td>
<td>2.11 ± 0.11</td>
<td>107 ± 4</td>
<td>3.09 ± 0.18</td>
<td>129 ± 1</td>
<td></td>
</tr>
<tr>
<td>(27) 1,2,4,5-Tetramethylbenzene</td>
<td>2.84 ± 0.28</td>
<td>102 ± 5</td>
<td>2.94 ± 0.18</td>
<td>128 ± 1</td>
<td></td>
</tr>
<tr>
<td>(28) 1,2,3,5-Tetramethylbenzene</td>
<td>3.97 ± 0.06</td>
<td>98 ± 1</td>
<td>2.87 ± 0.18</td>
<td>129 ± 1</td>
<td></td>
</tr>
<tr>
<td>(29) Pentamethylbenzene</td>
<td>5.11 ± 0.22</td>
<td>104 ± 2</td>
<td>2.67 ± 0.18</td>
<td>128 ± 1</td>
<td></td>
</tr>
<tr>
<td>(30) Hexamethylbenzene</td>
<td>7.31 ± 0.66</td>
<td>109 ± 5</td>
<td>2.53 ± 0.18</td>
<td>128 ± 1</td>
<td></td>
</tr>
<tr>
<td>(31) Biphenyl</td>
<td>1.75 ± 0.14</td>
<td>130 ± 5</td>
<td>3.03 ± 0.16</td>
<td>128 ± 1</td>
<td></td>
</tr>
<tr>
<td>(32) 3,3'-Dimethylbiphenyl</td>
<td>3.90 ± 0.18</td>
<td>119 ± 3</td>
<td>2.74 ± 0.18</td>
<td>129 ± 1</td>
<td></td>
</tr>
<tr>
<td>(33) 4,4'-Dimethylbiphenyl</td>
<td>4.41 ± 0.23</td>
<td>117 ± 3</td>
<td>2.63 ± 0.18</td>
<td>128 ± 1</td>
<td></td>
</tr>
<tr>
<td>(34) 2,2'-Dimethylbiphenyl</td>
<td>1.03 ± 0.07</td>
<td>87 ± 4</td>
<td>3.17 ± 0.18</td>
<td>128 ± 1</td>
<td></td>
</tr>
<tr>
<td>(35) 2,2',4,4',6,6'-Hexamethylbiphenyl</td>
<td>0.97 ± 0.02</td>
<td>80 ± 4</td>
<td>2.94 ± 0.18</td>
<td>128 ± 1</td>
<td></td>
</tr>
<tr>
<td>(36) 2,2',4,4',6,6'-Hexamethylbiphenyl</td>
<td>0.43 ± 0.02</td>
<td>76 ± 4</td>
<td>3.12 ± 0.18</td>
<td>128 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

* Data from ref. 26, converted to 20 °C with published values of $\Delta H$ from ref. 36. Values of $\Delta H$ for isomers were taken equal.

# Figure 1
Figure 1 shows plots of log $K$ for a series of trinitrobenzene complexes against the energy ($v_{CT}$) of the charge-transfer transition; data from Table 1.

Figures 1—3 show plots of log $K$ against the energy $v_{CT}$ 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, (19), (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. 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).

\[
E_{\text{stab}} = b^2D - b^2A - 2ab\beta_{DA} + b^2\psi_{es} + G_0 \tag{6}
\]

\( D \) 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. \( -\psi_{es} \) is the contribution of the Coulomb energy.

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).

\[
E_{\text{stab}} = b^2D - b^2A - 2ab\beta_{DA} + b^2\psi_{es} + G_0 \tag{7}
\]

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, \( \beta_{DA}, \psi_{es}, \) and \( G_0 \) remain nearly constant. Thus we obtain equation (8),

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

where \( C_1 \) is constant. If in such series of complexes variations in the equilibrium constant \( K^D \) 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 \( -D \) is equal to the ionisation potential \( I_P \) of the donor.\textsuperscript{37} Thus we obtain equation (10).

\[
RT \ln K \approx b^2D + C_1 \tag{9}
\]

\[
RT \ln K \approx b^2I_P + C_1 \tag{10}
\]

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 \( \Delta_1 \) [in equation (2)] does not vary by introduction of a phenyl residue in a donor will be correct. Changes in \( \Delta_1 \) will then only be due to differences in \( \Delta_a \) 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 \( \Delta_a \) 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.

\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, J. Chem. Soc. (B), 1970, 528.

\textsuperscript{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. 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 $A_1$ to $A_0$ [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 $\Delta_0$ 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 $A_1$ and $A_a$ remain constant no information about the structure of the complexes can be obtained from these data. With the help of tables values of $A_a$ 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 1.39 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 ($\Delta_a$) 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 ($\Delta_a^e$) of the second ring (11).

Table 6 compares the $\Delta_0$ values of the various biphenyl complexes and the $\Delta_0^{av}$ 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 $\Delta_a^e$ for
three models [Figure 6; formulae (IV), (V), and (VI), corresponding with (I), (II), and (III), respectively] it appears that the experimental values of $\Delta_a^e$ 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 as 20° and the central C-C bond length 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.

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 $\Delta_a$ 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 straightforward conclusions about the structure can be drawn.

Table 6 shows that $\Delta_a$ values are substantially smaller than $\Delta_a^{av}$ of the corresponding 'half' molecules. The experimental values of $|\Delta_a - \Delta_a^{av}|$ are much larger than is calculated for models (IV) and (V), even if a much larger angle of twist (70° or 90°) is taken (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 $\Delta_a$, which would also contribute to the relatively low $\Delta_a$ values.

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

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**Table 6**
Comparison of the $\Delta_a$ values of the biphenyl complexes of trinitrobenzene and picric acid with the average values of $\Delta_a$ ($\Delta_a^{av}$) of their corresponding 'half' molecules

<table>
<thead>
<tr>
<th>Acceptor, trinitrobenzene</th>
<th>$\Delta_a$/Hz</th>
<th>$\Delta_a^{av}$/Hz</th>
<th>$\Delta_a - \Delta_a^{av}$/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'-dimethoxy-biphenyl</td>
<td>65</td>
<td>92</td>
<td>-27</td>
</tr>
<tr>
<td>(16) 2,2',6,6'-Tetramethyl-4,4'-dimethoxy-biphenyl</td>
<td>41</td>
<td>92</td>
<td>-51</td>
</tr>
<tr>
<td>(17) 3,3',5,5'-Tetramethyl-4,4'-dimethoxy-biphenyl</td>
<td>99</td>
<td>81</td>
<td>+18</td>
</tr>
<tr>
<td>(31) Biphenyl</td>
<td>122</td>
<td>105</td>
<td>+17</td>
</tr>
<tr>
<td>(32) 3,3'-Dimethylbiphenyl</td>
<td>87</td>
<td>105</td>
<td>-18</td>
</tr>
<tr>
<td>(33) 4,4'-Dimethylbiphenyl</td>
<td>80</td>
<td>105</td>
<td>-25</td>
</tr>
<tr>
<td>(34) 2,2'-Dimethylbiphenyl</td>
<td>78</td>
<td>105</td>
<td>-29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acceptor, picric acid</th>
<th>$\Delta_a$/Hz</th>
<th>$\Delta_a^{av}$/Hz</th>
<th>$\Delta_a - \Delta_a^{av}$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>(13) 2,2'-Dimethyl-4,4'-dimethoxy-biphenyl</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'-dimethoxy-biphenyl</td>
<td>65</td>
<td>89</td>
<td>-24</td>
</tr>
<tr>
<td>(16) 2,2',6,6'-Tetramethyl-4,4'-dimethoxy-biphenyl</td>
<td>35</td>
<td>89</td>
<td>-54</td>
</tr>
<tr>
<td>(17) 3,3',5,5'-Tetramethyl-4,4'-dimethoxy-biphenyl</td>
<td>97</td>
<td>77</td>
<td>+20</td>
</tr>
<tr>
<td>(31) Biphenyl</td>
<td>128</td>
<td>112</td>
<td>14</td>
</tr>
<tr>
<td>(32) 3,3'-Dimethylbiphenyl</td>
<td>92</td>
<td>112</td>
<td>20</td>
</tr>
<tr>
<td>(33) 4,4'-Dimethylbiphenyl</td>
<td>88</td>
<td>112</td>
<td>-24</td>
</tr>
</tbody>
</table>

* $\Delta_a$ average of (31), (32), (33). $\Delta_a$ Of the corresponding 2,6-dimethylanisole complex.
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 $\Delta_1$ 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 ($^{19}$F resonance) are about three times as 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 $\Delta_0$ for various complexes are due to differences in $\Delta_1$ rather than in $\Delta_a$ and less apt for a study as in this paper.

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