Intramolecular Charge Transfer in (Dialkylamino)nitrobiphenyls

By Ewald Daltrozzo, Franz Effenberger, and Peter Fischer*[

The deep color of the new biaryls reported in the previous Communication12 must be ascribed to a charge transfer (CT) transition. Since within the region 7.5·10⁻⁴ to 7.5·10⁻⁶ mole/liter the absorption is independent of concentration, intermolecular origin of this CT interaction can be ruled out. For interpretation of intramolecular charge-transfer processes, knowledge of the molecular geometry is a prerequisite: information about the structure of the biphenyls (I) to (3) may be gained from the ¹H-NMR spectra.

In (Ia) and (2a) to (2f), the signals of the ortho-pyrroli- dino groups are shifted to higher field by about 0.30 ppm (β-methylene protons) and 0.60 ppm (N-CH₃) respectively, relative to those of the para-amino substituents (Table 1). Improved shielding due to steric hindrance of resonance by the nitrophenyl substituents[22] does not suffice to account for these large shifts, especially of the β-CH₃ hydrogen nuclei[3]; it must rather be assumed that the ortho-dialkyl-

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amino groups protrude deep into the diamagnetic anisotropy field of the nitrobenzene. The characteristic structure of the methylene multiplets, though, is not split further; within the NMR-time scale, the NR groups must therefore be placed symmetrically with respect to the plane of the nitroarene [cf. (4)].

Admixture of contact charge transfer in chlorinated hydrocarbons gives a bathochromic shift. As has been observed for tetracyanoethylene(69), CH3Cl2 is a far more effective donor than CCl4; for interaction of the amino system with halomethanes as acceptors(77), the opposite effect is to be expected.

Table I. 'H-NMR data and longest-wave UV absorptions of biphenyls (1) to (3).

<table>
<thead>
<tr>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>NMR (r values); 0.5 M in DCCI, int. TMS, 30°C</th>
<th>λmax (nm), H Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1a)</td>
<td>Pyr</td>
<td>CH3</td>
<td>NO2</td>
<td>NO2</td>
<td>8.28 (o) 7.22 (o)</td>
</tr>
<tr>
<td>(2a)</td>
<td>Pyr</td>
<td>H</td>
<td>NO2</td>
<td>NO2</td>
<td>8.30 (o) 7.26 (o)</td>
</tr>
<tr>
<td>(2b)</td>
<td>Pyr</td>
<td>H</td>
<td>CN</td>
<td>NO2</td>
<td>8.29 (o) 7.23 (o)</td>
</tr>
<tr>
<td>(2c)</td>
<td>Pyr</td>
<td>H</td>
<td>COOH</td>
<td>NO2</td>
<td>8.32 (o) 7.28 (o)</td>
</tr>
<tr>
<td>(2d)</td>
<td>Pyr</td>
<td>H</td>
<td>COOH</td>
<td>NO2</td>
<td>8.22 (o) 7.14 (o)</td>
</tr>
<tr>
<td>(2e)</td>
<td>Pyr</td>
<td>H</td>
<td>H</td>
<td>NO2</td>
<td>8.31 (o) 7.26 (o)</td>
</tr>
<tr>
<td>(2f)</td>
<td>Pyr</td>
<td>H</td>
<td>H</td>
<td>CN</td>
<td>8.31 (o) 7.24 (o)</td>
</tr>
<tr>
<td>(3a)</td>
<td>H</td>
<td>H</td>
<td>NO2</td>
<td>NO2</td>
<td>8.23 (o) 7.09 (o)</td>
</tr>
</tbody>
</table>

[a] (o) denotes pyrrolidino substituents in the 2- and 6-positions, (p) those in the p-position to the biphenyl linkage; in each case, the center of the characteristic multiplet is given as the signal position.

[b] 7.5 × 10⁻³ M in CH3CN.

In (2d), a hydrogen bridge can be formed from the COOH group to the ortho-dialkylamino-nitrogen; the resulting decrease in electron density on the N-atom shifts the N–CH3 signal by −0.14 ppm. This shows how sensitive the NMR signals are even to small changes in structure.

Gradation of band positions in the order (2a) → (1a) → (3a) (561.5, 548.5, 533 nm), as well as for the sequence (2a) → (2f), shows the energy of the CT transition to be determined by both the electron density of the amino and the electron affinity of the acceptor component. There is no straightforward correlation, though, with the Eα values of the nitroarenes.

For an interpretation of the charge transfer several possible mechanisms must be taken into account:

(a) interaction of the n-electron pair of one ortho-nitro-oxygen atom and orbitals of C-2 and C-6 of the aromatic amine;

(b) direct interaction between the lone pair of the ortho-pyrrolidino nitrogen and, particularly, positions 1', 2', and 6' of the aromatic nitro compound [see (4)];

(c) "normal" charge transfer from the electron-rich amino to the electron-deficient nitro component (overlap between π orbitals of one aromatic system and σ orbitals of bonds 1–2 and 1–6 of the other arene).

Transfer between the amino benzene and the ortho-nitro groups as in (a) is rather unlikely since, on the basis of orbital symmetry, there is no bonding interaction between any of the molecular orbitals participating in the long-wave transitions. By PPP calculations(68), position and intensity of the lowest-energy absorption may be repro-

![Image](4)
uced satisfactorily even without taking process (b) into account, and without specific adjustment of parameters\(^9,10\).

Thus, in the first electron transition (CT band), charge is transferred primarily from the ortho nitrogen atoms and from C-1 of the aminobenzene to C-1' and the ortho-nitro groups of the second component; hyperconjugative \(\sigma\pi\) interaction as in (c) has been taken into account by introducing pseudo-\(\pi\) centers.

Table 2. Lowest-energy UV-absorption bands of (2a) in various solvents.

<table>
<thead>
<tr>
<th></th>
<th>(C_6H_{12})</th>
<th>(CCl_4)</th>
<th>Dioxane</th>
<th>Dimethoxyethane</th>
<th>(CH_2Cl_2)</th>
<th>Acetone</th>
<th>(CH_3CN)</th>
<th>(CH_3OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_1)</td>
<td>31.2</td>
<td>32.5</td>
<td>36.0</td>
<td>38.2</td>
<td>41.1</td>
<td>42.2</td>
<td>46.0</td>
<td>55.5</td>
</tr>
<tr>
<td>(\nu)</td>
<td>17940</td>
<td>17610</td>
<td>17970</td>
<td>17950</td>
<td>17040</td>
<td>17860</td>
<td>17850</td>
<td>18050</td>
</tr>
<tr>
<td>(\Delta\nu)</td>
<td>3730</td>
<td>3930</td>
<td>4620</td>
<td>5010</td>
<td>4620</td>
<td>5090</td>
<td>5090</td>
<td>5250</td>
</tr>
<tr>
<td>(\epsilon_{max})</td>
<td>7240</td>
<td>7030</td>
<td>5720</td>
<td>5740</td>
<td>6300</td>
<td>5690</td>
<td>5750</td>
<td>5560</td>
</tr>
</tbody>
</table>

An estimate as to the relative contributions of mechanisms (b) and (c) to the charge transfer observed will be possible as soon as dialkylation biphensyls become available with different gradation between N-basicity and \(\pi\)-electron density at the free aromatic ring positions.

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\(^{[3]}\) The appreciably more bulky isopropyl group causes a shift to higher field of only 0.25 (\(\delta\)-H) or 0.07 ppm (\(\beta\)-H); because of the strongly anisotropic NO\(_2\) groups an additional paramagnetic shift is also to be expected.


\(^{[10]}\) We thank Drs. G. Hohneicher and S. Schneider for supplying the computer program. The calculations were carried out on the TR4 installation at the Leibniz-Rechenzentrum of the Bayerische Akademie der Wissenschaften.