

Intramolecular Charge Transfer in (Dialkylamino)nitrobiphenyls^[1]

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The deep color of the new biaryls reported in the previous Communication^[2] must be ascribed to a charge transfer (CT) transition. Since within the region $7.5 \cdot 10^{-4}$ to $7.5 \cdot 10^{-6}$ 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 (1) to (3) may be gained from the ¹H-NMR spectra.

In (1a) and (2a) to (2f), the signals of the *ortho*-pyrrolidino groups are shifted to higher field by about 0.30 ppm (β -methylene protons) and 0.60 ppm (N—CH₂) respectively, relative to those of the *para*-amino substituents (Table 1). Improved shielding due to steric hindrance of resonance by the nitrophenyl substituents^[2] does not suffice to account for these large shifts, especially of the β -CH₂ hydrogen nuclei^[3]; it must rather be assumed that the *ortho*-dialkyl-

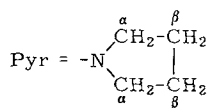
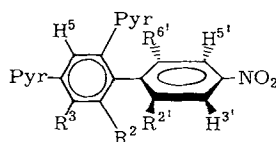
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amino groups protrude deep into the diamagnetic anisotropy field of the nitrobenzene. The characteristic structure of the methylene multiplets, though, is not split further; within the NMR-time scale, the NR₂ groups must therefore be placed symmetrically 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^[6], CH₂Cl₂ is a far more effective donor than CCl₄; for interaction of the amino system with halomethanes as acceptors^[7], the opposite effect is to be expected.

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

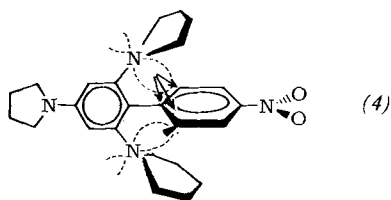


	R ²	R ³	R ^{2'}	R ^{6'}	NMR (τ values); 0.5 M in DCCl ₃ , int. TMS, 30 °C		λ _{max} (nm);	
					Pyr, β-H [a]	Pyr, α-H [a]	H ^{3,5}	H ^{3',5'} (ε _{max}) [b]
(1a)	Pyr	CH ₃	NO ₂	NO ₂	8.28 (o) 8.05 (p)	7.22 (o) 6.73 (p)	3.57	1.19 548.5; (3520)
(2a)	Pyr	H	NO ₂	NO ₂	8.30 (o) 7.99 (p)	7.26 (o) 6.65 (p)	4.01	1.26 561.5; (5750)
(2b)	Pyr	H	CN	NO ₂	8.29 (o) 7.99 (p)	7.23 (o) 6.63 (p)	3.97	H ^{3'} 1.36 532.5; (5940) H ^{5'} 1.19
(2c)	Pyr	H	COOCH ₃	NO ₂	8.32 (o) 7.99 (p)	7.28 (o) 6.65 (p)	4.01	1.31 530.5; (5660) 1.28
(2d)	Pyr	H	COOH	NO ₂	8.22 (o) 7.96 (p)	7.14 (o) 6.65 (p)	3.97	1.41 466 ; (3480) 1.22
(2e)	Pyr	H	H	NO ₂	8.31 (o) 7.99 (p)	7.26 (o) 6.65 (p)	4.01	H ^{3'} 1.32 510.5; (5790) H ^{5'} 1.71 H ² 2.31
(2f)	Pyr	H	H	CN	8.31 (o) 7.99 (p)	7.24 (o) 6.64 (p)	3.99	H ^{3'} 1.52 472 ; (6230) H ^{5'} 1.70 H ² 2.32
(3a)	H	H	NO ₂	NO ₂	8.23 (o) 7.98 (p)	7.09 (o) 6.65 (p)	H ² 3.14 H ³ 3.61 H ⁵ 3.93	1.32 533 ; (5960)

[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 × 10⁻⁵ 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—CH₂ signal by -0.14 ppm. This shows how sensitive the NMR signals are even to small changes in structure.



Therefore the fact that the H^{3',5'} signal position is almost identical for (2a) to (2f) (while electron affinities of the nitrophenyl units differ widely) seems to us good proof that in the ground state there is no significant interaction between the two aromatic component systems.

While several papers on intramolecular CT complexes have recently been published^[4], intramolecular CT interaction in biphenyls has not been observed previously. The near constancy of the band position for (2a) over a series of solvents (Table 2) again ascertains the intramolecular origin of the longest-wave absorption of (1) to (3).

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 E_{1/2}^{red} 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 p_z 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^[8], position and intensity of the lowest-energy absorption may be reproduced.

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 σ - π interaction as in (c) has been taken into account by introducing pseudo- π centers.

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

	C ₆ H ₁₂	CCl ₄	Dioxane	Dimethoxyethane	CH ₂ Cl ₂	Acetone	CH ₃ CN	CH ₃ OH
E_T -value [5]	31.2	32.5	36.0	38.2	41.1	42.2	46.0	55.5
$\tilde{\nu}$ (cm ⁻¹)	17940	17610	17970	17950	17040	17860	17810	18050
$\Delta\tilde{\nu}_{1/2}$ (cm ⁻¹)	3730	3930	4620	5010	4620	5090	5090	5250
ϵ_{\max}	7240	7030	5720	5740	6300	5690	5750	5560

An estimate as to the relative contributions of mechanisms (b) and (c) to the charge transfer observed will be possible as soon as dialkylamino biphenyls become available with different gradation between N-basicity and π -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 (α -H) or 0.07 ppm (β -H); because of the strongly anisotropic NO₂ groups an additional paramagnetic shift is also to be expected.

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