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THE INTRAMOLECULAR CHARGE-TRANSFER INTERACTION IN N-[ω-(p-NITROPHENYL)ALKYL]ANILINES[1)]

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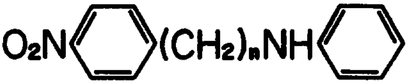
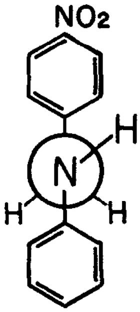
In the study of intramolecular N-H...π interaction, certain forces, such as intramolecular charge-transfer (CT) complex formation, have been suggested to be operating in some homologs (I) of N-(p-nitrobenzyl)aniline (2).



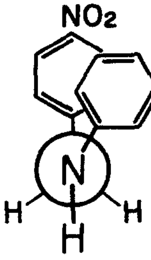
I

In Fig. 1 is reproduced the relation between the intensity ratio of N-H stretching bands and n, where A_l and A_h denote the integrated intensities of the lower (at ca. 3420 cm^{-1}) and the higher (at ca. 3445 cm^{-1}) bands, respectively. The ratio of higher homologs (n=4,5, and 7) is nearly as large as that of N-propylaniline (3) within experimental errors. Considering that there are only two rotamers with regard to the C-N bond and the absence of N-H...π interacting species in alkylanilines, it is clear that the ratio of these higher homologs is representing mostly that of rotamers about the C-N bond. On this basis the ratio of lower homologs (n=1,2, and 3) must be considered abnormal.

The matter will be clearer if N-(p-nitrobenzyl)aniline (4) is taken as an example. There are two rotamers (II and III) in this compound, in which II is an N-H...π interacting species. The ratio $\log(A_l/A_h)$, i.e. $\log(A_{II}/A_{III})$, is negative, the value showing that III is favored. This value is unexpectedly low, because N-H...π interaction is known to stabilize II and repulsive force(s) between the two benzene rings would destabilize III. Both effects should increase



II



III

the ratio over that of the alkylaniline. Another abnormal point has been found in the determination of the thermodynamic parameters for the N-H...π interaction (5). In a series of N-benzylanilines investigated, only the p-nitro derivative has possibly a positive ΔH value, in contrast to the other compounds of negative ΔH's (generally the interaction is exothermic). The possibility of CT type interaction between the two benzene rings has been suggested on these grounds, which makes the rotamer III more advantageous than II.

In order to test this possibility, the ultraviolet absorption spectra of the compounds of type I in which n is 1,2,3,4,5, or 7 have now been studied. As is seen in Fig. 2, the absorption bands of the lower homologs show some extra extinction in comparison with the higher one (n=7). Assuming that the p-nitrophenyl and the anilino groups in the latter are sufficiently apart from each other for making the intramolecular interaction nil, its spectrum may be used as a standard of chromophores which lack the intramolecular interaction. Subtraction of this standard spectrum from the others shows an absorption maximum in the region longer than 300mμ. The results are summarized in Table I.

TABLE I. The Subtraction Band in the System I in 95% EtOH

n	1	2	3	4 and 5
λ_{max} (mμ)	345∼55 (broad)	335	ca. 330 (shoulder)	———
ε_{max}	270	980	?	

The subtraction band may be assigned to the expected CT band, as it is present only in the homologs which show anomaly in their N-H stretching bands.

Further evidence for the CT complex formation was obtained by studying the spectra of the system IV, where Ar groups are 2,4-dimethylphenyl, p-anisyl and

IV

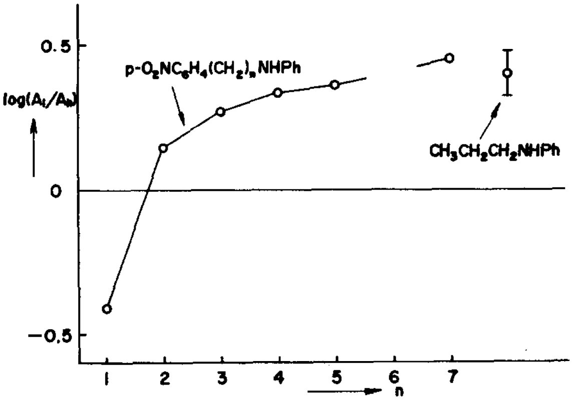


FIG. 1. Correlation of $\log(A_1/A_h)$ with n in the System I.

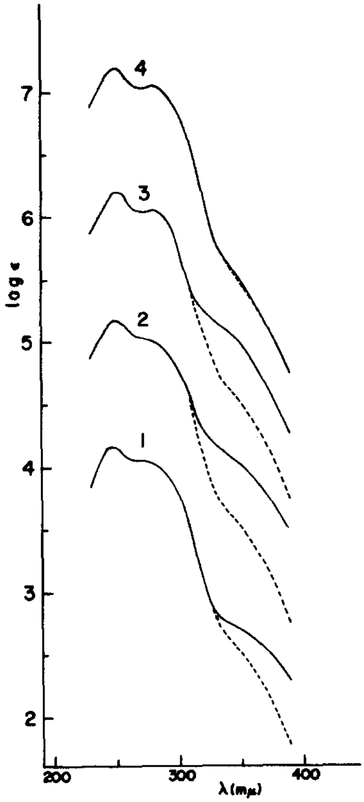


FIG. 2.

The Ultraviolet Absorption Spectra of the Homolog $p\text{-}O_2NC_6H_4(CH_2)_nNHPh$ in 95% Ethanol.

Curves 1, 2, 3, and 4 correspond to absorptions of the compounds, n=1, 2, 3, and 4, respectively. The broken line represents the absorption of the compound n=7. Curves (2), (3), and (4) are displaced upward by one, two, and three units, respectively, from (1).

α-naphthyl. Subtraction band maxima are shown in Table II.

TABLE II. The Effect of Aromatic Ring on the Subtraction Band* in the System IV, $p\text{-}O_2NC_6H_4(CH_2)_nNHAr$. (95% Ethanol Solution)

Ar	n=1		n=2	
	λ_{max}	(ε_{max})	λ_{max}	(ε_{max})
2,4-Dimethyl-phenyl	355 mμ 370	(230) (230)	340 mμ	(770)
p-Anisyl	362	(305)	350	(715)
α-Naphthyl	387	(250)	373	(565)

* The corresponding compound (n=7) was taken as a standard in each case.

It is obvious that the stronger the electron-donating power of the Ar group, the longer the absorption maximum. Unfortunately there is no available data on the ionization potentials of the above donor groups. Therefore it is impossible to test the linear correlation between the frequency of the absorption maximum and the donor ionization potential. But the tendency mentioned above naturally supports the presence of the CT complex.

Comparing the data in Table I and II, it is evident that the wavelength of the CT band of benzyl type homolog (n=1) is always longer than that of phenethyl type (n=2) regardless of the Ar group. Additional feature of interest is the maximum intensity which is much stronger in phenethyl type. Though the intensity might be correlated with the population of the CT complex, the difference of its conformation (degree of overlapping of π-electron cloud, relative positions of the two aromatic rings, etc.) in these homologs does not allow any hasty conclusion.

When the solvent was changed from 95% ethanol to pure acetic acid, the CT band remains in these two (n=1, and 2) in spite of the considerable decrease in intensity. Whereas, the CT band of the homolog (n=3) disappears in acetic acid. This fact can be readily explained by the strong hydrogen bonding of the solvent with the nitrogen atom, which decreases the complex forming power of the donor group.

White (6) has studied the system p-$O_2NC_6H_4(CH_2)_nC_6H_4NH_2$-p for the intramolecular CT interaction and concluded that the CT band appears at 310∼318 mμ with ε_{max} of 1300∼1600, when n is 1, 2, or 3. Though the wavelengths of the maxima and intensities are somewhat different, the data can be a support for the above assignment, because both systems have closely resembling donor and acceptor groups.

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