The Intramolecular Interaction between the N–H Group and π-Electrons. III.[1] Intramolecular Interaction in *N*-(ω-Phenylalkyl)anilines

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In the previous papers of this series the existence of intramolecular interaction between the N–H group and π-electrons has been reported for *N*-benzylaniline[2] and *N*-phenethylaniline.[1] The predominance of the interacting form over the free form in the latter has now prompted the authors to investigate the higher homologs of *N*-(ω-phenylalkyl)aniline, Ph·$(CH_2)_n$NHPh. In the alcoholic analogs, benzyl[3] and phenethyl[4] alcohols have been reported to show the same type of interaction.

In 3-phenylpropyl alcohol the interaction is absent unless the electron density is raised by the introduction of an electron-donating substituent into the benzene ring.[4] It would be interesting to know the limitation of the interaction by the chain length, since the N–H in an anilino group is known to be favorable toward the interaction.[1] Thus, the present paper is concerned with the determination of the limit of the chain length (the number, *n*) for the interaction and with an examination of its characteristics.

Experimental

Spectral Measurements and Calculations.—They were performed as has been described previously.[1]

Materials.—The materials used for the measurement are known compounds, unless otherwise stated. Their physical constants agreed with those in the literature.

N-(ω-p-Nitrophenylalkyl)anilines.—All nitro derivatives of this type was prepared by the following method. A corresponding ω-phenylalkyl chloride or bromide was nitrated with a mixture of nitric acid and sulfuric acid. The ω-nitrophenylalkyl halide (*o*- and *p*-isomeric mixture) thus obtained was heated with ca. 4 equivalents of aniline at 180—200°C for 1—1.5 hr. The unreacted aniline was then removed by steam distillation, and the residue was extracted with ether. The solvent was distilled off, and the remaining oil was charged on a column of alumina. Elution with a petroleum ether - benzene mixture gave the desired product in a first eluate. The melting points and the results of elemental analyses are given in the following table.

p-$NO_2C_6H_4(CH_2)_n$NHPh

n	M. p. °C	Carbon, %		Hydrogen, %		Nitrogen, %		Yield %
		Calcd.	Found	Calcd.	Found	Calcd.	Found	
3	52—53	70.29	70.44	6.29	6.40	10.93	10.97	48
4	105—106	71.09	71.32	6.71	6.80	10.36	10.29	33
5	59—60	71.75	71.80	7.36	7.09	9.73	9.85	23
7	52—53	73.04	72.84	7.74	7.87	8.97	8.79	36

N-(3-Arylpropyl)- and N-(4-Arylbutyl)aniline.—An appropriate hydrocinnamic acid or γ-phenylbutyric acid was heated with ca. 2 equivalents of aniline at a refluxing temperature to give anilide. This anilide, structure of which was confirmed by its infrared spectrum, was then recrystallized from 70% ethyl alcohol and reduced with lithium aluminum hydride, as has been described in a previous paper.[1] Probably because of the poor solubility of the anilide in ether, the yields were generally low.

The physical constants and the results of elemental analyses are given in the following table.

N-(4-Phenylbutyl)aniline. — 4-Phenylbutyl chloride (12.0 g. or 0.07 mol.) was heated with 25 ml. of aniline at 190—200°C for 1 hr. The reaction mixture was neutralized with an aqueous sodium carbonate solution, the unreacted aniline was removed by steam distillation, and the organic layer was extracted with ether. After the solvent had been removed on a water-bath, the residue was distilled under reduced pressure, affording 8.3 g. (51% yield) of a pale yellow oil; b. p. 158—163°C (2.5 mmHg), n_D^{22} 1.5836.

Found: C, 85.38; H, 8.73. Calcd. for $C_{16}H_{19}N$: C, 85.28; H, 8.50%.

N-(5-Phenylpentyl)aniline. — This compound was prepared by the same procedure as was *N*-(4-phenylbutyl)aniline. Pale yellow oil. Yield, 48%. B. p. 160—165°C (2.5 mmHg). n_D^{22} 1.5740.

Found: C, 85.45; H, 9.00. Calcd. for $C_{17}H_{21}N$: C, 85.30; H, 8.84%.

N-(7-Phenylheptyl)aniline. — This compound was

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[1] Part II: M. Ōki and K. Mutai, This Bulletin, **40**, 387 (1965).

[2] M. Ōki and K. Mutai, ibid., **33**, 784 (1960).

[3] M. Ōki and H. Iwamura, ibid., **32**, 955 (1959).

[4] M. Ōki and H. Iwamura, ibid., **32**, 1135 (1959).

N-(3-ARYLPROPYL) ANILINE $RC_6H_4(CH_2)_3NHPh$

R	B. p. °C/mmHg	n_D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Yield %
p-MeO	175—181/2	1.5848 (25°C)	79.63	79.83	7.94	8.10	5.80	5.91	63
p-CH_3	170—173/3	1.5760 (25°C)	85.28	85.52	8.50	8.70			39
p-Cl	181—186/3	1.5910 (23°C)	73.32	73.50	6.52	6.70	5.70	5.72	53
N-(4-ARYLBUTYL) ANILINE $RC_6H_4(CH_2)_4NHPh$									
p-MeO	194—199/3	1.5742 (20°C)	79.96	80.23	8.29	8.41	5.23	5.49	48
p-Cl	183—189/3	1.5841 (22°C)	73.99	74.02	6.94	7.05	5.35	5.57	40

prepared from crude 7-phenylheptananilide (m. p. 71—75°C) by reduction with lithium aluminum hydride; it was obtained as a pale yellow oil. Yield, 45%; b. p. 180—185°C (2 mmHg), n_D^{22} 1.5599.

Found: C, 85.13; H, 9.69. Calcd. for $C_{19}H_{25}N$: C, 85.34; H, 9.42%.

Results and Discussion

N-(3-Arylpropyl)anilines.—Three of the absorption curves measured in the N–H stretching region are shown in Fig. 1.

The shapes of the curves are similar to those of N-phenethylanilines. The two apparent maxima and the change in the relative absorption coefficients of the two with the substituent suggest the presence of the N–H···π interaction. Each curve was divided into two symmetric bands, each obeying the Lorentz function. No additional band was necessary to achieve a complete division. The data are summarized in Table I, in which the lower wave number band is assumed to be the interaction band.

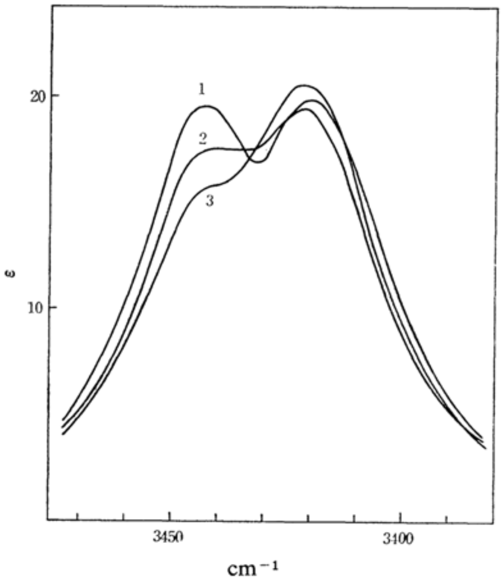

Fig. 1. ν_{N-H} Absorptions of N-(3-arylpropyl)-anilines: (1) p-nitro, (2) p-chloro and (3) p-methoxy.

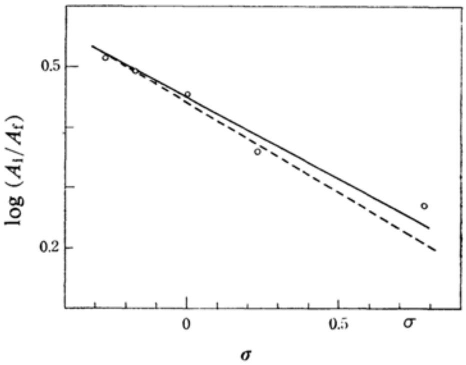

Fig. 2. The relationship between σ value and log (A_i/A_f) for N-(3-arylpropyl)aniline. Solid line; the value for p-nitro derivative (σ=0.78) is included. Broken line; the value for p-nitro derivative is excluded.

In the conventional approach, the log(A_i/A_f) value is compared with the Hammett σ value[5] and, as Fig. 2 shows, a linear correlation is obtained. Hence, it may be said that the interaction exists in this compound.

A comparison of the data in Table I with those for N-phenethylanilines shows some interesting points: (1) the straight line is obtained only when the σ value is so adopted as to indicate the interaction on the ring carbon atom attached to the aliphatic side chain*; (2) the slope (ρ=−0.24 for the solid line) of the line in Fig. 2 is gentler than that observed for N-phenethylaniline (ρ=−0.85);

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[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York (1940); H. H. Jaffé, *Chem. Revs.*, 53, 191 (1953); D. M. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1958).

* This linearity may have to be discussed with some reserved significance, since the contribution of a free from to the absorption at a lower wave number cannot be neglected, as will be discussed later.

TABLE I. ν_{N-H} ABSORPTION OF *N*-(3-ARYLPROPYL)ANILINES
$RC_6H_4(CH_2)_3NHPh$

R	Band	ν_{max} cm^{-1}	$\Delta\nu_{max}$ cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1}·l.·cm^{-2}	log (A_i/A_f)
p-CH_3O	i[a)] f[b)]	3420.4 3447.5	27.1	37.6 25.0	2.58 0.79	0.516
p-CH_3	i f	3420.5 3447.2	26.7	36.6 27.2	2.88 0.92	0.493
H	i f	3420.5 3446.7	26.2	35.8 26.2	2.85 0.99	0.457
p-Cl	i f	3420.5 3446.4	25.9	39.0 26.8	2.40 1.04	0.362
p-NO_2	i f	3418.2 3446.1	27.9	39.6 27.2	2.48 1.32	0.272

a) i denotes interacting form of N–H group.
b) f denotes free form of N–H group.

(3) the half-band width of the band assigned to the interacting form is narrower than that in *N*-phenethylanilines; (4) $\Delta\nu_{max}$ does not change appreciably with the substituent, but, again, it is smaller than that observed for *N*-phenethylanilines by ca. 4 cm^{-1}, and (5) log (A_i/A_f) is positive even when a nitro group is introduced to the ring of the π-electron source, but the value is smaller than that of *N*-phenethylaniline with any corresponding substituent except the nitro derivative.

A comparison of the log (A_i/A_f)'s for *N*-(3-phenylpropyl)anilines with those for *N*-phenethylanilines show that the formation of a six-membered ring is less likely than that of a five-membered ring. The steeper slope for the latter (n=2) may be the result of the more sufficient overlap of the orbitals belonging to the N–H group with those of π-electrons in the five-membered ring. That is, the higher interaction energy is sensitively affected by a little change in π-electron density. Of the derivatives of *N*-phenethylaniline and *N*-(3-phenylpropyl)-aniline, only log (A_i/A_f) value which is higher in the higher homolog is obtained for the *p*-nitro derivative.

This result seems inconsistent with the consideration established above. This anomaly may be explained in the following way. As was noted in an earlier paper,[2)] the free form can take two different states, corresponding to the two rotamers observed for *N*-ethylaniline, one of which absorbs at ca. 3420 cm^{-1}. As the electron-withdrawing power of the substituent increases in *N*-(3-arylpropyl)aniline, the number of the N–H group in the free form increases. In the *p*-nitro derivative the population of one of the rotamers, the presence of which can be regarded as negligible in lower homologs, may become sufficiently noticeable in the spectrum and may contribute to the intensity to an appreciable extent. Thus, the band assigned to the interacting form in the derivative may be in fact a composite of the interacting form and the free form, both absorbing at nearly the same position. There is supporting evidence for this explanation. As is illustrated in Fig. 2, the value for the *p*-nitro derivative falls above the line. This deviation suggests an overestimation of A_i, to which the intensity due to one of the free forms contributes as well as that of the interacting form. Accordingly, the correlation line in Fig. 2 should be drawn with a modification of the slope (the broken line). By a least-square method, disregarding the *p*-nitro derivative, the slope is −0.31.

The ratio of the free form to the interacting form in A_i will not be large enough to preclude the presence of the interaction in the derivative, since the log (A_i/A_f) of *N*-(7-*p*-nitrophenylheptyl)aniline (see Table III), which is free from the interacting N–H group, is appreciably greater than that of this lower homolog.

***N*-(4-Arylbutyl)anilines.**—The data on *N*-(4-arylbutyl)anilines are given in Table II.

As is shown by the filled circles in Fig. 3, a plot with σ_p's for *p*-substituents does not allow a correlation significant enough to confirm the presence of the interaction. On the other hand, a plot with σ_m's changes the situation fairly favorable for its presence. As the open circles in Fig. 3 show, the log(A_i/A_f)'s are in the order of corresponding σ values, though not linear. Since one of the free rotamers doubtlessly makes a certain contribution to the intensity assigned to the interaction band, it would be rash to conclude that the improvement of the σ–log (A_i/A_f) relationship by the adoption of the σ_m value reflects the actual site of the interaction. Nevertheless, it may be safe to conclude that the interaction does exist in *N*-(4-phenylbutyl)-anilines, for a comparison of the log (A_i/A_f)'s of

TABLE II. ν_{N-H} ABSORPTION OF *N*-(4-ARYLBUTYL)ANILINES
$RC_6H_4(CH_2)_4NHPh$

R	Band	ν_{max} cm^{-1}	$\Delta\nu_{max}$ cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1}·l.·cm^{-2}	log (A_i/A_f)
p-CH_3O	i[a)]	3422.2	26.0	35.6	2.26	0.414
	f[b)]	3448.2		31.2	0.87	
H	i	3421.2	25.7	39.4	3.13	0.540
	f	3446.9		31.0	0.90	
p-Cl	i	3421.8	25.4	36.2	2.22	0.396
	f	3447.2		26.4	0.89	
p-NO_2	i	3420.8	25.7	36.8	2.44	0.326
	f	3446.5		27.6	1.15	

a) i denotes interacting form of N-H group.
b) f denotes free form of N-H group.

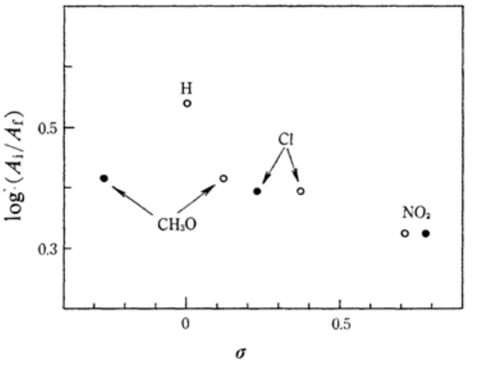

Fig. 3. The relationship between σ value and log (A_i/A_f) for *N*-(4-arylbutyl)aniline. Filled circles, σ_p; open circles, σ_m.

unsubstituted (0.540) and *p*-nitro (0.326) derivatives shows a significant difference, one which cannot be explained by any other reason than the N–H···π interaction.

This conclusion is important in that, in the hydroxy analog, $C_6H_5(CH_2)_4OH$, no O–H···π interaction was observed[4)]. Although the conditions for the interaction, especially the distance between the X–H group and the π-electron source, seem to be unfavorable in these compounds, the following may be added as supporting evidence.

Martin and Gleicher[6)] determined the NMR spectra of ω-phenyl-2-methyl-2-alkenes, $C_6H_5\cdot(CH_2)_nCH{=}C(CH_3)_2$. They concluded from the chemical shift of the terminal *cis*-methyl group that the group spends a considerable portion of the time over the plane of the benzene ring in those compounds in which n is 2 and 3. This conclusion suggests the likely importance of the number of the ring member in the X–H···π interaction and, at the same time, the significance of the restriction of the rotation around the CH_2–XH bond, which may be the main reason for the different behavior of the OH and NHPh groups in the interaction.

Higher Homologs with $n=5$ and 7.—As an extention, the infrared spectra of *N*-(5-phenylpentyl)- and *N*-(7-phenylheptyl)anilines and of *p*-nitro derivatives were recorded. The N–H stretching absorption curves are shown in Figs. 4 and 5, and the analyzed data, in Table III. The observed spectra (Fig. 4) for *N*-(5-phenylpentyl)aniline and its nitro derivative are slightly different in the higher wave number band, with a higher intensity for the *p*-nitro derivative. The data given in Table III indicate this point more clearly. The log (A_i/A_f) of the *p*-nitro derivative is smaller than that of the unsubstituted compound, but nearly

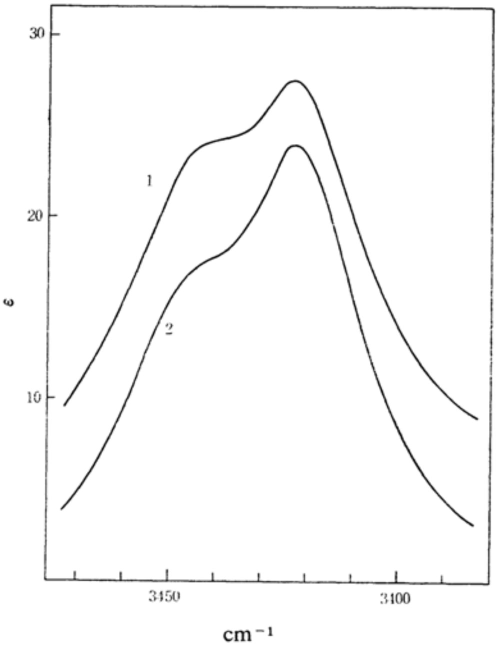

Fig. 4. ν_{N-H} Absorptions of *N*-(5-*p*-nitrophenylpentyl)- (1) and *N*-(5-phenylpentyl)anilines (2). Curve (1) is displaced upward by 5 units.

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6) M. M. Martin and G. J. Gleicher, *J. Am. Chem. Soc.*, **86**, 238 (1964).

TABLE III. ν_{N-H} ABSORPTION OF HIGHER HOMOLOGS OF $RC_6H_4(CH_2)_nNHPh$ (n=5 and 7)

n	R	Band	ν_{max} cm^{-1}	$\Delta\nu_{max}$ cm^{-1}	$\Delta\nu^a{}_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1}·l.·cm^{-2}	log (A_i/A_f) or log (A_I/A_{II})
5	H	i[a)	3421.6	25.2	33.4	2.63	0.428
		f[b)	3446.8		27.4	0.98	
5	p-NO$_2$	i	3421.6	25.2	36.4	2.59	0.361
		f	3446.8		27.6	1.13	
7	H	I	3422.7	25.6	33.8	2.12	0.421
		II	3448.3		26.8	0.81	
7	p-NO$_2$	I	3422.4	25.3	34.4	2.68	0.450
		II	3447.7		26.2	0.95	

a) i denotes interacting form of N-H group.
b) f denotes free from of N-H group.

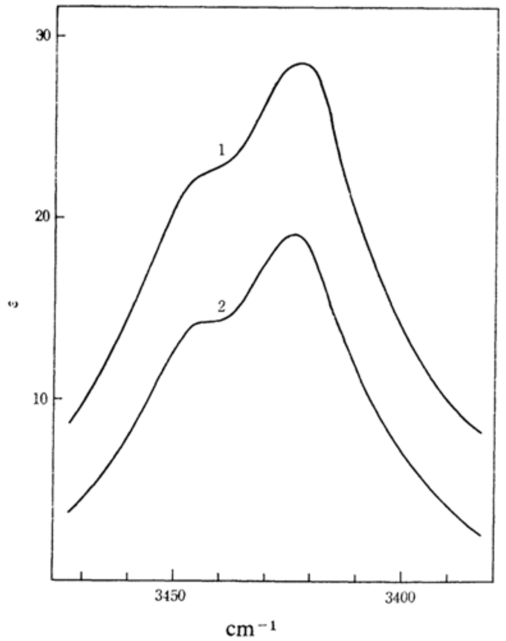

Fig. 5. ν_{N-H} Absorptions of *N*-(7-*p*-nitrophenylheptyl)- (1) and *N*-(7-phenylheptyl)anilines (2). Curve (1) is displaced upward by 5 units.

within the range of experimental error (ca. 0.05). If the observed effect of the substituent is meaningful, that fact should be interpreted as a reflection of the presence of the N–H···π interaction. Although the matter should be treated with great care, it seems that the apparent spectrum which shows the stronger absorption at higher wave number for the nitro compound suggests the existence of such interaction.

Two absorption curves of the higher homolog (n=7) (Fig. 5) indicate no substantial difference. Analyzed data also show the same result. The log (A_I/A_f)'s for two derivatives are similar within the range of experimental error. From these data, it can safely be concluded that the interaction is absent in *N*-(7-phenylheptyl)aniline.

General Discussion.—In summarizing the data for this series of compounds, $Ar(CH_2)_nNHPh$, one can conclude that the intramolecular interaction of the N–H group with π-electrons is present in the cases where n is 1, 2, 3 and 4, and possibly 5. In contrast to this, in the hydroxy analog, $Ar(CH_2)_nOH$, it has been reported[3,4) that the O–H···π intramolecular interaction is present only in the cases where n is 1, 2 and 3. From these results, it is tempting to conclude that the N–H group is more favorable for the interaction with π-electrons than is the O–H group, at least in these species.

As for chemical reactivity, the O–H group is more reactive and has more proton-releasing power than the N–H group. Additionally, and more significantly, it is generally accepted that the tendency of amines to associate is less than that of hydroxylic compounds.[7) The association of aniline in the liquid phase has been investigated by several workers[8–12) by infrared spectroscopy; it has been concluded that the shift of the N–H stretching bands of aniline with a change in concentration is due to N–H···N hydrogen bonding, with a very low energy. Recent ultraviolet spectroscopic studies[13) also show that hydrogen bonding in aniline is not very strong. Although Bellamy and Williams[14) have postulated that the steady shift of the bands to lower frequencies with

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7) M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936).
8) E. L. Kinsey and J. W. Ellis, *J. Chem. Phys.*, **5**, 399 (1937).
9) W. Gordy, ibid., **7**, 167 (1939).
10) E. Williams, R. Hofstadter and R. C. Herman, ibid., **7**, 802 (1939).
11) A. N. Buswell, J. R. Downing and W. H. Rodebush, *J. Am. Chem. Soc.*, **62**, 2759 (1940).
12) N. Fuson, M. L. Josien, R. L. Powell and E. Utterback, *J. Chem. Phys.*, **20**, 145 (1952).
13) J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **38**, 896 (1960).
14) L. J. Bellamy and R. L. Williams, *Spectrochim. Acta*, **9**, 341 (1957).

an increase in the concentration can be explained by dielectric constant and dipolar effects in the liquid, Rao and his co-workers[15] studied the problem by NMR spectroscopy and confirmed the presence of a N-H⋯N hydrogen bond in aniline with quite a low energy. All these data suggest that the N-H group, especially in aniline, is much less proton-donating in hydrogen bonding than is the O-H group.

These opposing pieces of evidence raise the question of whether or not the bands observed in the N-H stretching region can be assigned to free and N-H⋯π interacting forms with certainty. Other possible causes affecting two bands may be the Fermi resonance, or the presence of an overtone or a combination band. An inspection of the spectra of some compounds used in this series of papers in the sodium chloride region indicates that such effects cannot be expected for the compounds; on normal vibration band appears between 1650 and 2900 cm^{-1}, and it has been reported that there are two N-D stretching bands in *N*-deuterio-*N*-benzylaniline.[16]

Additional evidence for the equality of N-H and O-H groups as hydrogen donors was obtained by the determination of the interaction energy (ΔH). The energies in the intramolecular O-H⋯π interaction reported so far do not, in general, exceed 2.0 kcal./mol. The values for the N-H group have also been found, by a brief study of the energetics of *N*-benzylanilines,[17] to be within the same limits. Hence, O-H and N-H groups should be regarded as, at least, equally affecting functions for intramolecular interaction with π-electrons.

Probably one of the factors which result in the N-H group being equal with or having the advantage over the O-H group is the different extent of populations of rotamers caused by the rotations around the CH_2-NH and the CH_2-OH bands in the corresponding compounds. Taking *N*-ethylaniline and ethyl alcohol as reference compounds, the ratios of the state of possible interaction to that of the impossible are 8.7[2] and 0.57[18] respectively. The discrepancy, by a factor of more than 15, may reasonably be attributed to the large steric requirement of the phenyl group.

Finally, mention should be made of the interesting features of the spectra for this series of compounds in connection with the change in log (A_i/A_f) with the substituent and the chain length. The values for non-substituted and *p*-nitro derivatives are especially worthy of consideration. As is shown in Fig. 6, log (A_i/A_f)'s for *N*-(ω-phenylalkyl)anilines change in a zigzag fashion with the number of chain carbon atoms (n) and approach a limited value with a decreasing amplitude. The prominent peak at $n=2$ is the reflection of the highly favorable conditions for the N-H⋯π interaction in this homolog. The following zigzag change with a small amplitude is interesting, but experimental uncertainties do not at present allow any unambiguous explanation for this.

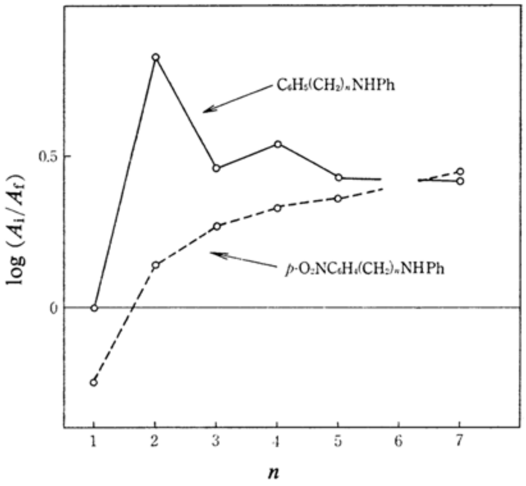

Fig. 6. The relationship between the number of the side chain carbon (n) and log (A_i/A_f) *N*-(ω-arylalkyl)aniline, $RC_6H_4(CH_2)_nNHPh$.

On the other hand log (A_i/A_f)'s for *p*-nitro derivatives increase with increasing n values and reach a limit. It may seem strange that the curve gives the impression that the longer the chain, the greater the ratio of the interacting form. However, as has been discussed, the A_i's for higher homologs are overestimated when the intensity due to a free form is included. The gradual decrease of $\Delta\nu_{max}$ and its approach to the value for the compound lacking the interaction may be cited as support for this interpretation. The values for $n=3$, 4 and 5 can be explained on this basis, because no complete Hammett correlation is observed for them. The values for $n=1$ and 2 should be regarded as true ratios of A_i and A_f, because the plots of log (A_i/A_f) against the σ value yield good linear correlations.

A comparison of the log (A_i/A_f) values for *p*-nitrobenzyl- and *p*-nitrophenethylanilines gives an interesting picture of the molecular conformation. The value for the former, -0.244, is appreciably lower than that for the

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[15] B. D. N. Rao, P. Venkateswarlu, A. S. N. Murthy and C. N. R. Rao, *Can. J. Chem.*, **40**, 963 (1960).

[16] A. G. Moritz, *Spectrochim. Acta*, **16**, 1176 (1960).

[17] M. Ōki and K. Mutai, Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

[18] M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

latter, 0.148. This remarkable discrepancy may be partly the consequence of the preference for the five membered ring conformation in the interacting states. However, the free form absorbing at ca. 3450 cm^{-1} in the *p*-nitrobenzyl derivative should be the conformer with two phenyl groups at an eclipsed or nearly-eclipsed position (see Ref. 2). In this conformation considerable repulsive forces will operate to prevent the two phenyls from becoming eclipsed; therefore, the state will be unstable compared with the interacting form in which phenyls are at trans and which is additionally stabilized by the interaction.

An explanation of this phenomenon will be published in a forthcoming paper.

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