*Tetrahedron.* Vol. 26, pp. 1181 to 1198. Pergamon Press 1970. Printed in Great Britain

# INTRAMOLECULAR CHARGE-TRANSFER INTERACTION IN N-[ω-(*p*-NITROPHENYL)ALKYL]ARYLAMINES[1]

M. ŌKI

Department of Chemistry, Faculty of Science, University of Tokyo, Hongo, Tokyo 113

and

K. MUTAI

Department of Chemistry, College of General Education, University of Tokyo,
Komaba, Meguro, Tokyo 153

(*Received in Japan* 6 *August* 1969; *Received in the UK for publication* 14 *October* 1969)

**Abstract**—The occurence of an intramolecular charge-transfer interaction has been confirmed by solvent effects and the change of $\pi$-base strength in a series of compounds, $p$-$O_2NC_6H_4(CH_2)_nNHAr$, where Ar groups are phenyl, 2,4-dimethylphenyl, mesityl, *p*-anisyl, α-naphthyl, and β-naphthyl. When the Ar group is phenyl, the interaction includes the homologs $n = 1 \sim 4$. The procedures to obtain the CT band by subtracting a reference spectrum have been discussed, especially with regard to the choice of reference compounds. The change of $\lambda_{max}$ and $\varepsilon_{max}$ with $\pi$-base strength and n has been discussed from the viewpoint of contact charge-transfer interaction. Throughout the series, mesityl and β-naphthyl groups show abnormal behaviour, which is explained by steric effects for the mesityl and by conformational effects for the β-naphthyl groups.

SINCE N-(*p*-nitrobenzyl)aniline (**1a**) shows an abnormal rotamer distribution with regard to its $CH_2$—N bond,[2] and since its solution is pale yellow even in a concentration less than $10^{-2}$ mole/l., it may be reasonable to expect intramolecular electron donor-acceptor or charge-transfer (CT) interaction* in this compound.

**1a**: n = 1
**1b**: n = 2
**1c**: n = 3
**1d**: n = 4
**1e**: n = 5
**1f**: n = 7

Although extensive theoretical and experimental attention has been given to the charge-transfer complex, most of the data are related to intermolecular interaction and not many[5-12] are concerned with the intramolecular case. The intramolecular CT interaction is, however, interesting and important, since the structural factors governing the characteristics of CT absorption are variable by choosing appropriate structures and the resulting effects may be useful for the analysis of the interaction.

---

* The terms "intramolecular charge-transfer interaction" and "intramolecular donor-acceptor interaction" have also been used for the phenomenon involving directly connected donor and acceptor groups.[3,4] There may be no essential difference in whether donor and acceptor groups are directly or indirectly bonded, since in either case the major process involved is transfer of a charge (i.e. of an electron) from a donor to an acceptor. However it is important from the viewpoint of approach whether the interaction occurs directly ("through bond") or indirectly (so to say, "through space"). The former has attracted the attention of the theoretical field, but the latter has been studied mostly by organic chemists. We feel it necessary to indicate this difference clearly in order to avoid misunderstanding.

Two representative types of structure have been used for the study of the intramolecular CT interaction. One the cyclophane type,[5–8] has rigidly fixed donor and acceptor groups, its spectral characteristics being easily subject to the analysis on the basis of established structural parameters. The other is the acyclic[9–12] type in which donor and acceptor groups are, in general, bound with a polymethylene chain. The analysis is not easy on account of the mobility allowed for the two groups, but this type has the greater advantage of being easily accessible and rich in variety.

The compound **1a** belongs to the latter type. The objectives of present paper are to provide evidence for the existence of the intramolecular CT interaction and to study, compare, and correlate the effects of various structural alterations on the CT absorption in a homologous series of compounds.

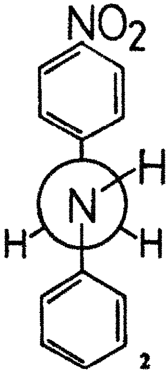
It should be mentioned here that Dewar and Thompson,[13] have pointed out "the appearance of a charge-transfer spectrum provides no evidence that charge-transfer plays a dominant, or even a significant, role in the binding." They have also indicated that the only requirement for a CT transition to occur with significant intensity is that the species involved should be close together. We consider these suggestions are also applicable to the present interaction. Therefore the term interaction, not complex formation, is used in this paper. As an approach, our concern is focused mostly on the electronic spectrum, i.e. CT band. Therefore the following discussion is mainly concerned with the characteristics of the CT band, but not with the forces bringing the donor and acceptor groups in close contact.

## RESULTS AND DISCUSSION

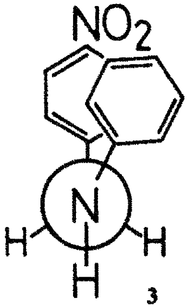
### *Infrared spectroscopy*

In the region of the N—H stretching absorption the compounds **1a–f** show two bands, at ca. 3420 and 3450 $cm^{-1}$. The former has been assigned as due to the intramolecular N—H ... π interaction and the latter to free N—H.[14,15] The relationship between the logarithmic ratio of the two band intensities, $\log (A_{lower}/A_{higher})$, and the number of methylene groups (n) in **1** is shown in Fig. 1. The gradual increase of the ratio with n has been interpreted as a consequence of the increase of another free N—H rotamer which absorbs at nearly 3420 $cm^{-1}$. It has been confirmed that the value for **1f** ($n = 7$) is the ratio of the two free rotamers as is observed in N-propylaniline.[15] The values for **1a**, **1b** and **1c** are abnormally low, because, if the N—H ... π interaction is present, the intensity of the lower band (interaction band) should be stronger, and if the interaction is absent it should be near to the value of **1f**, in which the absence of the interaction has been confirmed.

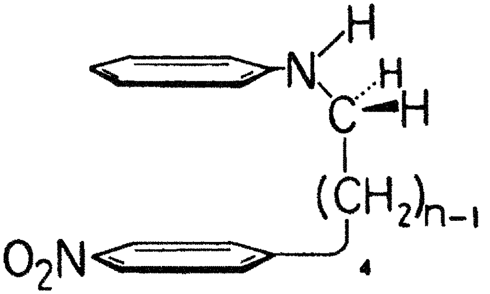
The anomaly will become clearer if **1a** is taken as an example. There are two rotamers (**2** and **3**) in this compound of which **2** is the N—H ... π interacting species. Since the observed ratio, $\log (A_{lower}/A_{higher})$ or $\log (A_2/A_3)$, is negative, the rotamer **3** is favoured over **2**. This value is unexpectedly low considering the circumstances that the N—H ... π interaction stabilizes **2** and repulsive force between the two benzene rings would destabilize **3**. Both effects should increase the population of **2** and the intensity ratio over that of **1f**. Hence, observed phenomenon must be explained by some attractive forces between the aromatic rings. The same conclusion has also been drawn from the determination of ΔH of **1a**.[16] For the cases **1b** and **1c**, the situation is nearly the same; the low intensity ratio suggests the high population of the conformer **4** in which the possibility of the aromatic rings being in close contact with each other is larger than other conformers. It is noteworthy that the N—H stretching absorption of the higher wavenumber does not show an appreciable change throughout the series of the homologs **1a–f**. This fact may suggest that the major force would not be the charge-transfer force, since if it were dominant the π-electron density in the anilino group would be reduced and appreciably effect the displacement of the band position.[2] The important thing deduced from these facts is that a great opportunity of close contact is provided for the aromatic rings in some homologs of **1**.



**2**



**3**



**4**

## ELECTRONIC SPECTROSCOPY

### *Electronic spectroscopy*

*Effect of the chain lengtn.* Electronic spectra in a region of 220 ~ 400 mμ of the homologous series of **1** have been measured in 95% ethanol and reproduced in Fig. 2. Comparing the absorption curves with that of **1f**, the lower homologs show some extra extinction in the longer wavelength region. The higher homologs, **1d** and **1e**, show nearly the same absorption curves as that of **1f**.

From these spectra it can be assumed that the *p*-nitrophenyl and the anilino groups in **1f** are sufficiently apart from each other to make any intramolecular interaction null, and that its absorption spectrum can be regarded as a reference or standard for comparison. Subtraction of this reference spectrum from others shows an absorption maximum in the region longer than 300 mμ. The results obtained in several solvents are summarized in Table 1.

As is seen in Table 1, **1a**, **1b**, **1c** and **1d** show the extra bands, with some differences in maximum position and extinction coefficient. Although the band in **1d** may appear uncertain on account of its small intensity, its presence is certain since the values are results of several measurements and since it is observed in three of four solvents (Table 1). It is notable that the extra band is observed in those compounds which have shown an anomalous value, log $(A_{lower}/A_{higher})$, mentioned above. Judging from the electronic spectrum, the value for **1d** (Fig. 1) could also be abnormal. Thus the circumstances that the *p*-nitrophenyl and anilino groups could be close together, seems, at least, one reason for the appearance of the extra band. Considering the band position and the nature of the two chromophores, it may be reasonable to conclude that the band is due to charge-transfer transition, where the *p*-nitrophenyl group plays a role of π-acid and the anilino group π-base.

TABLE 1. THE INTRAMOLECULAR CT BANDS OF **1** IN SEVERAL SOLVENTS

| Solvent | **1a** |  | **1b** |  | **1c** |  | **1d** |  |
|---|---|---|---|---|---|---|---|---|
|  | $\lambda_{max}$ | ($\varepsilon$) | $\lambda_{max}$ | ($\varepsilon$) | $\lambda_{max}$ | ($\varepsilon$) | $\lambda_{max}$ | ($\varepsilon$) |
| 95% Ethanol | 347 mμ | (280) | 333 mμ | (950) | 334 mμ | (185) | 345 mμ* | (40) |
| Acetic acid | 340 | (250) | 328 | (330) | not observed |  | not observed |  |
| $CCl_4$ | 344 | (315) | 332 | (930) | 325 | (340) | 336* | (25) |
| Dimethylformamide | 363 | (310) | 345 | (865) | 337 | (435) | 350* | (35) |

* Broad band, with an accuracy of ±5 mμ.

Various types of intramolecular interaction have been reported. Approaches for the study and the strength of the interactions are manifold. As a measure of the strength, limitation by the chain length, namely a number of atoms involved in the chain binding interacting groups may be used. Within the scope of weak interactions in acyclic compounds excluding H-bonding, compounds similar to the present case, $p\text{-}O_2NC_6H_4(CH_2)_nC_6H_4NH_2\text{-}p$, are known to show the CT band when n is 1, 2 and 3.[9] In the case of this study n = 2 and 3 correspond to **1a** and **1b** in chain length, respectively. In a series of pyridinium salt, $[Ar(CH_2)_nN^+C_5H_4R]X^-$, the appearance of the CT absorption has been reported in n = 1, 2, 3 and 4.[10, 11] Unfortunately, in both cases the limit of interaction has not been reported. In a series of pyridyl diradicals,[12] $Py\cdot(CH_2)_n\cdot Py$ where Py· denotes 4-methoxycarbonyl-1-pyridyl, the intramolecular association and at the same time CT band are observed in n = 3 and 4, but not in n = 5 which corresponds to **1d** in chain length. Several kinds of compounds

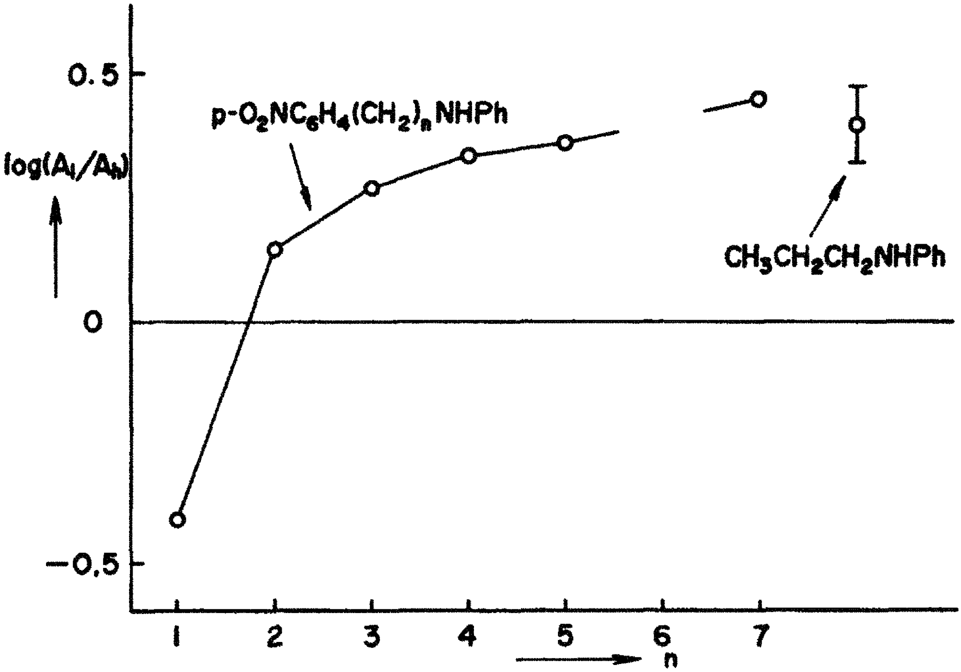


FIG. 1. Correlation of the number of methylenes (n) with the intensity ratio, log ($A_{lower}/A_{higher}$).

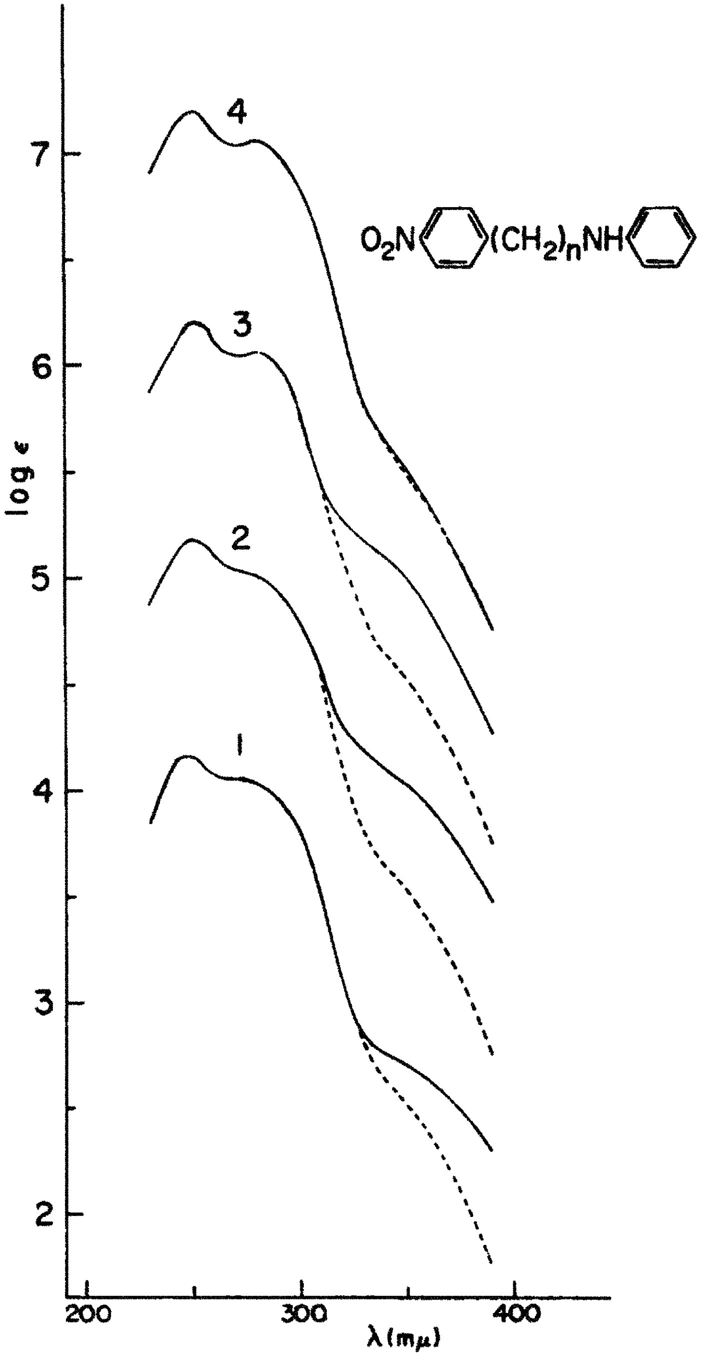


FIG. 2. The absorption spectra of 1 in 95% ethanol. Curves 1, 2, 3, and 4 correspond to the spectra of **1a**, **1b**, **1c**, and **1d**, respectively. The broken line represents that of **1f**. The curves have been displaced upward on the ordinate axis by one log ε unit increments from the curve immediately below.

have been used for the study of intramolecular interactions,[17–24] but their structural variety is limited in regard to the chain length. In most cases the investigation has not been extended to higher homologs in order to detect the limit of the interaction. The limited data available suggests that a chain length of four or five atoms is the limit to intramolecular interaction in acyclic compounds, especially involving two aromatic rings. The effects of chain length on the characteristics of the absorption are obvious, but discussion will be postponed to the later part of this paper.

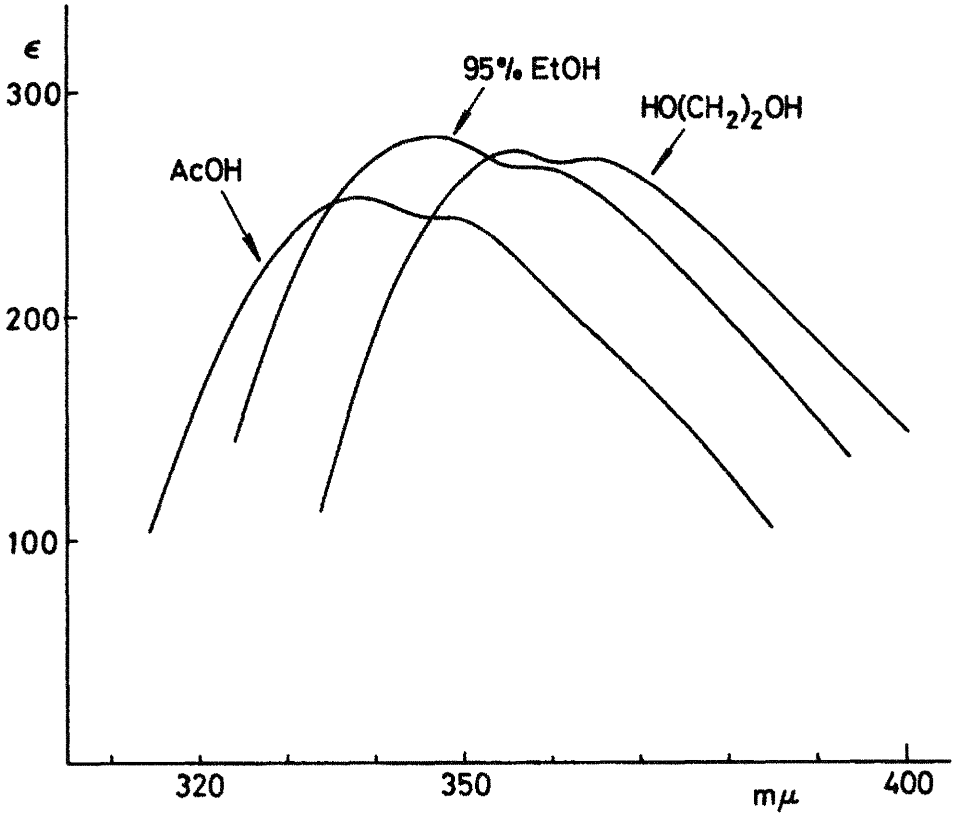


Fig. 3. The extra bands of **1a** in protic solvents.

*Solvent effects.* Since the influence of solvent on CT absorption is sometimes noted in intermolecular CT complex,[25–29] it would be interesting to know the effects in an intramolecular case since this may provide evidence for CT interaction. The subtraction bands of **1a** in several solvents are shown in Figs 3 and 4, with a summary of data in Table 1. Though the choice of solvents is limited by the solubility of the compounds and the transmittancy of solvents, from these data it may be said that in protic solvents (Fig. 3) the band appears very broad and, in some cases, probably has more than one peak. On the other hand in aprotic solvents (Fig. 4) the band is relatively sharp and apparently has one peak. The observed difference in the type of solvents would be explained on the basis of solute-solvent interaction.

In aprotic solvents, the effects are apparent in both maximum position and extinction coefficient; as a tendency, the shorter the wavelength, the higher the intensity. The band broadening is also observed, but less marked than in protic solvents. The broad bands observed in dioxan, bromobenzene, and dimethylformamide are explained on the basis of the solute-solvent interaction, in which the N—H group of the solute amine is a proton-donor and the oxygen or π-electrons of these solvents a proton-acceptor. Under these conditions, there may be many possible states of the CT interaction corresponding to various conformations and strength of the interaction. Accordingly, a broad band should be observed as a composite of the bands due to these various states. Only H—bonding is not an effective force. In dimethylformamide (Table 1), maximum positions are red-shifted by 10 ~ 20 mμ, $\varepsilon_{max}$'s slightly decreased in **1a** and **1b**, but rather increased by 30 ~ 40% in **1c** and **1d** in comparison with those in $CCl_4$. These effects should be considered in connection with dipole moment, dielectric constant, polarizability of the solvent, etc as well as H-bonding.

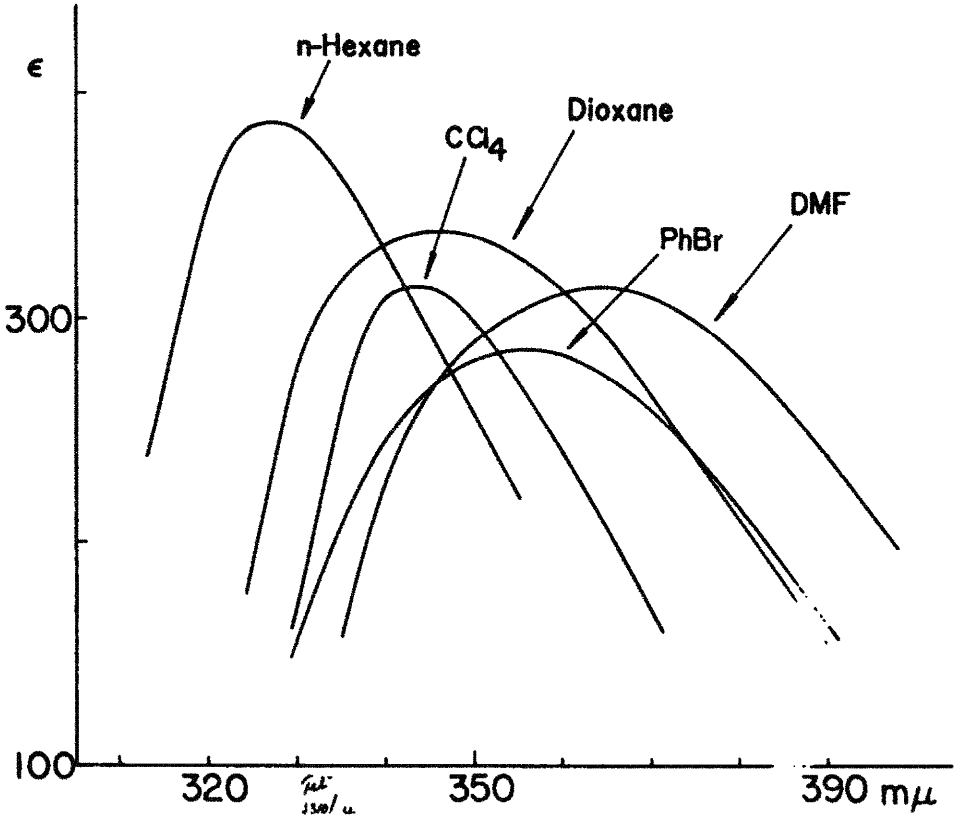


FIG. 4. The extra bands of **1a** in aprotic solvents.

Even $CCl_4$ is not an inert solvent in comparison with n-hexane (Fig. 4). The slight band broadening and reduction in the intensity observed in this solvent should also be attributed to a weak interaction with the solute aromatic amine.[30–32]

In protic solvents, this interaction is mainly intermolecular H-bonding where the nitrogen in the solute molecule is a proton-acceptor and a solvent molecule a proton-donor. This effect decreases the π-base strength of the anilino group to a greater extent than in aprotic solvents, resulting in weaker extinction coefficient as observed in Fig. 3. Of course, the N—H group of the solute can also be a proton-donor and the solvent oxygen a proton-acceptor, probably to a lesser extent than the O—H group of the solvents on account of the bonding energy.[33] In addition, O—H . . . π type, O—H . . . $O_2N$ type interactions, etc are also possible depending on the structures of the components and the bonding energies. All these effects are probably responsible for band broadening and two apparent peaks.

The band observed in acetic acid is blue-shifted with a considerable decrease in intensity (Table 1). A dramatic change is observed for **1c** and **1d**, the band in question completely disappearing in this solvent. Considering the fact that acetic acid solvates the solute amine far more strongly than the other protic solvents in salt-like mode, the observed effect could be explained by the sharp decrease of π-basicity in the anilino group. If this is true, the effect of acetic acid is further evidence of the presence of CT interaction.

It is therefore clear that protic solvents are not appropriate for the present study. For this reason $CCl_4$ was chosen as a standard solvent, as it is relatively inert and has good dissolving power.

*Reference compound.* In the homologous series of **1**, **1f** has been chosen as a reference or standard compound and its absorption spectrum subtracted from the others, and the resulting extra bands discussed on the basis of CT interaction. For this purpose, **1e** is also suitable, since in $CCl_4$, there is no difference between the spectra of **1e** and **1f**. Hereafter, this method of setting a reference is called the higher homolog method (HH method). In some cases the separate chromophores (SC) method has been applied. A compound is divided into two (or more) chromophoric groups, and representing these by simple or easily available compounds, the sum of the spectrum is taken as a reference. For instance, for the series of **1** the sum of the spectra of *p*-nitrotoluene and N-methylaniline is used instead of **1f**.

Before discussing the relative merits of these methods, it must be noted that the more important problem to be solved lies in obtaining the extinction of the extra band by simple subtraction of a reference spectrum in both methods. Here, we have assumed that the molecule in the CT interacting state should only add the extra spectrum to that of the non-interacting state. This assumption has not been proved yet. Fortunately, the assumption is not quite meaningless,* since the band appears in the region where the effect of a change in the original transitions on the absorption intensities of the interaction, if it occurs, is expected to be small (in ε unit) on account of the low extinction. Consequently it may seem of little value to discuss which of the two methods is superior so long as the extent of the uncertainties originating in this assumption are not known. But it is interesting to compare the reference spectra by these methods. By doing this, a criterion may be obtained to decide whether both methods are applicable on the same level or either of them should be adopted throughout a series of experiments.

As separate chromophores, N-methylaniline, N-ethylaniline, N-butylaniline,

---

* The same consideration should be taken into account in intermolecular complex. For instance, see Experimental Part of ref 38.

*p*-nitrotoluene, and *p*-nitrobutylbenzene were chosen. The data are summarized in Table 2.

TABLE 2. COMPARISON OF REFERENCE SPECTRA BY THE SC METHOD AND THE HH METHOD (IN $CCl_4$)

| Compounds | Absorption Coefficient* | | | | | |
|---|---|---|---|---|---|---|
| | 320 mμ | 330 | 340 | 350 | 360 | 370 |
| MeNHPh | 790 | 220 | 63 | 21 | 8 | 3 |
| EtNHPh | 840 | 230 | 65 | 21 | 9 | 5 |
| n-BuNHPh | 950 | 270 | 78 | 25 | 10 | 5 |
| *p*-$MeC_6H_4NO_2$ | 307 | 268 | 229 | 181 | 133 | 89 |
| *p*-n-$BuC_6H_4NO_2$ | 410 | 322 | 274 | 222 | 160 | 107 |
| MeNHPh + *p*-$MeC_6H_4NO_2$ | 1097 | 488 | 292 | 202 | 141 | 92 |
| EtNHPh + *p*-n-$BuC_6H_4NO_2$ | 1250 | 552 | 339 | 243 | 169 | 112 |
| n-BuNHPh + *p*-n-$BuC_6H_4NO_2$ | 1360 | 592 | 352 | 247 | 170 | 112 |
| *p*-$O_2NC_6H_4(CH_2)_nNHPh$ (1e and 1f) | 1290 | 575 | 340 | 244 | 170 | 111 |

* All values are averages of more than three measurements.

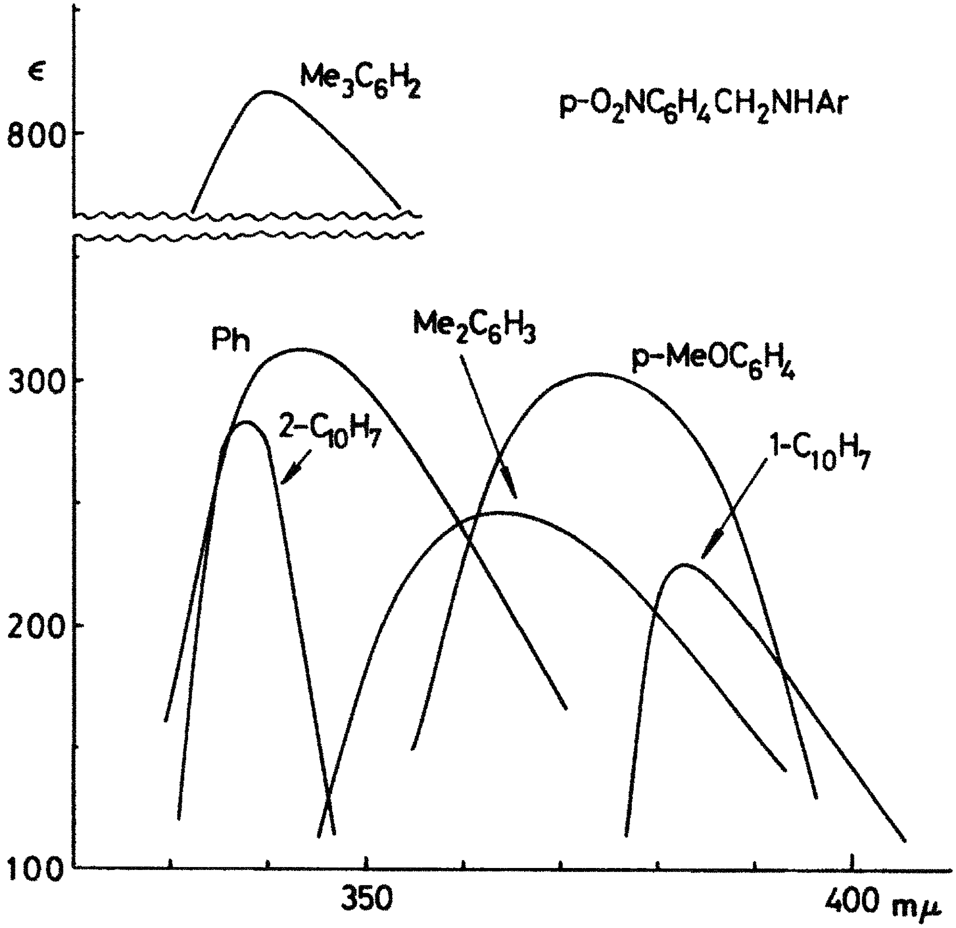


FIG. 5. The intramolecular CT bands of 5 in $CCl_4$.

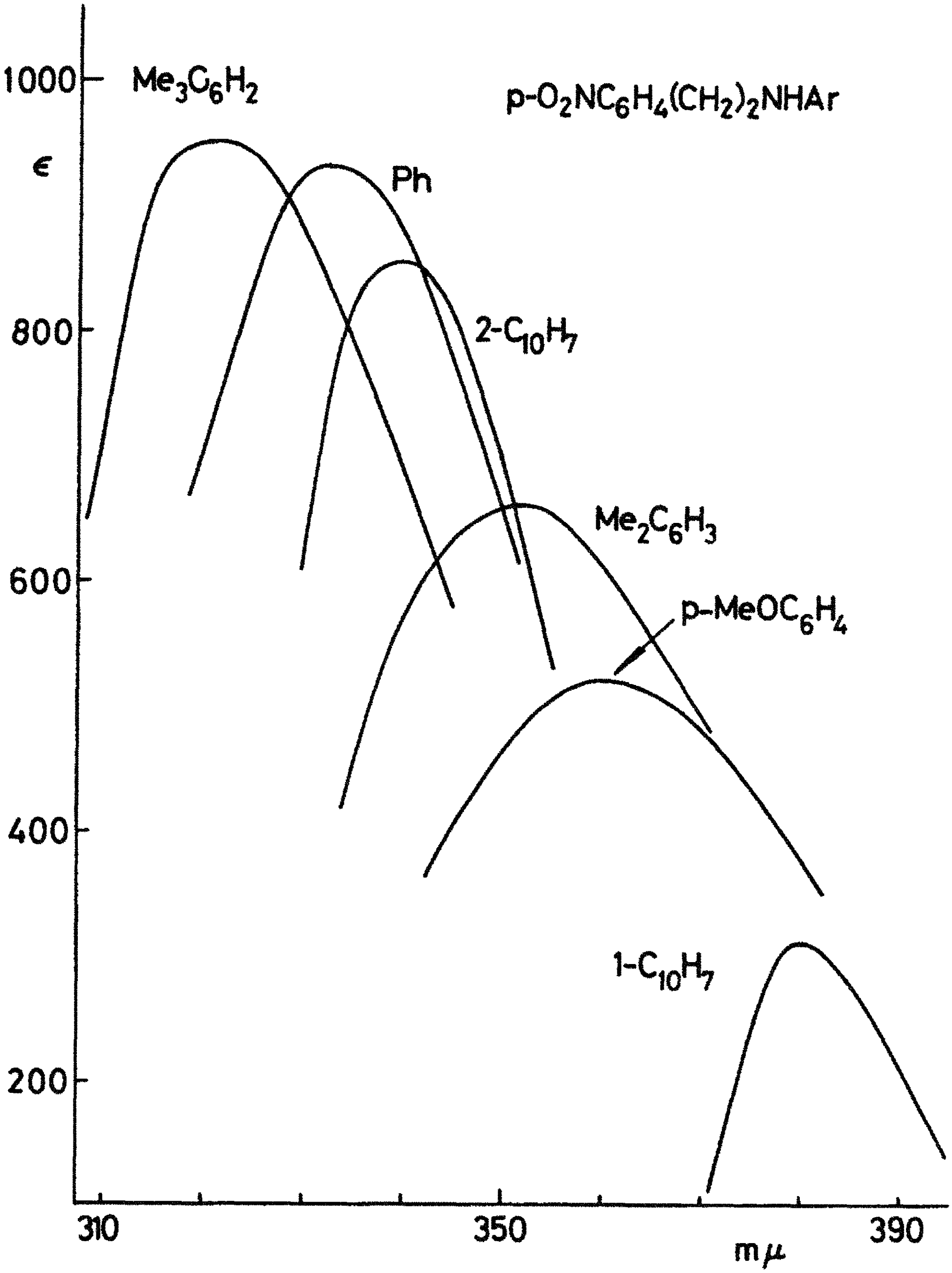


Fig. 6. The intramolecular CT bands of 6 in $CCl_4$.

Obviously there is a difference, slight but beyond errors, between Me, Et and Bu groups as a substituent in both types of chromophores. However it is also significant that the sum of the extinctions of N-butylaniline and p-nitrobutylbenzene or N-ethylaniline and p-nitrobutylbenzene is nearer to the average extinction of the higher homologs than the sum of the two chromophores substituted by a Me group. From these data it may be concluded that in the SC method if the methylene chain is substituted by a Me group, the resultant reference spectrum is very different from that obtained in the HH method, but if substituted by Et or Bu groups, the resultant spectrum is a good reference for the HH method, allowing a ±3% for experimental uncertainty of the observed coefficient. This difference brought about by introducing Me, Et and Bu groups may be explained by the difference in the substitution of the original methylene groups by Me or a methylene group. In this connection the different effect of the alkyl groups on the π-basicity of N-alkylanilines and N,N-dialkylanilines has been reported in their intermolecular CT complexes with trinitrobenzene.[27, 34] In conclusion, in order to compare the data obtained by these methods, Et or higher alkyl groups should be used instead of a Me group as substituent for methylene or a polymethylene chain in the SC method.

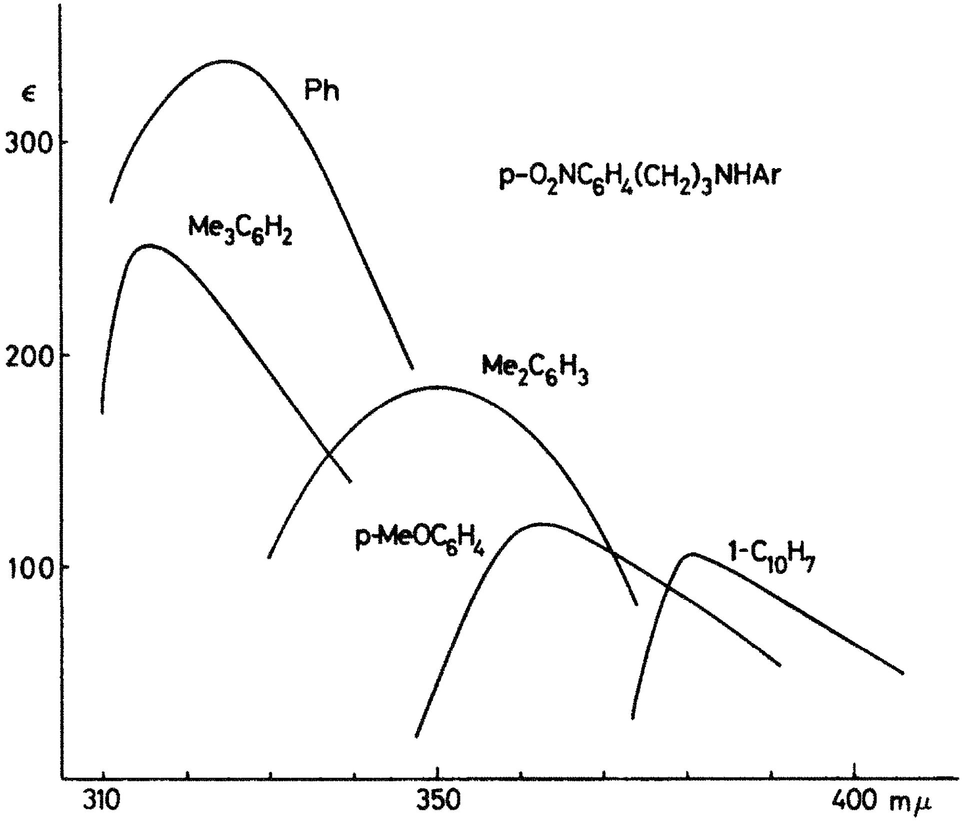


FIG. 7. The intramolecular CT bands of 7 in $CCl_4$.

*Effect of π-base strength.* A more reliable approach to intramolecular CT interaction is to determine the effects of π-base strength on the spectrum. If the band in question is ascribed to CT absorption as defined by Mulliken,[35] the charge-transfer transition energy should be closely connected with ionization potential or, in a qualitative sense, electron-donating ability of the π-base. Consequently, the spectra of several analogous compounds, **5**, **6**, and **7**, were synthesized and their spectra measured.

**5**: n = 1
**6**: n = 2
**7**: n = 3

**a**: Ar = $C_6H_5$ (= **1**)
**b**: = 2,4-$Me_2C_6H_3$
**c**: = 2,4,6-$Me_3C_6H_2$]
**d**: = p-$MeOC_6H_4$
**e**: = α − $C_{10}H_7$
**f**: = β-$C_{10}H_7$]

The extra bands are shown in Figs 5, 6, and 7, and data given in Table 3.

The effects of aryl groups are obvious. Some quantitative relationships between the absorption frequency and ionization potential (Ip) of π-donor have been proposed for the CT absorption of intermolecular CT complex.[36, 37] In fact, a linear or smooth correlation has been reported,[38–42] as is also the case in intramolecular interaction.[10] Unfortunately the data available for Ip as a comparison is insufficient. For instance, even if the value for N-methylarylamine is used instead of the N-Et or N-Bu derivative, only this value for N-methylaniline is known among those required. The values for even arylamines are limited, Consequently the presence of the CT interaction can only be determined qualitatively.

If it is assumed that the introduction of an amino group into an aromatic hydrocarbon has nearly the same effect on the Ip for all the parent hydrocarbons used in this study, the order of the π-basicity of the aryl groups is expected to be phenyl- < 2,4-dimethylphenyl < mesityl (2,4,6-trimethylphenyl) < p-anisyl < α- and β-naphthyl. Accordingly, the $\lambda_{max}$'s of **5** should be in the order, **5a** < **5b** < **5c** < **5d** < **5e** < **5f**, the same relation being expected for **6** and **7**. However the observed order for **5** is **5c** < **5f** < **5a** < **5b** < **5d** < **5e**. If **5c** and **5f** are considered as exceptions, the order is as expected, and it may safely be said that the extra bands are due to the intramolecular CT interaction. The abnormal behavior of **5c** and **5f** is considered later in this paper.

TABLE 3. THE INTRAMOLECULAR CHARGE-TRANSFER BANDS IN p-$O_2NC_6H_4(CH_2)_nNHAr$ IN $CCl_4$.

| Aryl Group | | **5** (n = 1) | | **6** (n = 2) | | **7** (n = 3) | |
|---|---|---|---|---|---|---|---|
| | | $\lambda_{max}$ | ε | $\lambda_{max}$ | ε | $\lambda_{max}$ | ε |
| $C_6H_5$ | (= **a**) | 344 mμ | 315 | 332 mμ | 930 | 325 mμ | 340 |
| 2,4-$Me_2C_6H_3$ | (= **b**) | 364 | 250 | 352 | 660 | 352 | 190 |
| 2,4,6-$Me_3C_6H_2$[a] | (= **c**) | 337 | 815 | 321 | 950 | 315 | 250 |
| p-$MeOC_6H_4$ | (= **d**) | 374 | 305 | 362 | 520 | 362 | 120 |
| α-$C_{10}H_7$ | (= **e**) | 383 | 220 | 379 | 310 | 380 | 100 |
| β-$C_{10}H_7$[b] | (= **f**) | 338 | 280 | 340 | 855 | — | — |

[a] The sum of the spectra of p-nitrobutylbenzene and N-ethylmesidine was used as a reference.

[b] The sum of the spectra of p-nitrobutylbenzene and N-ethyl-β-naphthylamine was used as a reference.

In the series 6 and 7, the order of the band position is almost similar to 5. Independent of the number of methylene groups, the common order of mesityl < phenyl- < 2,4-dimethylphenyl < p-anisyl < α-naphthyl is observed. Excepting the position of mesityl group, this order is as expected from the ionization potential of the parent hydrocarbons.

*Abnormal behavior of mesityl and β-naphthyl group.* It is obvious that the effect of a mesityl group would be abnormal. On the basis of Ip of mesitylene (8·40 eV)[43] and the CT absorption observed for its intermolecular complexes,[38, 44, 45] the parent hydrocarbon itself is a stronger electron donor than benzene (Ip = 9·25 eV)[43] or m-xylene (Ip = 8·50 eV).[43] The facts suggest that the abnormal behaviour should be explained not by the steric effects of the Me groups in the mesityl on, for instance, the accessibility of the aromatic rings, but by some effects originating in the mesitylamino group. Introduction of an amino or a methylamino group generally reduces the Ip of aromatic hydrocarbon by 1·5 or 1·9 eV, respectively.[43] The expected order of the aryl groups mentioned above is based on the assumption that an amino (or a methylamino) group would reduce the Ip of the parent hydrocarbon to nearly the same degree.

The steric effect on the resonance structure is probably the most important of possible causes for this anomaly; two Me groups in the 2 and 6 positions hinder the resonance interaction of the amino group with a benzene ring. This supposition is supported by the fact that the N-H stretching frequency of N-methylmesidine (3398 $cm^{-1}$) is unusually low as compared with N-methylaniline (3443 $cm^{-1}$).[2] The decrease in frequency is accompanied by a reduction in intensity of ca. 1/3. These effects are probably due to the N-Me group, since there is no appreciable difference between the N–H stretching frequencies of mesidine[46] and aniline.[47] The same effects are expected for N-substituted mesidine. The observed effects are not as remarkable as in the aliphatic secondary amines,[48] but their trend suggests a pyramidal structure of the nitrogen. The same conclusion is also obtained by the measurement of the dipole moment of mesidine derivatives.[49] Additional evidence is obtained by measuring the CT spectra of intermolecular complexes of N-methyl and N-ethylmesidine with 1,3,5-trinitrobenzene in $CCl_4$. N-Methylmesidine shows an absorption at 440 ± 10 mμ as a broad shoulder, and N-ethylmesidine at 445 mμ (broad): admitting the uncertainties of $\lambda_{max}$, these values are very close to N-methyl- and N-ethylanilines,[27] and effect of three Me groups becomes practically nil.

Another notable fact is the different behaviour of α- and β-naphthyl derivatives. Considering the Ip of naphthalene (8·12 eV),[43] the behaviour of α-naphthyl derivatives is normal. On the other hand, the behaviour of β-naphthyl derivatives is inexplicable. In the β-naphthyl group, the steric effect is of no account, but it should be taken into consideration in the α-isomer.[50] From the $pK_a$ values of naphthylamines[51] naphthols,[52] and naphthoic acids,[53] it is apparent that there is a difference in the inductive effect of an aryl group in different positions. In other words, a substituent in α- and β-positions should have a different effect on the π-basicity of naphthalene. However, it has been reported that there is only a small difference between α- and β-naphthylamines when they form intermolecular CT complexes with trinitrobenzene; the CT bands in $CHCl_3$ are 464 mμ (2·67 eV) for α- and 444 mμ (2·79 eV) and 456 mμ (2·72 eV) for β-isomers,[38] and the Ip's calculated from their CT band positions are 7·4 eV for α- and 7·5 eV for β-naphthylamine.[39] The difference observed in the present case is more than expected from the data of intermolecular interaction. When calculated from band maxima, the energy difference of the CT transitions in the two isomers is nearly 0·4 eV for both **5** and **6**.

A possible explanation may be the difference of interacting conformations or orientation isomers. In the case of intermolecular interaction, an acceptor and a donor have a freedom of choice of conformation to achieve the most stable complex, the situation being only somewhat disturbed by external conditions such as temperature, medium, etc. In the intramolecular case, the most favourable conformation cannot necessarily be assumed on account of restriction due to the polymethylene chain: the most favourable conformation is determined by both the chain length and relative position of the two aromatic rings in space. In this sense, we can regard this interaction as a forced one. The restriction on their contact area may result in considerably different conformations contributing to the CT bands: A Dreiding model shows that, in the β-naphthyl series, the *p*-nitrophenyl group can overlap with only one ring of the naphthalene, but, in the α-naphthyl series, it overlaps two rings almost equally. This effect may be a major cause for the difference of the α- and β-naphthyl groups. The possibility of a few or a number of conformations contributing to the CT band, has also been discussed in the intermolecular CT complex of naphthalene with tetracyanoethylene,[54] and is probably the case in the present intramolecular interaction. Contribution of varying mixture of conformations or orientation isomers to the CT band may also be the case in other derivatives to a greater or lesser extent, and in this regard the CT band is a typical absorption due to contact charge-transfer as has been pointed out by Orgel and Mulliken.[55] Complications of the interpretation of the difference arise from the symmetry properties of the molecular orbitals of ground and excited states of the interacting groups, and this problem should be postponed till the contributing conformations are established.

*$\lambda_{max}$, $\varepsilon_{max}$, and n.* The position of the CT band is in the longest wavelength when n is 1. The position generally blue-shifts as n increases, but in the α- and β-naphthyl series it does not change appreciably. Judging from the $\lambda_{max}$, the transition energy is the smallest in **5**, and, in this regard, **5** is the most favourable homolog for the interaction.

On the other hand, absorption coefficient ($\varepsilon_{max}$) is in the order **7** < **5** < **6** in most of the homologous series. It may be argued that **6** is the most favourable homolog for the interaction on account of its highest intensity (here, "the most favourable" means "in the highest population"). However, as has been shown by the intensity ratio of $\nu_{N-H}$'s, this possibility cannot be supported. From the viewpoint of entropy of the interaction, addition of a methylene group to the chain makes it more unfavourable for two aromatic rings to come close together. Furthermore, it was found that the fluorescence spectrum of **5e** is quenched almost completely, but that of **6e** is not, though it is weaker than N-[7-(*p*-nitrophenyl)heptyl]-α-naphthylamine by a factor of ca. 1/50.[56] This effect indicates that the quenching interaction between a *p*-nitrophenyl group and a naphthylamino group is greater in **5e** than **6e**. Although the quenching efficiency is not necessarily related directly to the strength of the CT interaction, this phenomenon could be supporting evidence for the greater degree of close contact of the two aromatic groups in **5e** than in **6e**.

Interacting conformations, therefore, probably affect the $\varepsilon_{max}$ as well as $\lambda_{max}$. Molecular models show that two aromatic rings can be in similar contact conformations in **6** and **7**. The small difference of $\lambda_{max}$ observed between **6** and **7** may be due to this situation, and a decrease in the intensity in **7** would result from the greater freedom allowed for the chain of **7**.

Examination of Table 3 shows that, in general, the shorter the $\lambda_{max}$, the higher the $\varepsilon_{max}$ in each series of **5**, **6**, and **7**. The mesityl group is also an exception here. A typical example is **6**, where a plot of $\varepsilon_{max}$ against $\nu_{max}$ shows a linear relationship (Fig. 8). A

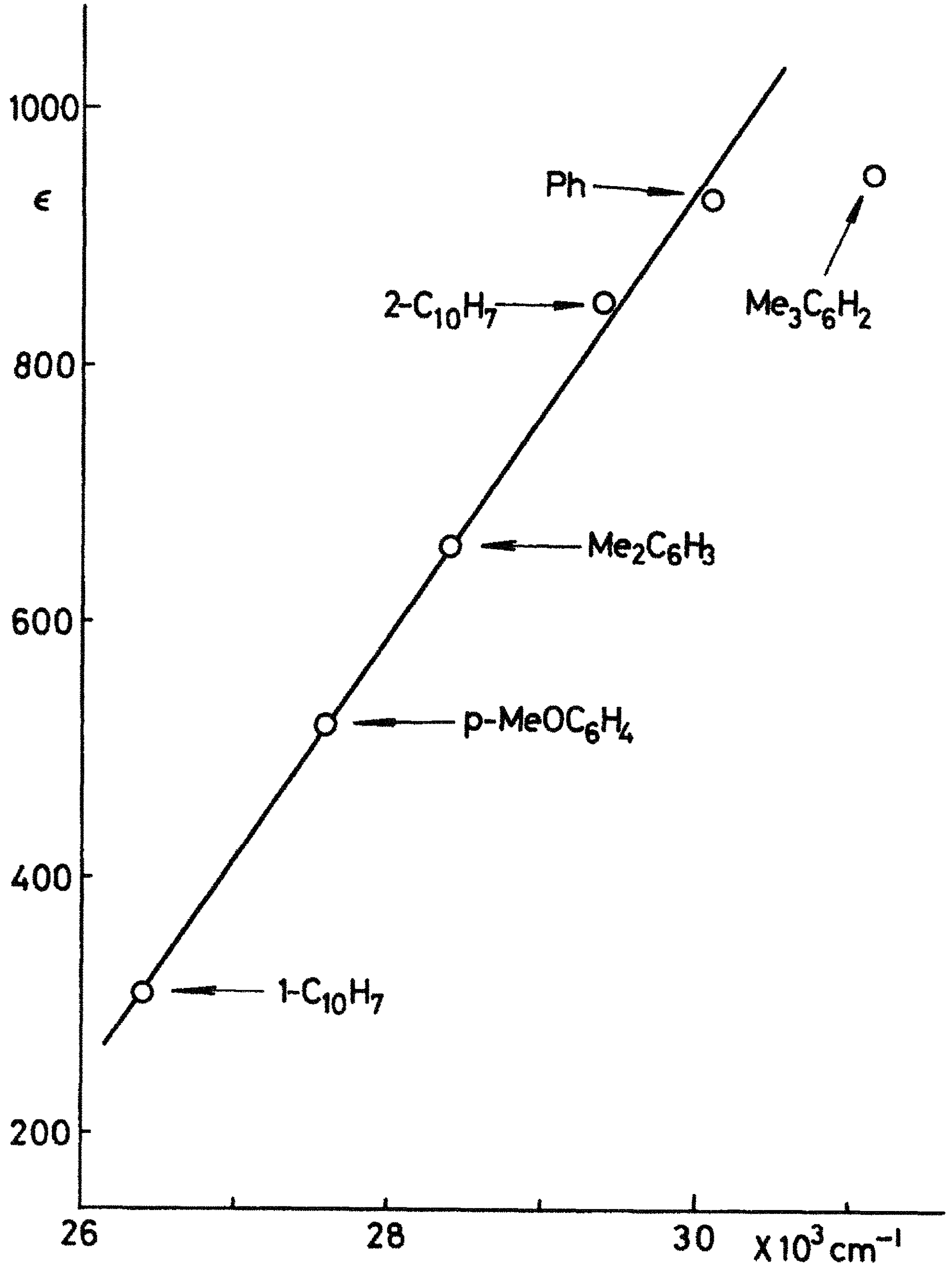


FIG. 8. Correlation of $\nu_{max}$ with $\varepsilon_{max}$ in **6**.

reasonable explanation for this linearity has not been found, but it should be pointed out that a similar trend, though not linear, has been reported in some intermolecular CT complexes.[38, 44, 45, 57] An explanation based on contact absorption has been advanced for the intermolecular case.[55] The present authors are inclined to support this explanation for the present case, since a nearly linear relationship is also observed in 7 where the long polymethylene chain allows more variety for the CT interacting conformations. In 5 the observed deviation from the linearity should be explained by limited interacting conformations. However, validity of this explanation needs further examination.

## EXPERIMENTAL

Unless otherwise specified, all m.ps and b.ps are uncorrected. Electronic spectra were measured with a Hitachi EPS-2U automatic recording spectrophotometer. Quartz cells of 1·0 cm in length were used. The concentration of $CCl_4$ soln was $10^{-5} \sim 10^{-4}$ mole/l for 220 ~ 320 mμ and $1 \sim 3 \times 10^{-3}$ mole/l for above 320 mμ. The IR spectra were recorded on a Perkin–Elmer Model 112-G grating infrared spectrometer, provided with a 2·0 cm quartz cell and a spectral slit width being 1·0 $cm^{-1}$ in the N—H stretching region. The concentration of $CCl_4$ soln was ca. 0·01 mole/l.

*Solvents.* Spectrograde or guaranteed reagents were used after careful distillation.

*Materials.* The compounds used in the present study were known, unless otherwise stated, and were purified through known methods. Their physical constants agreed well with those reported. The structures of some compounds were confirmed by NMR and IR spectra.

N-[ω-(p-*Nitrophenyl)alkyl*]*anilines* (**1**). The syntheses of this series of compounds have been reported.[14] However, mp's of **1c**, **1d** and **1e** were misreported. They should read 74–75° for **1c**, 109–110° for **1d**, and 74·5–75·5° for **1e**.

*General procedure for alkylation of arylamines.* A mixture of arylamine (0·03 mole) and ω-(*p*-nitrophenyl)-alkyl halide (0·01 mole) was heated to fuse at 90 ~ 150° and maintained at that temp for 1 hr. The mixture was poured into 10% $Na_2CO_3$ aq and extracted with ether. The solvent was distilled off, and the unreacted amine removed by distillation under reduced press. The residue if solid after cooling was recrystallized from

Table 4. Elemental analyses and yields of new compounds used in this study
$p\text{-}O_2NC_6H_4(CH_2)_nNHAr$.

| n | Ar | Yield, % | mp, °C | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Nitrogen, % Calcd. | Nitrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2,4-$Me_2C_6H_3$ | 32 | 90–91 | 70·29 | 70·03 | 6·29 | 6·33 | 10·93 | 10·77 |
| 2 | 2,4-$Me_2C_6H_3$ | 41 | 70–71 | 71·09 | 70·99 | 6·71 | 6·71 | 10·36 | 10·30 |
| 3 | 2,4-$Me_2C_6H_4$ | 41 | 96–97 | 71·80 | 71·55 | 7·09 | 6·86 | 9·85 | 9·83 |
| 7 | 2,4-$Me_2C_6H_4$ | 14 | 57–58* | 74·08 | 73·88 | 8·29 | 8·25 | 8·23 | 8·29 |
| 1 | 2,4,6-$Me_3C_6H_2$ | 40 | 100–101 | 71·09 | 71·09 | 6·71 | 6·81 | 10·36 | 10·20 |
| 2 | 2,4,6-$Me_3C_6H_2$ | 81 | 106–107 | 71·80 | 71·86 | 7·04 | 7·22 | 9·85 | 9·68 |
| 3 | 2,4,6-$Me_3C_6H_2$ | 25 | (196–200/2·5)† | 72·45 | 72·54 | 7·43 | 7·45 | 9·39 | 9·24 |
| 2 | *p*-$MeOC_6H_4$ | 52 | 89–90 | 66·16 | 66·20 | 5·92 | 5·98 | 10·29 | 10·47 |
| 3 | *p*-$MeOC_6H_4$ | 18 | 101–102 | 67·11 | 66·87 | 6·34 | 6·15 | 9·78 | 9·54 |
| 7 | *p*-$MeOC_6H_4$ | 14 | 57–58* | 74·08 | 73·88 | 8·29 | 8·25 | 8·23 | 8·29 |
| 2 | α-$C_{10}H_7$ | 24 | 108–109 | 73·95 | 73·73 | 5·52 | 5·44 | 9·58 | 9·46 |
| 3 | α-$C_{10}H_7$ | 8 | 58–59* | 74·49 | 74·64 | 5·92 | 5·69 | 9·15 | 9·22 |
| 7 | α-$C_{10}H_7$ | 8 | 108–109* | 76·21 | 76·12 | 7·23 | 6·97 | 7·73 | 7·57 |
| 2 | β-$C_{10}H_7$ | 20 | 62–63 | 73·95 | 73·88 | 5·52 | 5·47 | 9·58 | 9·62 |

* Purified by distillation under reduced pressure with a simple apparatus for sublimation.

† Boiling point. $n_D^{20}$ 1·5776.

EtOH, but if it remained as an oil, it was charged on a column of alumina. Elution with a light petroleum benzene (1:1), benzene, or benzene-ether (1:2) gave the desired product. The m.ps and the results of elemental analyses of the products are given in Table 4.

## REFERENCES

[1] Preliminary communication: M. Ōki and K. Mutai, *Tetrahedron Letters* 2019 (1968).
[2] M. Ōki and K. Mutai, *Bull. Chem. Soc. Japan* **33**, 784 (1960).
[3] S. Nagakura and J. Tanaka, *J. Chem. Phys.* **22**, 236 (1954).
[4] H. A. Bent, *Chem. Rev.* **68**, 588 (1968).
[5] D. J. Cram and R. H. Bauer, *J. Am. Chem. Soc.* **81**, 5971 (1959).
[6] D. J. Cram and A. C. Day, *J. Org. Chem.* **31**, 1227 (1966).
[7] S. J. Cristol and D. C. Lewis, *J. Am. Chem. Soc.* **89**, 1476 (1967).
[8] A. Ishitani and S. Nagakura, *Mol. Phys.* **12**, 1 (1967).
[9] W. N. White, *J. Am. Chem. Soc.* **81**, 2912 (1959).
[10] S. Shifrin, *Biochim. Biophys. Acta* **96**, 173 (1966).
[11] J. W. Verhoeven, I. P. Dirks and Th. J. de Boer, *Tetrahedron Letters* 4399 (1966).
[12] M. Itoh and E. M. Kosower, *J. Am. Chem. Soc.* **90**, 1843 (1968).
[13] M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron Suppl. No.* **7**, 97 (1966); see also ref 20.
[14] M. Ōki and K. Mutai, *Bull. Chem. Soc. Japan* **38**, 387 (1965).
[15] M. Ōki and K. Mutai, *Ibid.* **38**, 393 (1965).
[16] M. Ōki and K. Mutai, *Ibid.* **39**, 809 (1966).
[17] J. F. A. Williams, *Tetrahedron* **18**, 1487 (1962).
[18] D. G. Garnum, *J. Am. Chem. Soc.* **89**, 2970 (1967).
[19] [a] E. F. Kiefer, W. L. Waters and D. A. Carlson, *J. Am. Chem. Soc.* **90**, 5127 (1968); [b] E. F. Kiefer and W. Gericke, *Ibid.* **90**, 5131 (1968).
[20] M. D. Bentley and M. J. S. Dewar, *Tetrahedron Letters* 5043 (1967).
[21] A. A. Lamola, P. A. Leermakers, G. W. Byers and G. S. Hammond, *J. Am. Chem. Soc.* **87**, 2322 (1965).
[22] D. E. Breen and R. A. Keller, *Ibid.* **90**, 1935 and 1940 (1968).
[23] R. D. Rauh, T. R. Evans and P. A. Leermakers, *Ibid.* **90**, 6896 (1968).
[24] D. T. Browne, J. Eisinger and N. J. Leonard, *Ibid.* **90**, 7302 (1968).
[25] A. Kuboyama, *Nippon Kagaku Zasshi* **81**, 558 (1960).
[26] S. D. Ross and M. M. Labes, *J. Am. Chem. Soc.* **77**, 4916 (1955).
[27] F. Foster and D. Ll. Hammick, *J. Chem. Soc.* **1954**, 2685.
[28] P. A. D. DeMaine and J. Peone, *J. Mol. Spectr.* **4**, 262 (1960).
[29] J. Czekalla and K. O. Meyer, *Z. physik. Chem.* **27**, 185 (1961).
[30] K. M. C. Davis and M. F. Farmer, *J. Chem. Soc.* (B), **1967**, 28.
[31] D. P. Stevenson and G. M. Coppinger, *J. Am. Chem. Soc.* **84**, 149 (1962).
[32] D. D. Deshpande and M. V. Pandya, *Trans. Faraday Soc.* **61**, 1858 (1965).
[33] L. N. Ferguson, *The Modern Structural Theory of Organic Chemistry* p. 128. Prentice-Hall, Englewood Cliffs, N. J., (1963).
[34] B. Dale, R. Foster and D. Ll. Hammick, *J. Chem. Soc.* **1954**, 3986.
[35] R. S. Mulliken, *J. Am. Chem. Soc.* **74**, 811 (1952); *J. Phys. Chem.* **56**, 801 (1952).
[36] H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.* **21**, 66 (1953).
[37] S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, *J. Am. Chem. Soc.* **75**, 2900 (1953).
[38] A. Bier, *Rec. Trav. Chim.*, **75**, 866 (1956).
[39] G. Briegleb and J. Czekalla, *Z. Elektrochem.* **63**, 6 (1959).
[40] R. Foster, *Nature, Lond.* **181**, 337 (1958); *Ibid.* **181**, 1253 (1959); *Tetrahedron* **10**, 96 (1960).
[41] H. Yada, J. Tanaka and S. Nagakura, *Bull. Chem. Soc. Japan* **33**, 1660 (1960).
[42] M. Chowdhury, *Trans. Faraday Soc.* **57**, 1482 (1961).
[43] K. Watanabe, T. Nakayama and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer* **2**, 369 (1962).
[44] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.* **80**, 2778 (1958).
[45] L. J. Andrews and R· M. Keefer, *Ibid.* **74**, 4500 (1952).
[46] H. W. Thompson, *Proc. Roy. Soc.* **A250**, 22 (1959).
[47] P. J. Krueger and H. W. Thompson, *Ibid.* **A243**, 143 (1957).
[48] R. A. Russell and H. W. Thompson, *J. Chem. Soc.* 483 (1955).

[49] J. W. Smith, *J. Chem. Soc.* 81 (1961).

[50] For reviews see V. Balasubramaniyan, *Chem. Rev.* **66**, 567 (1966).

[51] N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.* **54**, 3469 (1932).

[52] H. Schenkel, *Experientia* **4**, 383 (1948).

[53] K. Lauer, *Ber. Dtsch. Chem. Ges.* **70B**, 1288 (1937).

[54] J. Kuroda, T. Amano, I. Ikemoto and H. Akamatu, *J. Am. Chem. Soc.* **89**, 6056 (1967).

[55] E. Orgel and R. S· Mulliken, *Ibid.* **79**, 4839 (1957).

[56] J. Aihara, K. Mutai, H. Inokuchi and M. Ōki, unpublished work.

[57] M. Tamres, D. R. Virzi and S. Searles, *J. Am. Chem. Soc.* **75**, 4358 (1953).