

250. *The Frequencies and Intensities of the N-H Stretching Vibrations in Primary Amines. Part II.<sup>1</sup> Polycyclic Aromatic Amines.*

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The positions, extinction coefficients, and band half-widths of the symmetric and antisymmetric N-H stretching vibration absorptions of some polycyclic aromatic amines have been measured in the  $3\mu$  region, and approximate values for the force constants and the HNH bond angles have been calculated from the results. These HNH bond angles increase as the  $\pi$ -electron charge density  $q_r$  at the exocyclic position of the carbanion corresponding to the amine falls, two relations being observed, one for the unhindered and the other for the *peri*-amines. The intensity of the symmetric stretching vibration band also increases as  $q_r$  falls in the series of unhindered amines, but not in the *peri*-series. It is concluded that conjugation between the amino-group and the aromatic nucleus is sterically hindered in the *peri*-amines.

IN monocyclic *N*-heteroaromatic amines it has been shown,<sup>1</sup> from the frequencies and the intensities of the N-H stretching vibrations, that the HNH bond angle, the N-H stretching force constant, and the N-H bond dipole gradient increase, relative to the values for aniline, as the lone-pair electrons of the amino-group are increasingly drawn into conjugation with the  $\pi$ -electron system of the nucleus by aza-substitution in the ring. These trends are due to varying hybridisation ratios in the orbitals of the nitrogen atom of the amino-group. As the lone-pair orbital becomes more nearly  $2p\pi$ , owing to conjugation with the nucleus, the "s" character of the N-H bonds increases, so that the HNH angle opens and the N-H bond becomes stronger and more polar, owing to, respectively, the better overlap of the nitrogen and hydrogen orbitals and the enhanced electronegativity of the nitrogen relative to the hydrogen atom. The effect upon the structure of the amino-group in aniline of another type of conjugation, that due to condensed or aromatic rings, has now been investigated by the measurement of the positions and the intensities of the symmetric and the antisymmetric N-H stretching vibration bands in a series of polycyclic aromatic amines. The observed frequencies, maximum extinction coefficients, and intensities are recorded in the Table.

In general, a condensed or aromatic ring is found to have a smaller influence than an aza-substituent upon the positions and the intensities of the N-H stretching vibrations of aniline. A given band has a frequency lying within a range of  $25\text{ cm.}^{-1}$  and an intensity which varies by a factor of two in the series of polycyclic aromatic amines (Table), but in the monocyclic amino-azine series the range is  $60\text{ cm.}^{-1}$  and the intensity varies by a factor of five.<sup>1</sup> The two series are comparable in that compounds with up to three "substituent," ring nitrogen atoms, or condensed rings, have been investigated. The smaller effect of the condensed ring upon the conjugation of an aromatic amino-group appears to be partly inherent, and partly due to steric factors. In a polycyclic aromatic hydrocarbon the *peri*- and *meso*-positions have a high conjugating capacity, but in those positions the conjugation of a substituent, such as an amino-group, may be sterically hindered.

It may be assumed, as previously,<sup>1</sup> that the two absorption bands in the  $3\mu$  region of the infrared spectra of primary amines are due to vibrations in which only the nitrogen and the hydrogen atoms move, and that these atoms vibrate along the N-H bond directions. With these assumptions the HNH bond angle ( $\theta$ ) and the N-H stretching force constant ( $k$ ) can be calculated from the frequencies of the symmetric ( $\nu_s$ ) and the antisymmetric ( $\nu_a$ ) absorption bands by using the valency force field equations due to Linnett,<sup>2</sup> namely

$$4\pi^2\nu_s^2 = k[1/m_H + (1 + \cos \theta)/m_N] \quad \dots \quad (1)$$

$$4\pi^2\nu_a^2 = k[1/m_H + (1 - \cos \theta)/m_N] \quad \dots \quad (2)$$

<sup>1</sup> The paper, *J.*, 1958, 3619, is regarded as Part I.

<sup>2</sup> Linnett, *Trans. Faraday Soc.*, 1945, 41, 223.

The positions ( $\nu$ ) and the intensities ( $I$ ) of the symmetric and antisymmetric N-H stretching vibration bands of some polycyclic aromatic amines and cyclohexylamine in carbon tetrachloride. The intensities ( $I$ ) are given as the product of the maximum extinction coefficient [ $E_{\max.} = (1/Cl) \log_{10} (T_0/T) \nu_{\max.}$ ] and the band half width. The N-H stretching vibration force constants ( $k$ ), the HNH bond angle ( $\theta$ ), and the  $\pi$ -electron charge density at the position of the exocyclic atom in the corresponding carbanion ( $q_r$ ).

Compound	Antisymmetric			Symmetric			$10^6 k^a$ (dyne cm. <sup>-1</sup> )	$\theta^a$ (deg.)	$q_r^b$
	$\nu$ (cm. <sup>-1</sup> )	$E_{\max.}$ (l. mole <sup>-1</sup> cm. <sup>-1</sup> )	$I$ (l. mole <sup>-1</sup> cm. <sup>-2</sup> )	$\nu$ (cm. <sup>-1</sup> )	$E_{\max.}$ (l. mole <sup>-1</sup> cm. <sup>-1</sup> )	$I$ (l. mole <sup>-1</sup> cm. <sup>-2</sup> )			
Unhindered									
1 Aniline .....	3473	22	960	3390	24	760	6.52	111.1	1.572
2 <i>m</i> -Aminodiphenyl ...	3476	23	970	3391	27	820	6.53	111.9	1.572
3 <i>p</i> -Aminodiphenyl ...	3480	22	960	3393	29	930	6.54	112.1	1.516
4 2-Aminofluorene ...	3475	22	980	3389	31	960	6.52	111.9	1.516
5 2-Naphthylamine ...	3477	24	970	3392	31	920	6.53	111.6	1.529
6 2-Phenanthrylamine	3477	26	1020	3394	39	1080	6.54	111.4	1.543
7 3-Phenanthrylamine	3480	27	1070	3393	40	1160	6.54	112.4	1.510
8 2-Anthrylamine .....	3480	25	930	3392	46	1220	6.54	112.7	1.471
Hindered									
9 <i>o</i> -Aminodiphenyl ...	3475	27	1260	3385	24	800	6.52	113.0	1.516
<i>peri</i>									
10 1-Naphthylamine ...	3470	21	810	3391	22	630	6.52	110.3	1.450
11 1-Phenanthrylamine	3471	23	850	3393	25	690	6.52	110.0	1.463
12 9-Phenanthrylamine	3464	22	800	3386	27	720	6.50	109.8	1.446
13 1-Anthrylamine .....	3468	21	810	3387	23	600	6.51	110.6	1.381
14 2-Aminochrysene ...	3469	18	750	3390	26	760	6.52	110.1	1.410
15 3-Aminopyrene .....	3482	24	960	3400	34	1080	6.56	110.8	1.364
<i>meso</i>									
16 9-Anthrylamine .....	3489	19	750	3412	22	690	6.60	109.4	1.286
Saturated									
17 cycloHexylamine ...	3375	3.3	155	3311	2.1	98	6.19	107.1	—

<sup>a</sup> Calculated by equations (1) and (2). <sup>b</sup> Calculated by the method of ref. (3).

where  $m_H$  and  $m_N$  are the mass of the hydrogen and the nitrogen atom, respectively. The bond angles and force constants of the polycyclic aromatic amines, calculated by means of equations (1) and (2), are recorded in the Table. The HNH bond angle in the *meso*- and the *peri*-amines is less than that of aniline, and in the series as a whole the angle varies only from 109 to 113° (Table), compared with the range 111—119° observed in the amino-azine series.<sup>1</sup>

A measure of the conjugating capacity of a given position in a polycyclic aromatic nucleus is afforded by the  $\pi$ -electron charge density,  $q_r$ , at the exocyclic position in the corresponding carbanion, *e.g.* the benzyl anion in the case of benzene. The greater the conjugation at the position of the exocyclic group, the more charge is drawn into the nucleus and the smaller the value of  $q_r$ . The charge densities,  $q_r$ , are readily found by Longuet-Higgins's method,<sup>3</sup> and the values for the carbanions analogous to the amines studied are recorded in the Table.

The lone-pair charge density,  $q_N$ , on the nitrogen atom of an aromatic amine is related to  $q_r$  by the expression

$$q_N = q_r + \pi_{r,r} \Delta\alpha_N \quad \dots \quad (3)$$

where  $\pi_{r,r}$  is the self-polarisability of the exocyclic atom in the corresponding carbanion, and  $\Delta\alpha_N$  is the increment in the Coulomb integral of nitrogen relative to carbon. Values of  $\pi_{r,r}$  have been derived<sup>4</sup> for the benzyl anion,<sup>5</sup> the 1- and 2-naphthylmethyl,<sup>6</sup> and the

<sup>3</sup> Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265.

<sup>4</sup> Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.

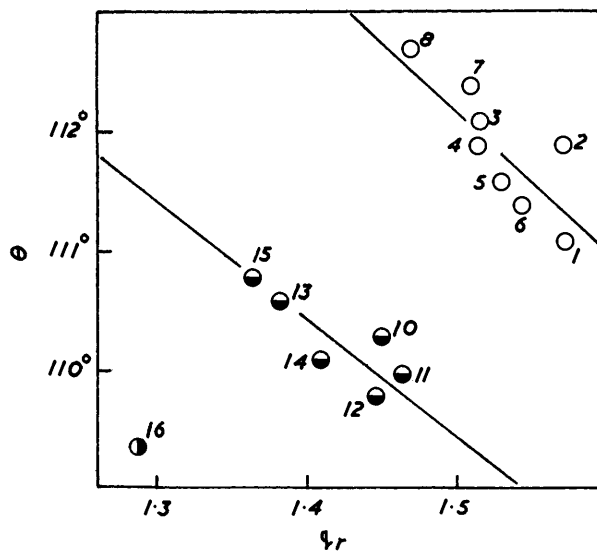
<sup>5</sup> Jaffe, *J. Amer. Chem. Soc.*, 1954, **76**, 3527.

<sup>6</sup> Present work.

9-anthrylmethyl ions,<sup>6</sup> namely, 0.412, 0.590, 0.501, and 0.724  $\beta^{-1}$ , respectively, where  $\beta$  is the carbon-carbon resonance integral. These values span the range of conjugating capacities studied in the present series, and they are smoothly related to the corresponding value of  $q_r$  (Table). The relation is probably general in the present series, so that  $q_r$  affords a semi-quantitative measure of  $q_N$ .

In aliphatic amines the HNH bond angle is  $\sim 107^\circ$  (Table), the "s" character of the nitrogen bonding orbitals being less than  $sp^3$  whilst that of the lone-pair orbital is greater. In aromatic amines the lone-pair orbital must assume a larger "p" character in order to conjugate with the  $\pi$ -electron system of the nucleus, and compensating hybridisation ratio changes in the nitrogen bonding orbitals result in a larger HNH bond angle. The angles

FIG. 1. The relations between the HNH bond angle,  $\theta$ , of some polycyclic aromatic amines and the charge density,  $q_r$ , at the exocyclic position of the corresponding carbanion. ● meso, ○ peri, and ○ unhindered amines. The numbers refer to the compounds listed in the Table.

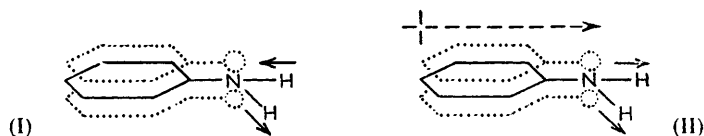


should increase in the series of polycyclic aromatic amines the more the lone-pair electrons of the amino-group are delocalised over the aromatic nucleus, that is, the smaller the value of  $q_N$ , or its measure,  $q_r$ . It is found (Table; Fig. 1) that the angles increase as the charge density,  $q_r$ , falls, but two distinct relations are observed, one for the unhindered and the other for the *peri*-amines, whilst the point for the *meso*-compound, 9-anthrylamine, lies off both correlations.

The HNH bond angles ( $\theta$ ) of the *meso*- and *peri*-amines are smaller than expected from the magnitudes of the corresponding charge densities,  $q_r$ , and the observed relation for the unhindered amines between these quantities (Fig. 1). The reduction appears to be due, partly to the compression of the HNH angle, and partly to the inhibition of resonance between the lone-pair electrons and the aromatic nucleus. The repulsion between a N-H and a *peri* C-H group results in the displacement of the centre of the 1s hydrogen orbital from the symmetry axis of the nitrogen bonding orbital, giving a "bent" bond, and in the twist of the amino-group so that the nodal plane of the *p*-component of the lone-pair orbital no longer coincides with the plane of the aromatic nucleus, reducing the interaction with the  $\pi$ -electron system.

The calculated N-H stretching force constants of the polycyclic aromatic amines allow these effects to be distinguished. In general, the N-H stretching force constant increases with the "s" character of the N-H bond, since the 2s orbital of nitrogen affords better overlap than does the 2*p* with the 1s orbital of hydrogen at an internuclear distance of  $\sim 1 \text{ \AA}$  and forms stronger bonds.<sup>1</sup> In the series of aromatic amines, 9-anthrylamine has

the largest force constant but the smallest HNH bond angle (Table), suggesting that the N-H bonds have the large "s" character appropriate to the high conjugating capacity of the 9-anthryl position and that the HNH angle is compressed. On the other hand, 9-phenanthrylamine has a smaller force constant and HNH bond angle than any of the unhindered amines (Table), indicating that, although the conjugating capacity of the 9-phenanthryl position is substantial, the delocalisation of the amine lone-pair electrons over the aromatic nucleus is partly inhibited.



The intensities of the N-H stretching vibration absorption bands in the series of polycyclic aromatic amines suggest that a change in the conjugation of the lone-pair electrons with the aromatic nucleus during the transition from the ground to the vibrationally excited state is also partly inhibited in the *meso*- and *peri*-amines. The intensity of an absorption band in the infrared region is proportional to the square of the change of dipole moment with the vibration. To a good approximation,<sup>1</sup> only the change of the N-H bond moment with bond length contributes to the transition moment of the antisymmetric

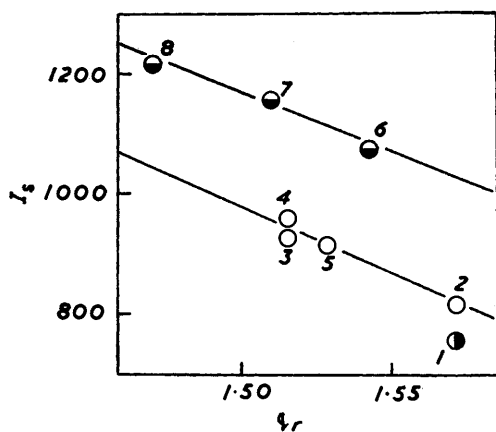


FIG. 2. The relations between the intensity of the symmetric N-H stretching vibration absorption band of some unhindered polycyclic aromatic amines,  $I_s$ , and the charge density at the exocyclic position of the corresponding carbanion,  $q_r$ . The numbers refer to the compounds listed in the Table. ● Mono-, ○ di-, and ○ tri-cyclic amines.

stretching vibration in primary amines, but there is an additional contribution from the variation of the atomic dipole of the lone-pair electrons to that of the symmetric stretching vibration.<sup>7</sup>

When a N-H bond is stretched the "s" character of the nitrogen hybrid orbital falls, as the  $2p$  orbital of nitrogen affords better overlap than does the  $2s$  with the  $1s$  orbital of hydrogen at large internuclear distances. In the antisymmetric stretching vibration (I) any change of hybridisation in one N-H bond is largely compensated by a converse change in the other, and the intensity of the corresponding absorption band should depend mainly upon the N-H bond dipole gradient and the HNH bond angle.<sup>1</sup> However, in the symmetric stretching vibration (II) both N-H bonds, on stretching, increase in "p" character, and compensating hybridisation changes must occur in the other nitrogen orbitals, notably, in the lone-pair orbital which undergoes an increase in "s" character.

In the ground state of aromatic amines the lone-pair electrons are delocalised over the

<sup>7</sup> Orville-Thomas, Parsons, and Ogden, *J.*, 1958, 1047.

nucleus, and when the lone-pair orbital assumes an increased "s" character during the symmetric stretching vibration these electrons are withdrawn from the aromatic system and localised upon the nitrogen atom, since the 2s orbital of nitrogen, with even symmetry, cannot combine with the  $\pi$  orbitals of the nucleus, which have odd symmetry with respect to the molecular plane. Accordingly, the  $\pi$ -electron component of the permanent dipole moment of aromatic amines varies in phase with the symmetric stretching vibration of the amino-group, and the variation contributes to the intensity of the corresponding infrared absorption band. The contribution should increase the larger the aromatic nucleus, and the greater the conjugation between the lone-pair electrons of the amino-group and the nucleus, that is, the smaller the charge density,  $q_r$ .

The intensity of the symmetric stretching vibration absorption band,  $I_s$ , in the unhindered polycyclic aromatic amines increases (Table, Fig. 2) with the number of aromatic rings in the molecule, and increases as the charge density,  $q_r$ , falls. The relation between  $I_s$  and  $q_r$  for the tricyclic amines (Fig. 2) lies above and parallel to the corresponding relation for the bicyclic amines (Fig. 2), which in turn lies above the point for aniline. In the series of *meso*- and *peri*-amines, except for 3-aminopyrene, the intensities of the symmetric stretching vibration bands do not vary widely, and they are smaller than those of the corresponding bands in the series of unhindered amines (Table), suggesting not only that conjugation between the lone-pair electrons of the amino-group and the aromatic nucleus is sterically hindered in the ground state of the *meso*- and *peri*-amines, but also that changes of conjugation with the symmetric stretching vibration are likewise hindered.

The intensities of the antisymmetric stretching vibration bands do not cover a wide range in either of the series of amines, although the antisymmetric bands of the *meso*- and *peri*-amines, in general, are somewhat less intense than those of the unhindered amines (Table). It is probable that the N-H bond dipole gradient does not vary widely in either series, and is reduced by steric hindrance between a N-H and a *peri*-C-H group, since the smaller HNH bond angles of the *meso*- and *peri*-amines do not account entirely for the smaller intensities of their antisymmetric stretching vibration bands.

The intensities of the antisymmetric and more particularly the symmetric stretching vibration bands of 3-aminopyrene are greater than those of any other *peri*-amine, and they fall, in fact, within the respective ranges typical of the unhindered amines (Table). In a parallel study of the basicities of the present series of amines in 50% ethanol-water, it has been found<sup>8</sup> that the entropy of ionisation of the conjugate acid of 3-aminopyrene is larger than that of any other *peri*-amine and is typical of an unhindered amine. The reduction of steric hindrance in the 3-position of pyrene is not peculiar to the amino-group, for the reduced rate of the  $S_N1$  reactions of the *peri*-arylmethyl chlorides, due to steric hindrance in the carbonium ion transition state,<sup>9,10</sup> is not observed in the case of 3-pyrenylmethyl chloride.<sup>10</sup>

Steric hindrance between a C-H bond and a methyl or amino-group in the *peri*-positions of pyrene may be small or absent because of the long nuclear carbon-carbon bonds separating these positions. In pyrene<sup>11</sup> the  $C_{(2)}-C_{(2a)}$  and the  $C_{(2a)}-C_{(3)}$  bonds have lengths of 1.45 and 1.42 Å, respectively, whilst in anthracene<sup>12</sup> the  $C_{(1)}-C_{(1a)}$  and the  $C_{(1)}-C_9$  bonds are 1.418 and 1.398 Å long, respectively, and the corresponding bonds in naphthalene have lengths<sup>12</sup> of 1.425 Å. The angle between the carbon-carbon bonds separating the *peri*-positions in pyrene is uncertain, but it is unlikely to be so small that those positions are as close together in pyrene as they are in naphthalene or anthracene.

The observed frequencies and intensities of the N-H stretching vibrations and the calculated force constants of the *peri*-amines are much more similar to those of the unhindered aromatic amines than to those of *cyclohexylamine* (Table), suggesting that the

<sup>8</sup> Unpublished result.

<sup>9</sup> Dewar and Sampson, *J.*, 1956, 2789; 1957, 2946, 2952.

<sup>10</sup> Fierens, Hannaert, Rysselberge, and Martin, *Helv. Chim. Acta*, 1955, **38**, 2009.

<sup>11</sup> Robertson and White, *J.*, 1947, 358.

<sup>12</sup> Ahmed and Cruickshank, *Acta Cryst.*, 1952, **5**, 852.

steric inhibition of conjugation between the amino-group and the nucleus of the *peri*-amines is not large. The differences between the positions and the intensities of the N-H stretching vibrations of aliphatic and aromatic amines may be due in part to the attachment of the amino-group to a  $sp^3$  and a  $sp^2$  carbon atom in the former and the latter, respectively, but the delocalisation of the lone-pair electrons of the amino-group over the nucleus of the aromatic amines is probably the more important factor.

#### EXPERIMENTAL

*Materials.*—*m*-Aminodiphenyl was obtained by the reduction<sup>13</sup> of *m*-nitrodiphenyl.<sup>14</sup> 1- and 2-Aminoanthracene were prepared from the corresponding anthraquinones,<sup>15,16</sup> and the 9-isomer by the reduction<sup>17</sup> of 9-nitroanthracene.<sup>18</sup> 1-, 2-, and 3-Aminophenanthrene were made by the method of Bachmann and Boatner<sup>19</sup> from 1-benzoyl-<sup>20</sup> and 2- and 3-acetyl-phenanthrene,<sup>19</sup> and the 9-isomer was prepared according to Bergstrom and Hornig's directions.<sup>21</sup> The remaining compounds were commercial specimens. Each amine was redistilled or resublimed at 0.2 mm. until it had the b. p. or m. p. recorded in the literature.

*Infrared spectra.*—These were measured with a Mervyn N.P.L. grating spectrophotometer with use of a *F*-centre filter for the  $3\mu$  region. The effective slit width was about  $10\text{ cm.}^{-1}$ . The aromatic amines were examined at concentrations in the range  $M/1000$  to  $M/250$ , and cyclohexylamine at  $M/50$ , a cell 5 cm. in length being used. The intensities were reproducible to within about 5%, and the frequencies to within  $2\text{ cm.}^{-1}$ , though the intensities diverge by up to 20% and the frequencies up to  $8\text{ cm.}^{-1}$ , from the corresponding quantities for the same amines measured with a prism instrument.<sup>1</sup> The intensities are recorded in the Table as the product of the maximum molar extinction coefficient and the width of the absorption band at half the maximum extinction. The correction factor<sup>22</sup> of  $\pi/2$  used previously<sup>1</sup> was not employed since only relative intensities were required in the present work.

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<sup>13</sup> Balcom and Furst, *J. Amer. Chem. Soc.*, 1953, **75**, 4334.

<sup>14</sup> Elkes, Haworth, and Hey, *J.*, 1940, 1285.

<sup>15</sup> Fierz-David, Blangey, and Streiff, *Helv. Chim. Acta*, 1946, **29**, 1718.

<sup>16</sup> Ruggli and Henzi, *ibid.*, 1930, **13**, 429.

<sup>17</sup> Meisenheimer, *Ber.*, 1900, **33**, 3547.

<sup>18</sup> Dimroth, *Ber.*, 1901, **34**, 221.

<sup>19</sup> Bachmann and Boatner, *J. Amer. Chem. Soc.*, 1936, **58**, 2097.

<sup>20</sup> Gore, *J. Org. Chem.*, 1957, **22**, 135.

<sup>21</sup> Bergstrom and Hornig, *ibid.*, 1946, **11**, 334.

<sup>22</sup> Ramsey, *J. Amer. Chem. Soc.*, 1952, **74**, 72.