723. *The Frequencies and Intensities of the* N–H *Stretching Vibrations in Primary Amines.*

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The positions, extinction coefficients, and band half-widths of the symmetric and antisymmetric stretching vibration absorptions of the amide anion, and some monocyclic aliphatic, aromatic, and *N*-heteroaromatic primary amides have been measured in the 3 μ region. Approximate values for the force constants, H–N–H bond angles, the " *s* " character of the hybrid orbitals bonding nitrogen to hydrogen, and the N–H bond dipole gradients have been calculated from the results. It is found that the force constant and the N–H bond dipole gradient increase linearly with the amount of " *s* " character of the hybrid orbitals of the N–H group, and that, in the aromatic series, these quantities increase as the π-electron charge density on the nitrogen atom of the amino-group falls.

IT is well known [1] that the mechanical and electrical properties of C–H bonds vary widely with the type of hybridisation of the carbon atom orbital, and there are indications that the properties of N–H bonds vary similarly. It has been observed that the H–N–H bond angle [2] and the N–H bond stretching force constant [3] in substituted aromatic amines increase with the electron-attracting power of the substituents, and more recently it has been found [4,5] that the frequencies and the intensities of the fundamental stretching vibration absorptions of the primary amino-group in substituted anilines are smooth functions of the Hammett σ constant of the substituent. In the present work a survey has been made of the positions and intensities of the symmetric and antisymmetric stretching vibration bands of a wide range of primary amines, varying from the amide anion, through *cyclo*hexylamine and aniline, to 3-amino-1 : 2 : 4-triazine, in order to obtain more extensive and more quantitative information of the effect of hybridisation and conjugation upon the mechanical and electrical properties of the N–H group. In the series of aromatic amines a single " substituent," * the aza-nitrogen atom, was employed as far as possible, so that the effect of substituents upon the π-electron charge density of the amino-nitrogen atom could be calculated quantitatively in terms of a single semi-empirical constant common to the series, the Coulomb integral of nitrogen. The use of ring-nitrogen substituents had the further advantage that conjugation in the *ortho*-" substituted " amines was not

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* Throughout this paper, " substituted," " substitution," and " substituent " refer to *replacement* of a CH-member of the benzene ring, specifically by nitrogen.

[1] Coulson, " Valence," Oxford Univ. Press, 1952.
[2] Flett, *Trans. Faraday Soc.*, 1948, **44**, 767.
[3] Short, *J.*, 1952, 4584.
[4] Califano and Moccia, *Gazzetta*, 1956, **86**, 1014; 1957, **87**, 58.
[5] Krueger and Thompson, *Proc. Roy. Soc.*, 1957, A, **243**, 143.

hindered sterically. The observed positions, maximum extinction coefficients, and band widths at half-maximum extinction of the amino-group stretching vibrations in the compounds studied are recorded in Tables 1 and 2.

TABLE 1. *The positions of the symmetric (ν_s) and antisymmetric (ν_a) stretching vibrations of the amino-group in the amide anion, and some monocyclic aliphatic and aromatic primary amines. The N–H stretching vibration force constants (k), the H–N–H bond angles (θ), the " s " character of the nitrogen hybrid orbitals of the N–H bonds expressed as the coefficient (b), where $\psi_{hybrid} = b\psi_s + \sqrt{(1 - b^2)} . \psi_p$, and the π-electron charge density on the nitrogen atom of the amino-group (q_N).*

No.	Compound	Solvent	ν_a (cm.$^{-1}$)	ν_s (cm.$^{-1}$)	$10^5 k$ [b] (dyne cm.$^{-1}$)	θ [b]	b [c]	q_N [d] (elec-trons)
1	Lithium amide	[a]	3315	3261	5·99	104·1°	0·436	—
2	*cyclo*Hexylamine	CCl$_4$	3381	3316	6·21	106·8	0·473	—
3	Aniline	,,	3481	3395	6·54	111·8	0·519	1·802
4	2-Aminopyridine	,,	3509	3410	6·62	115·3	0·547	1·742
5	2-Aminopyridine	CHCl$_3$	3512	3408	6·62	116·5	0·557	—
6	3-Aminopyridine	CCl$_4$	3481	3396	6·54	111·6	0·518	1·774
7	3-Aminopyridine	CHCl$_3$	3484	3400	6·56	111·3	0·516	—
8	4-Aminopyridine	CCl$_4$	3505	3413	6·62	113·5	0·535	1·730
9	4-Aminopyridine	CHCl$_3$	3512	3415	6·64	114·7	0·544	—
10	2-Aminopyrimidine	CCl$_4$	3540	3425	6·72	119·3	0·573	1·682
11	2-Amino-4 : 6-dimethyl-pyrimidine	CHCl$_3$	3533	3422	6·69	118·5	0·567	—
12	4-Aminopyrimidine	CCl$_4$	3536	3421	6·70	119·3	0·573	1·658
13	5-Aminopyrimidine	,,	3485	3399	6·56	111·8	0·520	1·745
14	5-Aminopyrimidine	CHCl$_3$	3488	3403	6·57	111·6	0·519	—
15	2-Aminopyrazine	CCl$_4$	3511	3410	6·62	115·8	0·551	1·714
16	2-Aminopyrazine	CHCl$_3$	3515	3410	6·64	116·8	0·558	—
17	3-Amino-6-methylpyrid-azine	,,	3509	3407	6·62	116·1	0·553	1·724
18	4-Aminopyridazine	,,	3514	3415	6·64	115·3	0·548	1·717
19	3-Amino-1 : 2 : 4-triazine	,,	3353	3420	6·70	119·0	0·572	1·664
20	3-Amino-5 : 6-dimethyl-1 : 2 : 4-triazine	CCl$_4$	3534	3423	6·68	118·5	0·569	—

[a] Solid in a potassium bromide disc: quoted from Mason, *J. Phys. Chem.*, 1957, **61**, 384. [b] Calc. by eqns. (1) and (2). [c] Calc. by eqn. (4). [d] Calc. by eqn. (5) with $\Delta\alpha_C = 0·2\Delta\alpha_N$ and $\Delta\alpha_N = 0·6\beta$.

I. Frequencies.—In the present work it is assumed that the two absorption bands in the 3200—3550 cm.$^{-1}$ region of the infrared spectra of primary amines are due to vibrations in which only the nitrogen and hydrogen atoms of the amino-group move. It is assumed further that the nitrogen and hydrogen atoms vibrate along the N–H bond directions, the stretching force constant being much larger than the deformation and interaction constants. In general, these assumptions are reasonable [6] for the vibrations of bonds to hydrogen atoms, and in the present case they are justified empirically, as a more exact treatment has shown [7] that the N–H stretching force constant is an order of magnitude larger than the deformation and interaction constants in the ammonia molecule. With these assumptions the H–N–H bond angle (θ) and the N–H stretching force constant (k) may be calculated from the frequencies of the symmetric (ν_s) and the antisymmetric (ν_a) absorption bands of a primary amine by using the valency force field equations given by Linnett,[6] namely:

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

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

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 primary amines studied, calculated by means of equations (1) and (2), are recorded in Table 1. Owing to the approximations used, no

[6] Linnett, *Trans. Faraday Soc.*, 1945, **41**, 223.
[7] McKean and Schatz, *J. Chem. Phys.*, 1956, **24**, 316.

claim can be made for the accuracy of the absolute values of the calculated bond angles and force constants, though it is probable that the relative values in the series of amines are reliable. The calculated bond angles are, however, acceptable. That of the amide ion (104·1°) is close to the bond angle of the isoelectronic molecule, water [8] (104·22°); that of *cyclo*hexylamine (106·8°) close to that of ammonia [8] (106·78°); and in the aromatic series the calculated angles increase with conjugation between the nucleus and the amino-group nearly up to the maximum value of 120° which is to be expected when the lone-pair electrons of the amino-group are fully delocalised over the aromatic nucleus (Table 1).

From the H–N–H bond angles of the primary amines the contribution of the $2s$ and the $2p$ atomic orbitals of the nitrogen atom to the hybrid orbitals binding the hydrogen atoms

TABLE 2. *The maximum extinction coefficients, $E = (1/cl) \log (T_0/T)$ $v_{max.}$, and the band half-widths $(\Delta v_{\frac{1}{2}})$ of the amino-group stretching vibrations in the amide ion and some monocyclic aliphatic, aromatic, and N-heteroaromatic amines. The apparent H–N–H bond angle (α), and the N–H bond moment gradient derived from the intensities of the symmetric $(dM/dr)_s$ and the antisymmetric $(dM/dr)_a$ stretching vibration bands.*

			Antisymmetric			Symmetric			
No.	Compound	Solvent	E (l. mole^{-1} cm.$^{-1}$)	$\Delta v_{\frac{1}{2}}$ (cm.$^{-1}$)	$(dM/dr)_a$ [b] (D/Å)	E (l. mole^{-1} cm.$^{-1}$)	$\Delta v_{\frac{1}{2}}$ (cm.$^{-1}$)	$(dM/dr)_s$ [c] (D/Å)	α [d]
1	Lithium amide	[a]	6·5	10	0·2	17·7	14	0·6	55°
2	*cyclo*Hexylamine	CCl$_4$	3·3	37	0·3	2·2	55	0·4	90
3	Aniline	,,	20	36	0·6	28	25	1·0	91
4	2-Aminopyridine	,,	44	34	0·9	66	23	1·5	90
5	2-Aminopyridine	CHCl$_3$	45	43	1·0	61	34	1·8	88
6	3-Aminopyridine	CCl$_4$	30	34	0·7	43	24	1·2	90
7	3-Aminopyridine	CHCl$_3$	32	40	0·8	47	28	1·3	89
8	4-Aminopyridine	CCl$_4$	41	34	0·9	67	23	1·4	87
9	4-Aminopyridine	CHCl$_3$	46	40	1·0	78	27	1·7	85
10	2-Aminopyrimidine	CCl$_4$	80	32	1·1	114	22	2·0	91
11	2-Amino-4 : 6-dimethyl-pyrimidine	CHCl$_3$	80	37	1·2	105	26	2·1	92
12	4-Aminopyrimidine	CCl$_4$	75	32	1·1	122	22	2·0	87
13	5-Aminopyrimidine	,,	39	33	0·9	56	24	1·3	89
14	5-Aminopyrimidine	CHCl$_3$	34	42	0·9	58	32	1·6	83
15	2-Aminopyrazine	CCl$_4$	57	33	1·0	89	23	1·8	88
16	2-Aminopyrazine	CHCl$_3$	66	41	1·2	90	31	2·1	88
17	3-Amino-6-methyl-pyridazine	,,	54	40	1·1	73	31	1·8	90
18	4-Aminopyridazine	,,	50	39	1·0	88	27	1·8	84
19	3-Amino-1 : 2 : 4-triazine	,,	108	36	1·4	149	24	2·4	92
20	3-Amino-5 : 6-dimethyl-1 : 2 : 4-triazine	CCl$_4$	91	32	1·2	134	22	2·2	90

[a] See Table 1. [b] Calc. according to eqns. (7), (9), and (11). [c] Calc. according to eqns. (7), (8) and (11). [d] Calc. according to eqns. (10) and (11).

may be derived. The values for the " s " character of the nitrogen orbitals are listed in Table 1 as the coefficient (b) of the $2s$-orbital of nitrogen in the hybrid,

$$\psi_{\text{hybrid}} = b\psi_{2s} + \sqrt{(1 - b^2)} \cdot \psi_{2p} \quad \cdots \cdots \quad (3)$$

If the two N–H bonds of a given primary amino-group are equivalent, and the hybrid orbitals of nitrogen binding the two hydrogen atoms are orthogonal, the coefficient (b) is related to the H–N–H bond angle by the expression:

$$b^2 = - \cos \theta/(1 - \cos \theta) \quad \cdots \cdots \quad (4)$$

The π-electron charge density upon the nitrogen atom of the amino-group (q_N) of the aromatic and N-heteroaromatic amines given in Table 1 was obtained from the charge

[8] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945.

density on the exocyclic atom [9] (q_r), and the atom–atom polarisabilities [10] of the benzyl anion according to the expression:

$$q_N = q_r + \sum \pi_{N \cdot N'} \Delta \alpha_N + \sum \pi_{C \cdot N'} \Delta \alpha_C \quad \cdots \quad (5)$$

where $\pi_{N \cdot N'}$ refers to the mutual polarisability of two positions occupied by nitrogen atoms, one of which, N', is the nitrogen atom of the amino-group, the sum being taken over all nitrogen atoms in the molecule including the case where N = N', and $\pi_{C \cdot N'}$ refers to the mutual polarisability of a position occupied by a carbon atom (C) adjacent to a nuclear nitrogen atom, and the position occupied by the exocyclic nitrogen atom (N'). $\Delta \alpha_N$ is the difference between the Coulomb integrals of the carbon and the nitrogen atom, and $\Delta \alpha_C$ the increment in the Coulomb integral of a carbon atom adjacent to a nitrogen atom.

FIG. 1. *Relations between the " s " character of the hybrid orbitals bonding the hydrogen atoms to the nitrogen atom of the amino-group, expressed as the coefficient (b) in equation (6), and (A) the N–H stretching vibration force constant (k), and (B) the N–H bond dipole gradient* $(dM/dr)_a$. *The numbers refer to the compounds listed in Tables 1 and 2.*

$$\text{Force constant } (k) \, (10^{-5} \text{dyne cm.}^{-1})$$
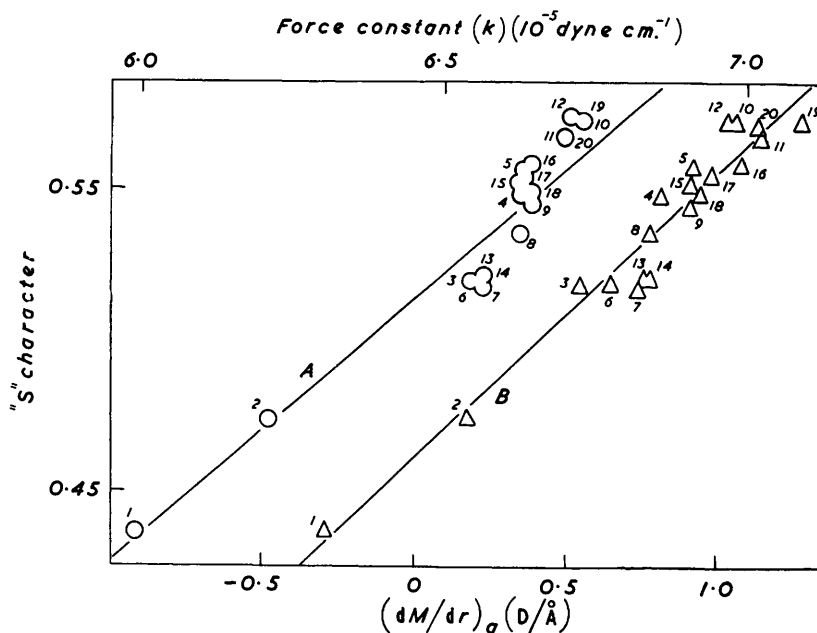
$\Delta \alpha_C$, which is a measure of the inductive enhancement of the electronegativity of a carbon atom by an adjacent nitrogen atom, is related to $\Delta \alpha_N$. Empirically it has been shown [11] that $\Delta \alpha_C = 0 \cdot 2 \Delta \alpha_N$, and a variety of evidence suggests [11] that $\Delta \alpha_N = 0 \cdot 6 \beta$, where β is the carbon–carbon resonance integral. These values were adopted in calculating, by equation (5), the values of q_N given in Table 1.

From the quantities listed in Table 1, it is found (Fig. 1A) that the N–H stretching vibration force constants (k) of the primary amines studied increase with the " s " character of the hybrid bonds from nitrogen to hydrogen, expressed as the coefficient (b) of equation (3). Such a correlation does not conform to the measure of sp hybrid-bond strength proposed by Pauling and Sherman,[12] which is known to be unsatisfactory for hybrid bonds between carbon and hydrogen.[1] According to Pauling and Sherman,[12] sp

[9] Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265.
[10] Jaffe, *J. Amer. Chem. Soc.*, 1954, **76**, 3527.
[11] Mason, *J.*, 1958, 674.
[12] Pauling and Sherman, *J. Amer. Chem. Soc.*, 1937, **59**, 1450.

hybrid bonds from a given atom have a maximum strength at tetrahedral hybridisation when, in the present terminology, $b = 0.5$, but the force constant of the N–H bond shows no maximum in the range ($b = 0.44$—0.57) covered in the present work (Fig. 1A). A more satisfactory measure of bond strength is provided by the overlap integral [1] of the hybrid orbital of the nitrogen atom with the 1s orbital of the hydrogen atom. By assuming a constant N–H bond distance of 1.0 Å in the range of amines covered, it is found, using Slater orbitals,[13] that the overlap integrals of the 2s- and the 2p-orbitals of nitrogen with

FIG. 2. *Relations between the π-electron charge density on the nitrogen atom of the amino-group (q_N) and (A) the N–H stretching vibration force constant (k), and (B) the N–H bond moment gradient (dM/dr_a), in the series of aromatic amines. The numbers refer to the compounds listed in Tables 1 and 2.*
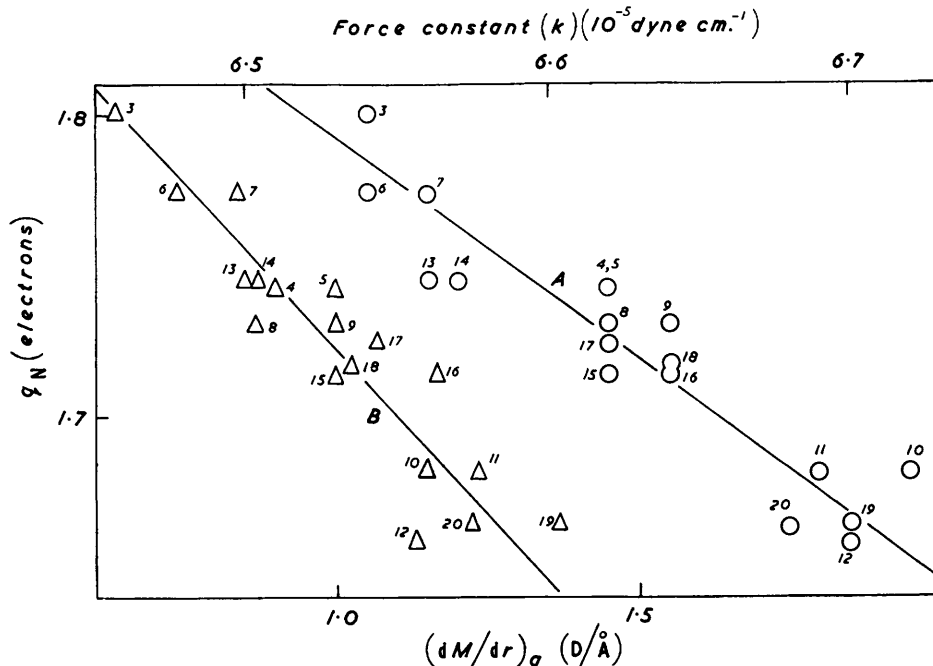
the 1s orbital of hydrogen are 0.55 and 0.42 respectively. Thus the overlap integral (S) for a hybrid orbital of nitrogen, given by equation (3), and a 1s orbital of hydrogen is:

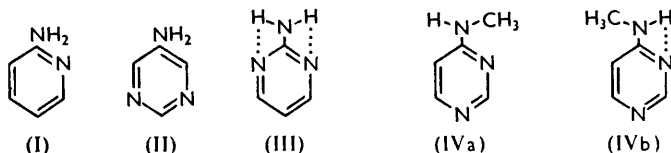$$S = 0.55b + 0.42\sqrt{(1 - b^2)} \quad \ldots \ldots \quad (6)$$

The overlap integral (S), given by equation (6), has a maximum value when $b = 0.79$, that is, when the N–H bond has slightly more than digonal " s " character. Over the range covered in the present work ($b = 0.44$—0.57), the overlap integral (S) increases approximately linearly with b, in accord with the observed increase in the force constant (k) with the " s " character (b) of the N–H bonds (Fig. 1A).

In the series of aromatic amines the N–H stretching vibration force constant (k) increases as the π-electron charge density (q_N) on the amino-nitrogen atom falls (Fig. 2A). The decrease of charge density (q_N) may be expected to have two effects upon the N–H bonds of the amino-group. First, the lone-pair orbital of the nitrogen atom of the amino-group should become more purely 2$p\pi$ as the non-bonding electrons are increasingly delocalised over the aromatic nucleus, so that the N–H bonds attain an increased " s " character and become stronger. Secondly, the electronegativity of the nitrogen atom of

[13] Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

the amino-group increases as the charge density (q_N) falls, so that the hydrogen atoms are bound more firmly. The two effects may be distinguished, for the N—H bonds have the same " s " character in aniline and in 5-aminopyrimidine, yet the force constant of the latter is larger than that of the former, corresponding to a fall in the charge density (q_N). Moreover, *ortho*-" substitution " with a single nitrogen atom results in a large increase in the " s " character of the N—H bonds, whilst two *meta*-nitrogen " substituents " result in no increase, though the charge densities (q_N) in 2-aminopyridine (I) and 5-aminopyrimidine (II) are closely similar (Table 1).

In general, ring-nitrogen " substituents " in aniline increase the H—N—H bond angle and the " s " character of the N—H bonds in the order, *ortho* > *para* > *meta* (Table 1). The greater influence of an *ortho*- than of a *para*-substituent (compare Nos. 4 and 8, 5 and 9, 17 and 18, Table 1) may be ascribed partly to intramolecular hydrogen-bonding between the nuclear and exocyclic nitrogen atoms, and partly to an inductive effect between these two nitrogen atoms in the *ortho*-compounds. The former effect may be important. Tak-

ing the bond distances in 2-aminopyrimidine (III) to be those obtained [14] by an *X*-ray diffraction study of 2-amino-4 : 6-dichloropyrimidine, with the H—N—H bond angle given in Table 1, and an assumed N—H bond distance of 1·0 Å, it is found, using Slater orbitals,[13] that the overlap integral between the sp^2-orbital of the lone-pair electrons of a nuclear nitrogen atom and the 1s-orbital of a hydrogen atom of the amino-group in (III) is 0·077. Thus intramolecular hydrogen-bonding between the nuclear and the exocyclic nitrogen atom of the *ortho*-compounds cannot be inconsiderable, and it must be responsible, at least in part, for the observed increase in the H—N—H bond angles of these amines (Table 1). As in the *peri*-*N*-heteroaromatic amines,[3] intramolecular N—H · · · N hydrogen-bonding in the *ortho*-" substituted " amines has only a small effect upon the position of the N—H stretching frequencies, in contrast to O—H · · · N intramolecular hydrogen-bonding where the O—H frequency is considerably lowered. The effect may be apparent in 4-methyl-aminopyrimidine (IV) which gives rise [15] to two N—H stretching vibration absorptions in dilute solution at 3443 and 3466 cm.$^{-1}$, the frequencies falling to 2555 and 2570 cm.$^{-1}$ on deuteration. The absorptions may be due to the " free " form (IVa) and the hydrogen-bonded form (IVb) respectively, the latter giving the higher frequency as the N—H · · · N angle is less than 90° and so causes a larger restoring force for the N—H stretching vibration. The two bands are of comparable intensity, suggesting that the two forms (IVa and b) are equally stable, the increase in stability due to hydrogen-bonding being offset by steric compression between the methyl and *ortho*-CH group in (IVb).

II. *Intensities.*—The integrated intensity (A) of an infrared absorption band is related to the change of the vector dipole moment with the normal co-ordinate of the vibration (dM/dQ) by the expression:

$$A = (N\pi/3c)(dM/dQ)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The stretching vibrations of the primary amino-group involve the motions of both of the N–H bonds in the group, and the intensities of the corresponding absorption bands afford a knowledge of the electrical properties of the N–H bonds in a given amine if it is assumed that only the change of the N—H bond moment with bond length (dM/dr) contributes to the transition moment, and that the contributions from the two N–H bonds are equal and additive. With these assumptions the dipole moment gradients of the

[14] Cochran, *Acta Cryst.*, 1948, **1**, 4.
[15] Brown, Hoerger, and Mason, *J.*, 1955, 4035.

normal co-ordinates of the symmetric (dM/dQ_s) and the antisymmetric (dM/dQ_a) stretching vibration of the primary amino-group lie along the internal and the external bisector of the H–N–H angle respectively, and they are connected with the N–H bond-moment gradient (dM/dr) by the relations:

$$(dM/dQ_s) = (2/\mu_s)^{1/2} \cos \theta/2 \ (dM/dr) \quad \ldots \ldots \quad (8)$$

$$(dM/dQ_a) = (2/\mu_a)^{1/2} \sin \theta/2 \ (dM/dr) \quad \ldots \ldots \quad (9)$$

where μ_s and μ_a are the reduced masses governing the amplitudes of the atomic motions from equations (1) and (2). By equations (7—9) two independent values of (dM/dr) may be obtained, by use of the intensities of the symmetric and the antisymmetric vibration absorption band respectively; and a measure of the H–N–H bond angle may be derived from the ratio of the two intensities through the approximate relationship:

$$A_a/A_s = \tan^2 \theta/2 \quad \ldots \ldots \ldots \quad (10)$$

The integrated intensity of an infrared absorption band can be found accurately only by graphical summation, but good approximate values can be obtained by fitting the envelope of the band, if it is symmetrically shaped, to a normal-error curve,[16] or to a Lorentz curve.[17] In the present work it was found that the latter curve corresponded more closely to the observed band envelopes, and, accordingly, the intensities were evaluated by means of the relation:[17]

$$A = (\pi/2)E\Delta\nu_{\frac{1}{2}} \quad \ldots \ldots \ldots \ldots \quad (11)$$

where E is the maximum extinction coefficient and $\Delta\nu_{\frac{1}{2}}$ the band half-width. Equation (11) is a good approximation [17] if the effective slit-width is less than 0·4 of the band half-width, or if the intensity is measured at about 75% absorption with larger slit-widths. These conditions were adopted in the present study. The intensities obtained by means of equation (11) were not corrected for the effect of the solvent used, since the expressions proposed [18] for the influence of solvents on the intensities of infrared absorption bands do not account for the relative intensities observed with a given amine in chloroform and carbon tetrachloride solutions.

The measured maximum extinction coefficients and band half-widths for the primary amines studied are recorded in Table 2, together with the change of the N–H bond moment with bond length obtained from the intensities of the symmetric $(dM/dr)_s$ and the antisymmetric $(dM/dr)_a$ stretching vibration bands, and the apparent H–N–H bond angle (α) derived from the ratio of the intensities (equations 7—11). The values obtained for the apparent bond angle (α) are too small, that of the amide ion being as low as 55°, and in the " substituted " aromatic amines the expected relative values are not reproduced (compare 0 of Table 1 with α of Table 2). Moreover, the two values of the bond dipole gradient (dM/dr) for a given amine do not agree, that derived from the intensity of the symmetric stretching vibration band being invariably larger than that obtained from the antisymmetric band (Table 2).

Thus the assumptions upon which equations (8) and (9) are based are not fully tenable. In particular, the assumption that the transition moment of the symmetric stretching vibration absorption contains only vector components from the N–H bond dipoles (equation 8) requires modification, as it is probable that the atomic dipole of the lone-pair electrons of the amino-group contribute to the transition moment.[19] During the antisymmetric vibration of the amino-group any change in the hybridisation of one N–H bond

[16] Richards and Burton, *Trans. Faraday Soc.*, 1949, **45**, 874.
[17] Ramsey, *J. Amer. Chem. Soc.*, 1952, **74**, 72.
[18] Polo and Kent, *J. Chem. Phys.*, 1955, **23**, 2376; Brown, *Spectrochim. Acta*, 1957, **10**, 149.
[19] Orville-Thomas, Parons, and Ogden, *J.*, 1958, 1047.

is compensated by a converse change in the hybridisation of the other, leaving the sp-ratios and the electron-distributions in the other orbitals of the molecule unaltered. Thus equation (9) is a good approximation. During the symmetric vibration, however, both of the N–H bonds undergo the same change of hybridisation, and a compensating change must occur in the other orbitals of the nitrogen atom, notably, in the lone-pair orbital. Tables of overlap integrals indicate [13] that the " s " character of a nitrogen hybrid orbital giving the maximum overlap with a hydrogen 1s-orbital falls as the N–H bond length increases. As the N–H bonds lengthen during the symmetric stretching vibration of the amino-group, the " s " character of the bonds falls whilst that of the lone-pair orbital increases, and the atomic dipole of the lone-pair electrons, which increases with the " s " character of the orbital,[20] makes a significant contribution to the transition moment of the vibration. The contribution is particularly important in the amide ion, which has two pairs of unshared electrons, for the symmetric band is some four times as intense as the antisymmetric band in this case (Table 2), whilst the intensities would be comparable if equation (8) were valid.

In the series of " substituted " aromatic amines the lone-pair electrons of the amino-group are extensively delocalised over the aromatic nucleus in the vibrational ground state. As the " s " character of the lone-pair orbital increases during the symmetric vibration, the lone-pair electrons become more localised on the amino-nitrogen atom, since the s-orbital, with even symmetry, cannot combine with the π-orbitals of the nucleus, which have odd symmetry with respect to the plane of the molecule. Accordingly, the π-electron component of the permanent dipole of the aromatic amines varies in phase with the symmetric vibration, and so contributes to the transition moment of that vibration, the contribution becoming larger the greater the conjugation between the amino-group and the aromatic nucleus. There are indications that the intensity of the symmetric band becomes progressively larger than required by equation (8) with increasing conjugation in the aromatic series. The apparent bond angle (α), which is an expression of the intensity ratio (A_a/A_s) by equation (10), progressively falls, relative to the bond angle (θ) derived from the frequencies, as the conjugation between the amino-group and the aromatic nucleus increases (Tables 1 and 2). Moreover, the fall is larger in the *para*-" substituted " amines than in their *ortho*-isomers (compare 4 and 8, 5 and 9, 10 and 12, 17 and 18, Tables 1 and 2), the *para*-compounds having larger permanent dipole moments than their *ortho*-isomers (2- and 4-aminopyridine have moments of 2·17 and 4·79 D respectively [21]).

Whilst the intensities of the symmetric stretching vibration bands of the primary amines do not depend upon the electrical properties of the N–H bonds alone, it is probable that the intensities of the antisymmetric bands afford good approximate values of the N–H bond dipole gradient (dM/dr) by equation (9). The values of $(dM/dr)_a$ obtained (Table 2) are ambiguous in sign, and it is found (Fig. 1B) that they correlate linearly with the " s " character of the N–H bonds if the value for the amide ion has a sign opposite to those of the aliphatic and aromatic amines. On electronegativity grounds it is probable that the N–H bond in the aliphatic and the aromatic amines has the polarity $\overset{-}{N}–\overset{+}{H}$, so that the polarity in the amide ion is $\overset{+}{N}–\overset{-}{H}$, the correlation of (Fig. 1B) suggesting that the electronegativity of the nitrogen atom increases with the " s " character of the N–H bonds.

In the aromatic series the N–H bond dipole gradient $(dM/dr)_a$ increases as the π-electron charge density on the amino-nitrogen atom (q_N) falls (Fig. 2B). In general, a decrease in the charge density (q_N) is accompanied by an increase in the " s " character of the N–H bonds, but in aniline and 5-aminopyridine the N–H bonds have the same " s " character though the bond dipole gradient of the latter compound is larger than that of former (Table 2, Fig. 2B), suggesting that the electronegativity of the amino-nitrogen atom is increased by a reduced charge density independently of any changes in hybridisation.

[20] Coulson, *Trans. Faraday Soc.*, 1942, **38**, 433.
[21] Goethals, *Rec. Trav. chim.*, 1935, **54**, 299.

EXPERIMENTAL

Infrared Spectra.—These were measured with a Perkin–Elmer model 12 C spectrometer, with a lithium fluoride prism and a quartz filter. The effective slit width was about 6 cm.$^{-1}$. The aromatic amines were examined at two or more concentrations in the range M/100 to M/1000, in cells of 1 cm. length with chloroform and also 2 and 5 cm. length with carbon tetrachloride as solvent. *cyclo*Hexylamine was examined at M/50-concentration in a 5 cm. path-length of carbon tetrachloride. The intensities recorded in Table 2 refer to solutions giving about 75% absorption with the longest path-lengths employed. These intensities were reproducible within 5%, though they are up to 5% larger than the intensities given by stronger solutions with shorter path-lengths.

Materials.—5-Aminopyrimidine was kindly supplied by Dr. N. Whittaker,[22] 3-amino-6-methyl- and 4-amino-pyridazine by Dr. J. Druey, and 2-aminopyrazine and 2- and 4-aminopyrimidine by Dr. D. J. Brown. 3-Amino- and 3-amino-5 : 6-dimethyl-1 : 2 : 4-triazine were prepared according to Erickson's directions.[23] The remaining compounds were commercial specimens.

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[22] Whittaker, *J.*, 1951, 1565.
[23] Erickson, *J. Amer. Chem. Soc.*, 1952, **74**, 4706.