The Vibrational Spectra of Compounds containing the Dimethylamino-group. Part II.† *p*-*NN*-Dimethylaminobenzonitrile and the *N*-Methyltoluidines

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The i.r. and Raman spectra of *p*-chlorobenzonitrile and *p*-*NN*-dimethylaminobenzonitrile have been recorded in the range 4000—10 cm^{-1}. The fundamental vibrational frequencies of these systems have been computed. On the basis of these calculations and by analogy with related molecules the observed spectral bands have been assigned. It is shown that several modes exist which might be characteristic of the dimethylamino-group and that considerable mixing occurs in some instances between the modes of the ring and the amino-group. Some tentative conclusions concerning the structure of the C_6–NC_2 skeleton are made. A survey of the spectra of the *N*-methyl-toluidines and -anilines has been made which supports the identification of the characteristic bands of the aromatic –NMe_2 and aromatic –NHMe entities.

THERE have been few detailed studies of the vibrational spectra of compounds containing the NMe_2 group. A number of i.r. absorption bands in the 3000 cm^{-1} region have been suggested to be characteristic of the grouping [1-3] and some attempts have been made to identify further characteristic bands in the fingerprint region.[4-6] It might be expected that when a complex grouping A, such as NMe_2, is attached to a common large grouping of nuclei, B, with a fixed geometry in a variety of molecules, then the variation in the vibrational frequencies associated with A would be much less than if B were varied. For this reason we have studied the NMe_2 and the NHMe

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[4] L. J. Bellamy, ' Advances in Infrared Group Frequencies,' Methuen, London, 1968, p. 9 *et seq.*

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groupings attached directly to aromatic six-membered rings.

Two problems arose in the interpretation: (*a*) there appears to be considerable uncertainty concerning the conformation of the NMe_2 group in this environment. *X*-Ray crystallography has established that in *NN*-dimethylamino-*p*-nitrobenzene the C_6–NC_2 skeleton is planar in the solid state and only slightly rotated from the plane of the aromatic ring.[7] On the basis of the u.v. spectra the NC_2 skeleton of *NN*-dimethylaniline was suggested to be in the plane of the ring [8] but the evidence for this is far less convincing. An electron-diffraction study of *NN*-dimethylaniline in the vapour phase [9] led to the conclusion that the tertiary amine skeleton was non-planar with CNC angles of *ca.* 116° which is intermediate between those required for planar and tetrahedral configurations. Aniline itself is definitely non-planar.[10,11] An estimate of the angle between the ring–N bond and the NH_2 plane of *ca.* 45° has been deduced from the electronic spectrum.[11] If these estimates are correct they imply that the structure is nearer tetrahedral in aniline than in its dimethyl derivative. We suggest that the difference in the vibrationl spectra of *NN*-dimethylaniline, and also those of the *NN*-dimethyltoluidines, from the spectra of the *p*-nitro-derivative, imply different conformations.[12] (*b*) Despite the enormous literature on the spectra of aromatic derivatives there seem to be many uncertainties in the assignment of aromatic ring modes when the substituents consist of more than one atom. This makes the interpretation of the spectra arising from the NMe_2 group much more complex. We aim to show that this problem arises from the severe mixing of the phenyl distortions with those of the complex substituent groupings.

In this paper we present an analysis of the spectra of *p*-chlorobenzonitrile and *p*-*NN*-dimethylaminobenzonitrile. In addition we summarise some of the results of an investigation of the spectra of aniline and *ortho*-, *meta*-, and *para*-toluidines and their *N*-methyl and *NN*-dimethyl derivatives. As these results are largely in accord with the earlier work of Katritzky and Jones [5] and since the spectra of these compounds have all been published in varying degrees of detail, we shall not reproduce our data here. Details of the spectra are available on request.

EXPERIMENTAL

All compounds were the highest purity commercial products from BDH, Koch–Light, or Emmanuel. Recrystallisation of *p*-chlorobenzonitrile and *p*-*NN*-dimethylaminobenzonitrile produced no spectral change and therefore most studies were carried out on the commercial samples. All the anilines and toluidines were distilled *in vacuo* before use. A zone-refined sample of *NN*-dimethyl-*p*-toluidine was kindly given to us by Professor R. A. Shaw. Spectra from this sample were identical to those from our distilled sample. Measurements of the i.r. spectra are summarised in Table 1. Raman spectra were obtained on a Cary 81 spectrometer with a Spectra Physics helium–neon 50 mW C.W. laser (6328 Å) for excitation. Samples (liquid and solid) were contained in Pyrex capillary tubes.

TABLE 1

Range/cm⁻¹	Sample state	Spectrometer
10—200	Nujol mull or CCl_4 soln.	Grubb–Parsons ' Cube ' interferometer
150—300	Nujol mull or CCl_4 soln.	Multigrating evacuated spectrometer built in this department
260—400	Nujol mull or CCl_4 soln.	Perkin-Elmer 457 spectrometer
400—4000	KBr disc or CCl_4 soln.	Unicam SP 100 or Perkin-Elmer 337 spectrometer

TABLE 2

The molecular parameters and force constants assumed in the calculations

Aromatic C═C	= 1·40 Å	N–Me	= 1·46 Å
Aromatic C–H	= 1·08 Å	C–H	= 1·08 Å
Aromatic C–N	= 1·40 Å	C≡N	= 1·16 Å
C–CN	= 1·42 Å	C–Cl	= 1·70 Å

All ring angles were taken as 120° and all angles around the carbon of the methyl groups taken as tetrahedral (109° 28′). The atomic masses of carbon, hydrogen, nitrogen, and chlorine, were taken as 12·011, 1·008, 14·0, and 35·5 a.m.u. respectively.

Diagonal force constants/N m⁻¹		Interaction force constants/N m⁻¹	
C≡N	1760	R–R ($o = -m = p$)	48
Ring–CN	600	R_i–β_i(H)	35
R (aromatic C═C)	687	R_i–α_i	31·6
Aromatic C–H	512·5	AN–NMe	60
Ring–NMe_2	600	NMe–NMe	64
C–Cl	370	NMe–δ	30
N–Me	460	α_i–α_{i+1}	−5
Methyl C–H	495	α_i–β_{i+1}(H)	4·2
α (ring CCC)	61·9	δ_i–δ_{i+1}	−3
β(H)	88·1	β_i(H)–β_{i+1}(H)	1·8
β(CN)	51	β_i(H)–β_{i+2}(H)	−1·9
β(N)	51	β_i(H)–β_{i+3}(H)	−2·7
θ(HCH)	44	γ_i(H)–γ_{i+1}(H)	1·23
δ(HCN)	61	γ_i(H)–γ_{i+2}(H)	−1·3
ε(C–C≡N)	30	γ_i(H)–γ_{i+3}(H)	−1·15
γ(C–C≡N)	30	γ_i(H)–ϕ_i	1·25
γ(H)	26·5	γ_i(Cl)–ϕ_i = γ_i(C)–ϕ_i	
γ(Cl)	12·3	= γ_i(N)–ϕ_i	−0·3
γ(N)	15·5	ϕ_i–ϕ_{i+1}	−0·7
γ(C≡N)	15·1		
χ	45		
φ	3·6		

Deformation co-ordinates of the angles ABC are multiplied by the bond length AB. β(X) Co-ordinates are multiplied by the CX bond lengths. The interaction force constants involving γ(X) and β(X) co-ordinates of the type β_i(X)–β_{i+1}(H) are obtained from the corresponding γ(H) and β(H) constants by multiplication with the ratio of the square-roots of the CH to CX bond lengths. All α–β(X), R–β(X), γ(X)–γ(H), and β(X)–β(H) are included.

RESULTS AND DISCUSSION

Calculations.—The computational procedure has been described.[13] The bond lengths and interbond angles adopted were as shown in Table 2. In computing the

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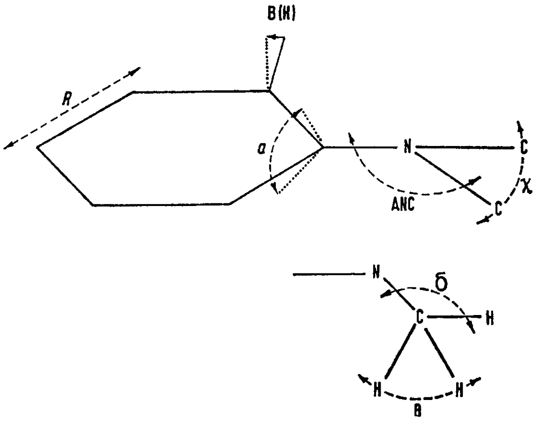
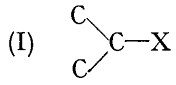
potential energy distribution (p.e.d.) we have ignored the contribution from off-diagonal force constant elements.

For *p*-chlorobenzonitrile, the in-plane frequencies were calculated by use of a force field due to Duinker which was derived from a study of chlorobenzenes.[14] Out-of-plane force constants for the substituted aromatic ring system were taken from the 15-parameter field for chlorobenzenes given in Table 3 of ref. 15. For the ring-substituent out-of-plane deformation it was assumed that the force required for a unit angular displacement is the same as for a Cl substituent. The latter approximation is necessary owing to lack of reliable force constants for these substituents and is justified elsewhere.[15] For the NMe_2 group the same force constants as those used in Part I [16] were taken. As in Part I the force constants associated with the methyl group are those due to King and Crawford.[17]



Definition of internal displacement co-ordinates

Some co-ordinates are defined in the Figure. Other definitions used are $\gamma(X)$, out-of-plane deformation of a CX bond from a planar system (I); $\beta(X)$, corresponding

(I) 

$$\begin{matrix}C \\ & \rangle C{-}X \\ C\end{matrix}$$

in-plane deformation of the CX bond from the internal bisector of the ring; ϕ Bell's torsion co-ordinate;[18] A–CN, aromatic-carbon to nitrile carbon stretch; A–N, aromatic-carbon to nitrogen stretch; and ε(CCN) and γ(CCN), angular deformations of the C–C≡N system in-the-plane and out-of-the-plane of the aromatic ring respectively. A value of 60 N m^{-1} was chosen for the ring-N–NMe interaction constant. This would be expected to be similar to the NMe–NMe interaction constants. For the C–C≡N grouping the best available guide to the force constants appears to be MeCN. From the work of Nakagawa and Shimanouchi [19] the force constants of the angular deformations of the C–C≡N, both in-the-plane and out-of-the-plane of the aromatic ring, were taken as 30 N m^{-1}, the value for MeCN. Conjugation to the aromatic ring would be expected to reduce the C≡N stretching force constant from its value in MeCN. An arbitrary value of 1760 N m^{-1} was chosen compared with the value of 1860 N m^{-1} for the aliphatic nitrile. Even this reduction is clearly too small as the computed νC≡N remains about 3% high. This suggests that the constant is still high by *ca.* 10%. Such a change would have a negligible effect on other frequencies.

Three different models were tried for the calculation of the frequencies of *NN*-dimethylaminobenzonitrile: (i) a coplanar arrangement of the NC_2 skeleton and the aromatic ring (C_{2v} point-group); (ii) a pyramidal distribution of bonds (tetrahedral bond angles) about the nitrogen atom while retaining a plane of symmetry perpendicular to the ring (C_s point-group). In both (i) and (ii) out-of-plane aromatic angular deformations were not included in the calculation; (iii) the same as model (ii) but with out-of-plane ring deformations included.

p-Chlorobenzonitrile was assumed to have C_{2v} symmetry. It is assumed here that the z-axis is coincident with the C_2 axis and the x-axis is perpendicular to the molecular plane. The in-plane vibrational species are then a_1 and b_2.

Computed and observed spectral data for *p*-chloro- and *p*-*NN*-dimethylamino-benzonitriles are in Tables 3 and 4 respectively.

p-*Chlorobenzonitrile*.—The Raman spectrum of *p*-chlorobenzonitrile has been reported by Kohlrausch and Pongratz.[20] A number of discrepancies occur between our results and these early data, particularly at small frequency shifts, but many of Kohlrausch's data are substantiated. The i.r. spectrum has been reported by two groups.[21,22] The spectra agree well though our interpretations differ.

The average discrepancy between our calculated and observed frequencies is 13 cm^{-1}, the largest difference being only 32 cm^{-1}. As most of the assignments are known beyond reasonable doubt, the good agreement between calculated and observed frequencies yields confidence in the use of the field in the vibrational calculations on dimethylaminobenzonitrile. There is some uncertainty concerning the b_1 and a_2 modes near 960 cm^{-1}. Two weak absorption bands (at 952 and 963 cm^{-1}) are assigned respectively to these modes. Comparison with the calculations suggests that the higher frequency is the a_2 mode absorbing in violation of the selection rules. The combination band arising from these γ(H) vibrations, which always appears with

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[14] J. C. Duinker, Thesis, Amsterdam, 1964.

[15] K. Radcliffe and D. Steele, *Spectrochim. Acta*, 1969, **25**, *A*, 597.

[16] A. Finch, I. J. Hyams, and D. Steele, *J. Mol. Spectroscopy*, 1965, **16**, 103.

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[18] R. P. Bell, *Trans. Faraday Soc.*, 1945, **41**, 293.

[19] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1962, **18**, 513.

[20] K. W. F. Kohlrausch and A. Pongratz, *Monatsh.*, 1935, **65**, 199.

[21] H. W. Wilson and J. E. Bloor, *Spectrochim. Acta*, 1965, **21**, 45.

[22] C. Garrigou-Lagrange, J. M. Lebas, and M. L. Josien, *Spectrochim. Acta*, 1958, **12**, 305.

reasonable intensity,[23] is at 1915 cm^{-1}, in perfect agreement with the frequency sum. The two highest a_2 modes give rise to a further combination band near 1780 cm^{-1} (observed at 1778 cm^{-1}). If we take the 963 cm^{-1} band as the a_2 mode then the second γ(H) a_2 mode is placed at 813 cm^{-1} (calculated at 826 cm^{-1}). No assignment was possible for the lowest a_2 mode. These assignments differ only in small details from those of Garrigou-Lagrange, Lebas, and Josien.[22] We did not observe an absorption band at 674 cm^{-1} as reported by these authors. We assume that the intense Raman band at 642 cm^{-1} is due to both b_1 and b_2 fundamentals. It is possible that one of these fundamentals gives rise to the weak Raman and i.r. bands at 704 cm^{-1}. The principal difference is in our assignment of the 1197 and 1176 cm^{-1} pair of bands as a Fermi resonance doublet. Following the calculations we prefer a greater spread between the a_1 frequencies and choose the 1260 cm^{-1} band, though much weaker, as the second a_1 fundamental. In this way we also differ from Wilson and Bloor.[21]

TABLE 3

Observed and calculated vibrational frequencies/cm^{-1} of *p*-chlorobenzonitrile

Observed [a]			
I.r.	Raman	Calculated	Assignment [b]
116w		97	b_1
163m	148s	151	b_2
250w	250vs	237	b_1
	303s	300	b_2
348w	350vs,p	354	a_1
		407	a_2
440w	443vs	419	b_1
	521w	542	b_1
542s	546vs	510	b_2
587s	590w	604	a_1
	642vs	646	b_2
		659	b_1
704w	705w		116 + 587 ($b_1 + a_1$)
779ms	779vs	797	a_1
	806m		$2 \times a_2$
828vs		818	b_1
813 [c]		826	a_2
880w			2×440 ($b_1 + b_1$)
952w		951	b_1
963w		964	a_2
1016s	1020w	1033	a_1
1090vs	1090vvs,p	1093	a_1
1115m		1100	b_2
1130w			350 + 779 ($a_1 + a_1$)
1176ms	1176vs,p	1173	a_1
1196m	1197vs,p		546 + 642 ($b_1 + b_1$)
1260m		1241	a_1
1280m		1284	b_2
1304m	1305w	1290	b_2
1400s		1382	b_2
1485vs	1484w	1478	a_1
1498m			
1583sh	1580sh	1568	a_1
1594s	1592vvs,p	1571	b_2
1778w			963 + 813 ($a_2 + a_2$)
1915w			963 + 952 ($a_2 + b_1$)
2222s	2230vvs,p	2298	a_1
N		3070	b_2
N		3070	b_2
N		3072	a_1
N		3073	a_1

[a] v, Very; s, strong; m, medium; w, weak; p, polarised; dp, depolarised; sh, shoulder; N, no measurement. [b] The 33 fundamental vibrations are distributed among the species of the C_{2v} point-group as follows: $12a_1 + 11b_2$ (in-plane) + $3a_2 + 7b_1$ (out-of-plane). [c] Assigned from γCH combination bands.

In agreement with Garrigou-Lagrange,[24] Kahane-Paillous,[25] and Jakobsen [26] the in-plane C–C≡N deformation is identified with the intense absorption near 540 cm^{-1}. This is in accord with the present calculations and with the high i.r. and Raman intensity associated with this frequency. The high i.r. intensity in particular makes its assignment as a ring mode, as suggested by Green [27] (for the analogous band of benzonitrile) and by Wilson and Bloor [21] less attractive. We tentatively assign the b_1 ring mode to the weak Raman band at 521 cm^{-1}. Another assignment on which we differ from Wilson and Bloor is in the higher a_2 and b_1 frequencies. They assign 968 cm^{-1} as a b_1 mode and correlate the a_2 mode with the 880 cm^{-1} band. On the basis of our calculations this seems to be very low (to obtain agreement between calculated and observed frequencies would necessitate reduction of all force constants by 17% or a correspondingly large change in selected constants) and also leads to difficulties in interpreting the combination bands.

Benzonitrile and perdeuteriobenzonitrile have been studied by Jakobsen.[26] On the basis of mode sensitivity to substituent in the C_6H_5X and C_6D_5X series, the γ(C–C≡N) mode was assigned at 160 cm^{-1}.

The calculated p.e.d. for modes in this frequency range for *p*-chlorobenzonitrile and for the *p*-*NN*-dimethylaminobenzonitrile show a most surprising difference. For the former molecule the mode calculated at 151 cm^{-1} is 87% γ(CCN) and yet in the dimethylamino-compound mixing is so strong with distortions of the NMe_2 group that in no vibration does γ(CCN) contribute more than 9% to the total potential energy. The band calculated to be at 180 cm^{-1} is that which contains 9%. As is seen from Table 3 it also contains 17% of the associated γ(C) motion; 17% of ring torsion and the bulk of the remainder of the potential energy is associated with the NMe_2 group. The extent of the difference is very surprising but has survived a careful rechecking.

p-NN-*Dimethylaminobenzonitrile*.—Despite the large number of published vibrational studies of *para*-substituted aromatic molecules, it is still very difficult to predict the intensity and position of the aromatic bands for new systems. Conversely it is very difficult to be certain of the identification of the aromatic bands in the spectra of complex systems. The assignments presented are based on (*a*) analogy with spectra of simple aromatic systems; (*b*) the calculations; and (*c*) analogy with spectra of *NN*-dimethylaniline, *N*-methylaniline, and the corresponding toluidines. (*a*) and (*c*) serve to identify the major 'characteristic' bands of the aromatic ring and the NMe_2 group respectively, whilst (*b*) helps to

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[23] D. H. Whiffen, *Spectrochim. Acta*, 1957, **7**, 253.

[24] C. Garrigou-Lagrange, Thesis, Bordeaux, 1962.

[25] J. Kahane-Paillous, *J. Chim. phys.*, 1960, **57**, 580.

[26] R. J. Jakobsen, *Spectrochim. Acta*, 1965, **21**, 127.

[27] J. H. S. Green, *Spectrochim. Acta*, 1961, **17**, 607.

TABLE 4

Observed vibrational bands and calculated frequencies/cm^{-1} of *p*-*NN*-dimethylaminobenzonitrile. Model (i) assumes a planar ring–NC$_2$ system. Model (ii) assumes tetrahedral angles about the nitrogen, but otherwise with maximum symmetry. Model (iii) is as model (ii) but includes the out-of-plane aromatic deformations, whereas models (i) and (ii) do not. In the column of Raman bands figures in parentheses denote measured depolarisation ratios

Observed bands/cm^{-1} [a]		Calculated frequencies/cm^{-1}					
I.r. (solution CCl$_4$ or CS$_2$)	Raman (solid)	Model (i) (C_{2v})	Model (ii) (C_s)	Model (iii) (C_s)	Species Model (i)	Species Models (ii) and (iii)	Approximate p.e.d. (%) (Major terms only) [Model (iii)]
N	N	3073	3074	3074	a_1	a'	ν(CH) of aromatic entity
N	N	3073	3073	3073	a_1	a'	ν(CH) of aromatic entity
N	N	3071	3071	3071	b_2	a''	ν(CH) of aromatic entity
N	N	3070	3070	3070	b_2	a''	ν(CH) of aromatic entity
N	N	3060	3054	3054	a_1	a'	ν(CH) antisymmetric of Me group
N	N	3057	3052	3052	b_2	a''	ν(CH) antisymmetric of Me group
N	N	3043	3052	3052	b_1	a'	ν(CH) antisymmetric of Me group
N	N	3043	3051	3051	a_2	a''	ν(CH) antisymmetric of Me group
N	N	2935	2932	2932	a_1	a'	ν(CH) symmetric of Me group
N	N	2934	2931	2931	b_2	a''	ν(CH) symmetric of Me group
2220vs	2210vs	2292	2292	2292	a_1	a'	83 C≡N, 16 A–CN
1602s	1602vs,dp	1668	1667	1667	a_1	a'	58 R, 16 A–N, 11 α, 11 β
	1560m,dp	1600	1600	1600	b_2	a''	80 R, 9 α
1527s	1528m (0·5)	1567	1564	1564	a_1	a'	36 R, 7 A–CN, 12 A–N, 31 β
	1488p						
1450ms	1448ms,dp	1480	1458	1458	a_1	a'	100 (δ, θ)
		1474	1455	1456	b_1	a'	100 (δ, θ)
		1476	1453	1453	b_2	a''	100 (δ, θ)
		1469	1450	1450	a_2	a''	100 (δ, θ)
	1418w,dp	1414	1392	1392	a_1	a'	47 δ, 36 θ, 6 β
		1397	1377	1377	b_2	a''	50 δ, 36 θ, 6 R
		1390	1386	1386	b_2	a''	52 R, 27 β, 18 α
1369vs	1373ms (0·1)	1377	1361	1361	a_1	a'	23 A–N, 24 β, 14 δ, 15 θ
1324w		1316	1313	1313	b_2	a''	95 β
1312w	1310w,dp	1288	1288	1288	b_2	a''	84 R, 14 β
1229ms	1228s (0·6)	1266	1263	1263	a_1	a'	30 R, 7 C≡N, 31 A–CN, 14 α, 11 β
1180s	1184vs (0·5)	1143	1171	1174	a_1	a'	51 δ, 18 N–C, 10 θ, 6 β, 7 χ
1168s	1172s (0·4)	1194	1193	1193	a_1	a'	90 β
1135w		1040	1113	1113	b_1	a'	67 δ, 10 θ, 11 R
1122w	1128w	1214	1173	1173	b_2	a''	48 N–C, 29 δ, 7 β, 6 α
		1081	1081	1081	b_2	a''	44 R, 40 β
		1086	1058	1058	a_2	a''	86 δ, 10 θ
1005m	1006vw,p	1038	1038	1038	a_1	a'	40 α, 12 β, 45 R
1062ms		1016	994	994	b_2	a''	48 N–C, 44 δ
				965		a''	72 γ(H), 28 ϕ
		928	946	953	a_1	a'	22 N–C, 12 δ, 45 γ(H), 15 ϕ
944ms	946w (0·2)			945		a	30 N–C, 14 δ, 38 γ(H), 12 ϕ
	833w (0·1)						
				832		a''	76 γ(H), 24 ϕ
818vs	816w			820		a'	70 γ(H), 6 γ(C), 12 ϕ
791w	790vs	816	834	835	a_1	a'	51 R, 18 α, 7 A–N, 6 γ(H)
732w	731m			731		a'	20 γ(N), 23 γ(C), 32 ϕ, 11 γ(H)
	720ms,dp						
		627	646	663	a_1	a'	20 R, 19 A–CN, 16 A–N, 12 α
652m	654s	651	658	650	b_2	a''	90 α, 5 R
594w	594w			572		a'	16 γ(N), 20 γ(C), 43 γ(CCN)
	488m						
540s	542w	521	521	521	b_2	a''	60 ε(CCN), 32 β(C)
466m	468m,dp			470		a'	20 ANC, 18 γ(N), 17 ϕ, 18 γ(CCN)
		455	447	419	a_1	a'	12 A–CN, 30 α, 21 χ, 11 γ(N)
				409		a''	30 γ(H), 49 ϕ
		414	387	386	b_2	a''	52 ANC, 13 N–C, 5 R
362m	355s (0·35)	281	354	357	a_1	a'	59 χ, 5 ANC, 3 α, 9 ϕ
	280m			275		a'	22 ANC, 11 χ, 12 γ(C), 13 ϕ
	181m	185	260	184	b_2	a''	37 β(C), 18 β(N), 16 ANC, 23 ε(CCN)
158s	151s	111	182	180	a_1	a'	29 ANC, 19 γ(N), 17 ϕ, 9 γ(CCN), 17 γ(C)
				117		a''	22 β(C), 5 R, 45 β(N), 16 ANC, 10 ε(CCN)
				79		a'	13 γ(N), 11 γ(H), 48 ϕ, 15 γ(C), 6 γ(CCN)

[a] N, No observation.

understand the interplay between the vibrations of the two groups and also assists in locating the approximate positions of weakly active modes.

A number of resonance Raman studies of *NN*-dimethylamino-*p*-benzonitrile have been reported (see, *e.g.*, ref. 28). The data referred to in Table 3 were obtained in the present work by use of 6328 Å radiation, that is, at much longer exciting wavelengths. The vibrational frequencies have previously been calculated

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[28] H. W. Schrötter and J. Brandmüller, Proc. Int. Meeting of Mol. Spectroscopy, Bologne, 1959, vol. 3, p. 1128, published 1962.

by use of a simplified C_6H_4XY model,[29] but this has proved inadequate for the present purposes.

As mentioned earlier we have also made an empirical study of *N*-methyl-toluidines and -anilines. In these systems a number of strong spectral features are seen which are not obviously correlated with the aromatic ring modes. These appear to be characteristic of the *N*-methylamino- and *NN*-dimethylamino-entities attached to an aromatic framework. We tabulate these in Table 5 where we have, for convenience, attached labels *dA* to *dF* for the modes associated with the dimethylamino-entity and *mA* to *mE* for those associated with the methylamino-group.

TABLE 5

Characteristic bands (cm^{-1}) of the NMe_2 and NHMe groups; letters following frequencies denote i.r. and Raman band strengths, respectively. (p) Indicates that the Raman band is polarised, (NI) means that no polarisation measurement was made

NMe_2 Group

Mode label	*NN*-Dimethylaniline	*NN*-Dimethyl-*m*-toluidine	*NN*-Dimethyl-*p*-toluidine	*NN*-Dimethyl-*o*-toluidine
dA	1346vs,s(p)	1350vs,ms(p)	1343vs,m(p)	1310s,br,m(NI)
dB	1193s,s(p)	1227s,s(p)	1190m,vs(p)	1203m,s(NI)
dC	1160s,vs(p)	1175s,m(p)	1160s,s(p)	1152s,coincidence
dD	1130m,w	1130m,wbr(p)	1129s,m	1105s,w(NI)
dE	1062s, —	1059s, —	1058s, —	1049,coincidence
dF	946s,s(p)	958s,m(p)	947s,m(p)	945s,w(NI)

NHMe Group

Mode label	*N*-Methylaniline	*N*-Methyl-*m*-toluidine	*N*-Methyl-*p*-toluidine	*N*-Methyl-*o*-toluidine
mA	1313vs,s(NI)	1328vs,m(NI)	1317s,m(p)	1319s,s(NI)
mB	1260s,m(NI)	coincidence	1261s,w(p)	1267,coincidence
mC	1178s,s(NI)	1182vs,w(NI)	1183s,vs(p)	1191w,vs(NI)
mD	1150s,s(NI)	1168vs,m(NI)	1152s,m(p)	1169s,s(NI)
mE	1070s,w(NI)	1070s	1061m,mw(p)	1068m,m(NI)

The analogous bands of *p*-*NN*-dimethylaminobenzonitrile are easily recognised (Table 6). In the case of band *dA* the frequency is significantly higher than in the toluidines and is overlapping the methyl umbrella region. It is identified however by the considerable intensity of the absorption band and by the high degree of polarisation of the Raman band.

TABLE 6

Comparison of the characteristic bands of the NMe_2 group (as derived from the *NN*-dimethylaniline and toluidines) with the observed and calculated bands of *NN*-dimethylaminobenzonitrile

Designation [a]	Frequency range/cm^{-1} in *NN*-dimethylaniline and toluidines	Activity I.r.; Raman	Frequencies/cm^{-1} in $Me_2N{\cdot}C_6H_4{\cdot}CN$ Obs. (in soln.)	Calc. (model iii)
dA	1350—1300	vs; m—s,p	1369vs; ms,p	1361
dB	1230—1190	m—s; vs—s,p	1180s; vs,p	1174
dC	1180—1150	s—w; vs—w,p	1135w; —	1113
dD	1130—1100	m; w—vw	1122w; —w	1173
dE	*ca.* 1058	m—s; —	1062ms; —	994
dF	960—940	s; m—s,p	944ms; w,p	945

[a] See text.

On the basis of the potential energy distribution calculations with use of model (iii) the nature of the modes can be seen from Table 4. It is striking that band *dA* is calculated to contain 24% of the β (in-plane aromatic CH bending) motion. The mode character is very mixed but it is probable that the considerable intensity arises primarily from the ring–N stretching motion (*ca.* 23%).

The methyl deformation modes near 1450 and 1420 cm^{-1} are well known and need no further discussion. In addition to these, two methyl torsions and six CH stretching modes, there will be ten further fundamental modes associated with a Me_2NX unit, three of which will lie below 500 cm^{-1}. Of the seven remaining higher-frequency modes we have located six (labelled *dA* to *dF*).

Katritzky and Jones [5] assigned the ring–N stretching vibration near 1350 cm^{-1} and Ritschl and Künkel [6] correlated the frequency variations of this mode with the Hammett σ functions of the ring substituents for various substituted *NN*-dimethylanilines. Our calculations confirm that this mode contains the highest proportion of potential energy arising from stretching of the ring–N bond, albeit only 23%. On the basis of the calculations the mode is of a highly mixed character with 24% of β (ring CH) deformation and 29% of methyl HCH and HCN deformations. Three other modes of the *A'* species, the two highest aromatic ring vibrations near 1600 and 1530 cm^{-1} and a mode near 660 cm^{-1}, also contain significant contributions from the ring–N stretching motion.

The symmetric and antisymmetric N–Me stretching modes have been identified [5] near 950 and 1050 cm^{-1} respectively. The band at 946 cm^{-1}, assigned as the symmetric $N–C_2$ stretch, is surprisingly weak in the Raman. However no more probable candidate appears within 150 cm^{-1}. Even extending the range another 100 cm^{-1} includes only a band at 790 cm^{-1} which can be discounted since it is not found in the other aromatic NMe_2 systems. Our calculations again show severe mixing of character. There are two modes computed to be near 950 cm^{-1}. Both show *ca.* 40% of ring character and 50% of NMe_2 character. This mixing may well be overestimated. The actual geometry is probably intermediate between that requiring tetrahedral angles

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[29] J. Brandmüller, E. W. Schmid, H. Schrötter, and G. Nonnenmacher, *Spectrochim. Acta*, 1961, **17**, 523.

and that involving a planar skeletal configuration. Mixing would be reduced with a more planar configuration. Only one other a' mode, that computed near 1170 cm^{-1}, shows any significant N–Me contribution.

In the case of the antisymmetric deformation the calculations again show a strong interaction between the antisymmetric N–Me stretch, and HCN angular distortions. The interaction results in considerable mixing and a splitting apart of the two resulting modes to 1173 and 994 cm^{-1}. The observed band is at 1069 cm^{-1} and we cannot find any second component. The predicted mixing should not be very dependent on the configuration about the nitrogen, as is supported by the calculations with models (i) and (ii), and we are unable to explain this discrepancy. Provided that we are correct in believing that we have not observed this other a'' component, then the remaining observed characteristic bands are readily correlated with the other two a' and the one a'' modes. All three are best described as CH_3 rocking or wagging modes, though only the a'' vibration can reasonably be described as pure. Only *dB* is not listed by Katritzky and Jones.[5] They investigated the i.r. spectra only whereas this mode leads to strong Raman rather than strong i.r. bands.

The interpretation of the band near 355 cm^{-1} is of considerable interest. A very strong, polarised Raman band occurs very near to this frequency in most *para*-substituted *NN*-dimethylanilines, *e.g.*, *p*-$Me_2N{\cdot}C_6H_4{\cdot}CN$, 358 cm^{-1} (s,p); *p*-$Me_2N{\cdot}C_6H_4{\cdot}Me$, 361 cm^{-1} (s,p), and *p*-$Me_2N{\cdot}C_6H_4{\cdot}CHO$, 357 cm^{-1} (s,p).[12]

The frequency is changed drastically in the NHMe systems and in *o*- and *m*-*NN*-dimethyltoluidines which suggests that it is a mixed NMe_2 and aromatic ring mode. This is in agreement with the calculations. Model (ii) and model (iii) show it to be largely a δ(CNC) mode, but in model (i) the frequency decreases by 20% showing a sharp change in character.

The major interest in this δ(CNC) mode arises from the dependence of its frequency on the angle between the planes defined by the aromatic ring and that of the NC_2 of the dimethylamino-entity. Comparison of the calculations of models (i) and (iii) [or (ii)] indicates that the frequency should rise with loss of planarity. *NN*-Dimethylamino-*p*-nitrobenzene is known to be almost planar in the crystal phase. The only strong Raman band between 460 and 200 cm^{-1} is at 320 cm^{-1}.[12] A band occurs near this frequency in *p*-chloronitrobenzene so a possibility exists that the mode is associated in part with the aromatic NO_2 component. Nevertheless it is clear that the frequency in question must be close to 320 cm^{-1}.

The observed decrease in frequency on going from $Me_2N{\cdot}C_6H_4{\cdot}CN$ to $Me_2N{\cdot}C_6H_4{\cdot}NO_2$ is half of that predicted for a change from tetrahedral angles to planar configuration. Provided that the force constants for the angular deformations do not change drastically in going from one to the other of these configurations, it seems reasonable to deduce that the angle between the ring–N and the N–C_2 plane is between 20° and 40° (64° 44′ for tetrahedral angles).

It should be noted that C_s symmetry has been assumed, but even if the symmetry of the ring–NC_2 system is lower then the coupling between the NMe_2 modes and the CN–ring, N–ring stretch, and immediately adjacent ring angle deformation modes, will be little affected. This follows since the relative directions of the distortion vectors are insignificantly altered.

The discrepancy between the observed and calculated frequencies (planar configuration) for the *p*-cyano-compound must be due to inadequacies in the force field. Actually the aromatic and dimethylamino modes are more mixed for the planar case than for model (iii). Any changes in the force field made in order to merge the observed and calculated frequencies would be open to doubt. Nevertheless the main arguments presented for a non-planar configuration, in other than the *p*-nitro-compound, hold. Unfortunately this uncertainty precludes any chance of being more precise as to the dihedral angle.

Of the characteristic aromatic modes listed by Randle and Whiffen[30] for *para*-substituted benzenes the three highest ring modes near 1610, 1580, and 1510 cm^{-1} are easily identified as 1602, 1560, and 1528 cm^{-1} respectively. Other characteristic bands listed by them are observed by us at 1172, 820, and 654 cm^{-1}. The band at 1007 cm^{-1} is surprisingly weak in absorption. The other aromatic modes above 400 cm^{-1}, of which many are of a highly mixed character and involve substituent motions, are in the ranges listed by Garrigou-Lagrange, Lebas, and Josien.[22] The lower-frequency modes are very mixed in character and the interested reader is referred to the potential energy distribution in Table 4 in lieu of further discussion.

Characteristic Frequencies of the Methylamino-group.—As indicated in Table 5 we have noted five characteristic bands in the range 1350—1000 cm^{-1}. If the CH stretching vibrations, the δCH vibrations, and the torsion are excluded, seven modes are expected for a MeNH–X system. The δCNC vibration must be below 500 cm^{-1}. This suggests that the observed bands should be correlated with the methyl rocking modes (degenerate for C_{3v} symmetry), the two CN stretches and the two δNH modes. Previous studies have found the δNH modes to be elusive but Hadzi and Škrbljak[31] have presented evidence for one of these modes to be near 1500 cm^{-1}. They failed to observe the second δNH mode but expressed the belief that it must be below 800 cm^{-1}. If all the bands observed in the present work are genuine fundamentals then the deductions or assumptions of Hadzi and Škrbljak must be modified. Katritzky and Jones[5] located only four characteristic bands in this region, noting only one of the close pair *mC* and *mD*. On the basis of the present evidence we can only note the existence of the extra band and point out the problems.

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[30] R. R. Randle and D. H. Whiffen, ‘ Report on the Molecular Spectroscopy Conference,’ London, 1954, p. 111, published by the Institute of Petroleum, London, 1955.

[31] D. Hadzi and M. Škrbljak, *J. Chem. Soc.*, 1957, 843.