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# Vibrational spectra of isomeric aminobenzonitriles

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Vibrational spectra of benzonitrile, its mono- and di-substituted derivatives have been studied by various workers (Jacobson 1965, Green and Harrison 1976, Joshi *et al* 1987, Aquil and Verma 1982, Rastogi *et al* 1990, 1991). Inspite of a large amount of spectral data available for these molecules, difference in the interpretation of the spectra are still considerable. As the complete vibrational data for three isomeric aminobenzonitriles is not available in literature, we undertook the study of the vibrational spectra of *o*-, *m*- and *p*-aminobenzonitriles.

The spectrally pure samples of *o*-, *m*- and *p*-aminobenzonitriles, hereafter referred to as OAB, MAB and PAB were obtained from M/S Aldrich Chemical Co, USA and used as such without further purification. The Raman spectra of *m*- and *p*-aminobenzonitriles in the solid phase were recorded on a Spex Laser Raman Spectrophotometer (Ramalog) using, for excitation, 514.5 nm of radiation from a 2W Argon ion laser from Spectra Physics. Spectral slit width was 10 $cm^{-1}$ in both the cases but the laser powers were varied from 100 mW to 300 mW depending upon the scattering property of the sample concerned. The detection was made by a thermoelectrically cooled PM tube (HAMMATSU R 995P) operated on PC mode. The compound *o*-aminobenzonitrile is too fluorescent and it was impossible to record its Raman spectra. The IR spectra were recorded on a Perkin-Elmer 577 grating spectrophotometer and Nicolet DX IR spectrophotometer in the 200-4000 $cm^{-1}$ (except for PAB in KBr and nujolmull matrices in which case spectra were recorded in 650-4000 $cm^{-1}$) region.

Figure 1 shows the structures of benzonitrile and *o*-, *m*- and *p*- aminobenzonitrile molecules with classical numbering of the atoms. From the structural point of view the compounds OAB and MAB belong to the point group $C_s$, while PAB to the $C_{2v}$ point group. The 39 normal modes of vibrations will be distributed over the possible species $27a' + 12a''$ in compounds OAB and MAB and $14a_1 + 4a_2 + 13b_2 + 8b_1$ in PAB. The analysis of the bands and the assignment of the

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fundamental frequencies are made on the basis of magnitude and relative intensities of the observed bands and help has been taken from the assignments made by earlier workers in the related molecules. The wavenumbers of the observed fundamental bands in IR and Raman spectra alongwith the proposed assignments are given in Table 1.

*Skeleton vibrations :*

The appearance of a group of four bands in the region 1350-1620 cm$^{-1}$ in the spectra of substituted benzenes represent the two doubly degenerate C—C stretching modes namely, $e_{2g}$ (1595 cm$^{-1}$) and $e_{1u}$ (1485 cm$^{-1}$). It is usually observed that one of the two components of these two frequencies is lowered while the other component retains the energy of the degenerate vibration in benzene. On the basis of this criterion the bands observed at 1592 and 1580 cm$^{-1}$ in OAB, 1606 and 1578 cm$^{-1}$ in MAB and at 1599 and 1520 cm$^{-1}$ in PAB have been assigned as the two components of the $e_{2g}$ vibration of benzene. Similarly the pairs of frequencies 1496 and 1460 cm$^{-1}$ in OAB, 1515 and 1438 cm$^{-1}$ in MAB and 1470 and 1388 cm$^{-1}$ in PAB have been assigned as two components of the $e_{1u}$ (1485 cm$^{-1}$) mode of vibration of benzene.

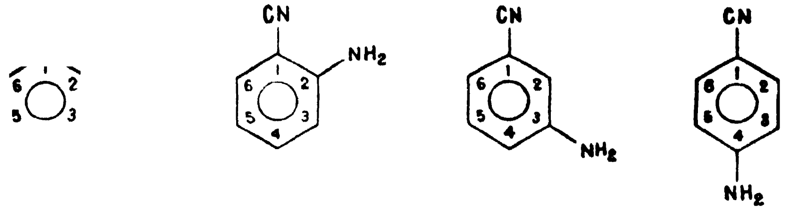

**Figure 1.** Structures of (1) benzonitrile, (2) o-, (3) *m*-, and (4) *p*-benzonitriles.

As pointed out by several workers the C—C ring breathing $a_{1g}$ (995 cm$^{-1}$) and C—C—C trigonal bending $b_{1u}$ (1010 cm$^{-1}$) vibrations of benzene give rise to combined modes in molecules belonging to the reduced symmetry. As a result of this, one of the modified modes is considerably reduced and lies between 700-900 cm$^{-1}$ depending upon the mass and nature of substituent, while the other keeps itself around 1000 cm$^{-1}$. These two vibrations have been identified at 1020 and 860 cm$^{-1}$ in OAB, 1008 and 827 cm$^{-1}$ in MAB and at 1016 and 819 cm$^{-1}$ in PAB. Corresponding to the other planar carbon bending vibration $e_{2g}$ (608 cm$^{-1}$) of benzene, there occurs two vibrations in substituted benzenes, one of which with considerably reduced frequency. These two vibrations have been observed at 582 and 498 cm$^{-1}$ in OAB and at 574 and 463 cm$^{-1}$ in MAB. In the case of PAB, only one vibration could be identified at 475 cm$^{-1}$ in IR and at 490 cm$^{-1}$ in Raman spectrum, while the other vibration could be observed neither in IR nor in Raman spectra.

It has been reported in literature (Varsanyi 1969, 1974) that in all primary aromatic amines, a strong band appears in the region 1250-1360 cm$^{-1}$ and the

**Table I.** Assignment of vibrational frequencies (in $cm^{-1}$) of isomeric aminobenzonitriles.

| Compound | | | | | | | | | | Vib. No. | Assignment |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OAB ($C_s$) Sym. species | IR | | MAB ($C_s$) IR | Raman | PAB ($C_{2v}$) Sym. species | IR | | | Raman | | |
| | KBr | Nujol | CsI | | | KBr | Nujol | CsI | | | |
| $a'$ | 3462 vs | 3460 s | 3484 vs | — | $a_1$ | 3490 w | 3460 m | — | — | — | $NH_2$ asym. stretch |
| $a'$ | 3369 vs | 3367 s | 3375 vs | — | $b_2$ | 3370 w | 3395 s | 3340 s | — | — | $NH_2$ sym. stretch |
| — | 3238 s | — | — | — | — | — | — | — | — | — | $\nu$ (N−H) } associated |
| — | 3228 s | — | 3218 s | — | — | — | — | 3205 s | — | — | $\nu$ (N−H) |
| $a'$ | — | — | 3120 vw | — | $a_1$ | — | 3120 vw | — | — | 20*b* | $\nu$ (C−H) |
| $a'$ | 3080 s | — | 3070 w | — | $a_1$ | — | — | — | — | 2 | $\nu$ (C−H) |
| $a'$ | 3045 s | — | 3058 sh | — | $b_2$ | — | — | 3048 vw | — | 20*a* | $\nu$ (C−H) |
| $a'$ | 2236 vs | 2236 m | 2210 vvs | 2232 s | $a_1$ | 2220 vs | 2235 vs | 2197 vs | 2210 vvs | — | $\nu$ (C≡N) |
| $a'$ | 1634 vvs | 1634 s | 1628 vvs | — | $b_2$ | 1630 sh | 1640 sh | — | 1628 w | — | $NH_2$ scissor |
| $a'$ | — | 1592 m | 1604 vvs | 1606 m | $b_2$ | 1610 vvs | 1617 vs | 1595 vs | 1599 vs | 8*b* | $\nu$ (C−C) |
| $a'$ | 1568 vvs | 1580 m | 1570 sh | 1578 w | $a_1$ | 1515 vs | 1510 w | 1516 m | 1520 w | 8*a* | $\nu$ (C−C) |
| $a'$ | 1496 vvs | 1496 sh | 1515 vs | — | $a_1$ | — | 1470 vs | 1500 m | — | 19*b* | $\nu$ (C−C) |
| $a'$ | 1460 vvs | 1466 vvs | 1438 w | — | $b_2$ | — | 1388 vs | — | — | 19*a* | $\nu$ (C−C) |
| $a'$ | 1346 s | 1358 m | 1332 sh | — | $b_2$ | — | — | — | 1340 vw | 7*b* | $\nu$ (C−$NH_2$) |

Table I. (Contd.)

| Compound | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OAB ($C_s$) Sym. species | IR | | MAB ($C_s$) IR | Raman | PAB ($C_{2v}$) Sym. species | IR | | | Raman | Vib. No. | Assignment |
| | KBr | Nujol | CsI | | | KBr | Nujol | CsI | | | |
| $a'$ | 1316 vs | 1328 s | 1317 vs | 1326 w | $b_2$ | 1322 vs | 1320 vs | 1319 vvs | 1314 vw | 14 | ν (C – C) |
| $a'$ | 1268 vvs | 1280s | 1300 sh | 1295 m | $b_2$ | — | — | — | — | 3 | β (C – H) |
| $a'$ | 1226 s | 1220 m | — | — | $a_1$ | 1220 m | 1222 m | 1217 m | 1220 m | 9*a* | β (C – H) |
| $a'$ | 1208 s | 1202 sh | 1210 m | -- | $b_2$ | — | — | — | 1196 vw | 9*b* | β (C – H) |
| $a'$ | 1172 s | 1172 s | 1175 vvs | 1169 vw | $a_1$ | 1182 vs | 1184 vs | 1177 vs | 1173 vs | 13 | ν (C – CN) |
| $a'$ | 1154 s | 1136 s | 1136 m | — | $b_2$ | 1145 s | 1148 s | 1140 s | 1138 w | 15 | β (C – H) |
| $a''$ | 1068 m | 1064 m | — | — | $b_1$ | 1076 vw | — | — | — | — | $NH_2$ twisting |
| $a'$ | 1020 m | 1012 w | 1008 w | 991 s | $a_1$ | 1016 m | — | 1012 m | — | 12 | φ (C – C – C) |
| $a''$ | 968 m | 960 w | 966 w | — | $b_1$ | 978 m | 980 m | 970 m | 976 vw | 5 | γ (C – H) |
| $a''$ | 912 w | 906 w | 943 w | 935 w | $b_1$ | 957 m | — | 948 m | — | 17*b* | γ (C – H) |
| $a''$ | 878 m | 874 sh | 835 vs | — | $a_2$ | 845 vs | 846 vs | 832 vvs | 842 s | 10*a* | γ (C – H) |
| $a'$ | 860 s | 858 w | 827 s | 795 vw | $a_1$ | — | — | — | 819 sh | 1 | ν (C – C) (ring breath) |
| $a''$ | 750 vvs | 750 s | — | 738 sh | $b_1$ | 734 w | 732 vw | 742 w | — | 10*b* | γ (C – H) |

**Table I.** (Contd.)

| Compound | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OAB ($C_s$) Sym. species | IR KBr | IR Nujol | MAB ($C_s$) IR CsI | Raman | PAB ($C_{2v}$) Sym. species | IR KBr | IR Nujol | IR CsI | Raman | Vib. No. | Assignment |
| $a''$ | 738 sh | 730 sh | 712 w | 720 m | $b_1$ | 715 s | 706 m | 717 w | 702 w | 4 | δ (C – C – C) |
| $a'$ | — | 620 w | 693 s | — | $a_1$ | 684 vw | 680 w | 682 vs | 651 m | — | $NH_2$ wagging |
| $a'$ | 582 m | 576 vw | — | 574 vw | $b_2$ | — | — | — | — | 6*b* | φ (C – C – C) |
| $a'$ | 564 m | 561 vw | 538 vs | 534 w | $b_2$ | — | — | 535 vs | — | — | β (C≡N) |
| $a'$ | 498 vvs | 498 m | 470 w | 463 w | $a_1$ | — | — | 475 vw | 490 vw | 6*a* | φ (C – C – C) |
| $a''$ | 410 vs | — | — | — | $a_2$ | — | — | — | 420 w | 16*a* | δ (C – C – C) |
| $a'$ | 380 s | — | 380 m | 393 w | $a_1$ | — | — | 372 sh | 389 vw | 18*a* | β (C – $NH_2$) |
| $a'$ | 278 sh | 278 vvs | 336 m | — | $b_2$ | — | — | 330 vs | — | 18*b* | β (C – CN) |
| $a''$ | 246 sh | 242 vvs | — | 245 vw | $b_1$ | — | — | 250 sh | 265 vw | — | γ (C≡N) |
| $a''$ | 233 sh | 230 vvs | — | — | $a_2$ | — | — | — | 240 sh | 17*a* | γ (C – $NH_2$) |
| $a''$ | 222 vs | 224 s | — | — | $b_1$ | — | — | 230 sh | — | 11 | γ (C – CN) |
| $a''$ | 212 vvs | 215 s | — | — | $a_2$ | — | — | — | — | — | $NH_2$ torsion |
| $a''$ | — | — | — | 170 s | $b_1$ | — | — | — | 170 w | 16*b* | δ (C – C – C) |

v = very, s = strong, w = weak, m = medium, sh = shoulder, β and φ = in-plane bending, γ and δ = out-of-plane bending, asym = asymmetric, sym = symmetric.

intensity of this band appears to be variable and probably it is associated with substituent and has been assigned to C – $NH_2$ stretching vibration. Goel *et al* (1978) have assigned the strong bands observed at 1312 and 1302 $cm^{-1}$ in 2,3- and 3,5-dichloro anilines respectively to this mode of vibration. In the present case the bands observed at 1346, 1332 and 1340 $cm^{-1}$ in OAB, MAB and PAB respectively have been assigned to the C – $NH_2$ stretching vibration.

Green (1961) and Jacobson (1965) have assigned a band at 1192 $cm^{-1}$ to the C – CN stretching mode. The strong bands observed at 1172, 1175 and 1182 $cm^{-1}$ in the IR spectra of OAB, MAB and PAB respectively have been assigned to this mode in accordance with the assignments proposed by Singh (1969) in *o*- and *m*-fluoro benzonitriles and by Sinha and Chatterjee (1976a, 1976b) in *m*- and *p*-methyl benzonitriles respectively. In Raman spectra also a strong band at 1173 $cm^{-1}$ in PAB and a weak band at 1169 $cm^{-1}$ in MAB has been observed corresponding to this mode of vibration.

### *CN group vibrations :*

Saito *et al* (1981) have suggested that a band at 2223 $cm^{-1}$ (a calculated value) in benzonitrile is highly localised at a C – C≡N part and is the band characteristic of the C≡N stretching vibration. They have also shown by a study on several *m*- and *p*-benzonitriles that the position of this band is not affected much by the kind of substituents. In the present study, the strong band at 2236 $cm^{-1}$, 2232 $cm^{-1}$, 2210 $cm^{-1}$ in the three molecules respectively have been assigned to this mode of vibration. The bands observed at 564, 538 and 535 $cm^{-1}$ have been assigned to the in-plane C≡N deformation mode in accordance with the assignments proposed by Kuwae and Machida (1979) for deuterated benzonitriles. The C≡N out-of-plane bending vibrations have been identified at 246, 245 and 250 $cm^{-1}$ respectively in these molecules.

### *$NH_2$ group vibrations :*

The $NH_2$ group involves the symmetric and asymmetric N – H stretching vibrations. In the case of nearly all the primary aromatic amines, two bands (Bell 1962, Ellis 1928) occur in the region 3300-3500 $cm^{-1}$. The bands around 3500 $cm^{-1}$ have been assigned by a large number of workers as asymmetric and that appearing around 3400 $cm^{-1}$ as symmetric stretching vibration. Both of these are subject to small changes with alteration of polarity of the solvent and to rather large changes in concentrated solutions in which intermolecular association can occur. Intramolecular bonding also lowers these frequencies. In view of these considerations, the strong IR bands observed at 3462 and 3369 $cm^{-1}$ in OAB, 3484 and 3375 $cm^{-1}$ in MAB and at 3490 and 3370 $cm^{-1}$ in PAB have been assigned to the N – H ($NH_2$) asymmetric and symmetric stretching vibrations respectively. It has been pointed out by Bellamy (1959) that in N-octamide in $CHCl_3$ solution, the $NH_2$ free absorption occurs at 3530 and 3415 $cm^{-1}$, but it also shows additional bands at 3498, 3345, 3300 and 3182 $cm^{-1}$, suggesting different types of simultaneous association of free and bonded NH bonds. Therefore, the additional bands observed at 3228 and 3238 $cm^{-1}$ in the IR spectra of OAB may be assigned to such $NH_2$ bonded absorption. Only one band at 3218 $cm^{-1}$ in MAB and at 3205 $cm^{-1}$ in PAB could be observed corresponding to such $NH_2$ bonded stretching vibration.

The $NH_2$ scissoring freqeuecy has been suggested to lie in the region 1590-1650 $cm^{-1}$ in nearly all primary aromatic amines (Rao 1963). The bands observed at 1634, 1628 and 1628 $cm^{-1}$ in OAB, MAB and PAB respectively have been assigned to this mode, which find support from literature values in the case of various substituted anilines (Singh *et al* 1966).

The $NH_2$ wagging vibration is analogous to the inversion mode of ammonia (Albert and Nelson 1945). The infrared band corresponding to inversion mode of ammonia is observed at 950 $cm^{-1}$ (mean of two bands). In methyl ammine (Cleaves and Phyler 1939), this bands is located at 783 $cm^{-1}$ and in aniline at 660 $cm^{-1}$. In the present investigation this vibration is observed at 620, 693 and 682 $cm^{-1}$ in OAB, MAB and PAB respectively. Sharma and Dwivedi (1976) and Ansari and Verma (1978) have also reported the $NH_2$ wagging vibration in this frequency range.

The assignments of the other vibrations in the compounds studied are presented in Table 1.

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