

Electronic Spectra of *o*-, *m*- & *p*-Aminophenols & Their Anions & Cations

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The electronic spectra of *o*-, *m*- and *p*-aminophenols have been studied both experimentally (absorption as well as emission) and theoretically. The absorption bands have been characterised and compared with theoretical results. The pH dependence of the spectra has been studied and the results are explained in terms of the species $\text{HOC}_6\text{H}_4\text{NH}_3^+$ and $^-\text{OC}_6\text{H}_4\text{NH}_2$. All the aminophenols give rise to fluorescence and phosphorescence in neutral and acidic media. However, no fluorescence is observed in alkaline medium. The charge density calculations in the ground and excited states are used to explain solvent shifts.

CURRENTLY, considerable interest¹⁻⁶ is being evinced in the photochemistry and photobiology of substituted benzenes. However, for understanding their photochemical behaviour it is imperative that electronic states of these molecules are well characterized. There have been only a few studies on the spectra of these molecules and the bands have not been properly characterised. The present work is a part of our systematic study^{7,8} on the spectra of disubstituted benzenes. Most of the work on disubstituted benzenes has so far been concentrated⁹⁻¹² on molecules of the type D-Ph-A, where one of the substituents is an electron donor (D) and the other an electron acceptor (A). The electronic spectra of a number of other disubstituted benzenes have also been studied¹³ but our main aim here is to understand the electronic spectra of molecules of the type D-Ph-D and A-Ph-A. In aminophenols both the substituents are donor groups. The donor character of —OH is enhanced when it is converted into —O⁻ but that of —NH₂ group is decreased when it is converted into —NH₃⁺ group.

Materials and Methods

Purification of aminophenols — Solutions of aminophenols (BDH, Analar) in water were treated with activated charcoal, filtered and kept aside to obtain aminophenols as crystalline solids. These were further purified by repeated crystallization in the dark from ethanol or ethanol-water mixtures until the absorbance spectra were reproducible and melting points, i.e. 443, 395, 457 K for *o*-, *m*-, *p*-isomers respectively agreed with the literature values.

Spectral measurements — Absorption spectra were taken on a Carl-Zeiss UV-VIS spectrophotometer. The fluorescence and phosphorescence measurements were made on a Perkin-Elmer MPF-44B spectrofluorimeter.

Semiempirical molecular orbital calculations — The Del Bene and Jaffe^{14,15} CNDO/S-CI program¹⁶ was used for the molecular orbital calculations in order to characterise the electronic states.

Standard bond lengths and bond angles were used in these calculations. Excited states were generated from the ground state occupied and virtual orbitals through a configuration interaction procedure between the sixty lowest energy singly excited states. The molecular axes and number of atoms are designated in Fig. 1 for aminophenols and the same set of axes have been used for the corresponding anions and cations.

The electron densities on various atoms in the excited state *j* are given by :

$$j\rho_A^* = \rho_A^0 + \sum_m \sum_u \frac{C_{jm}^u}{C_j} (C_j^2 - C_i^2)$$

in which ρ_A^0 is the ground state electron density on atom A and C_{jm} being the coefficient of the *m*th configuration contributing to the *j*th state. C_j and C_i are the orbital coefficients of the final and initial

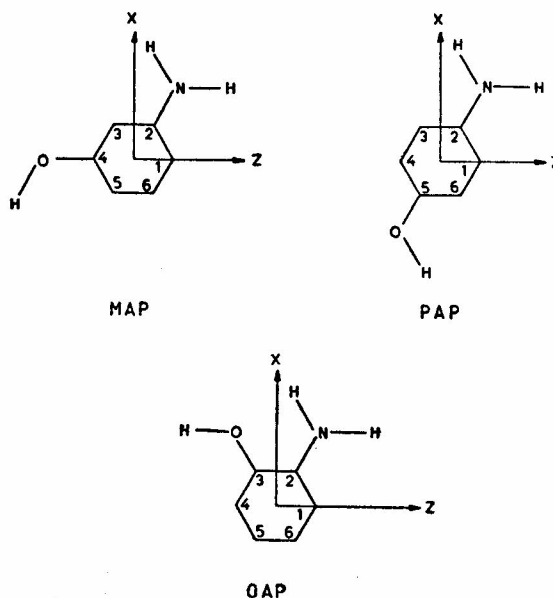


Fig. 1 — Designation of axes for CNDO/S calculation. [y-Axis is out of plane]

MO involved in the m th configuration. The characterization of different states has been done on the basis of configurational analysis. All calculations have been done on DEC-2050 machine.

Results and Discussion

The MOs involved in the low energy transitions together with the orbital description for all the aminophenols and corresponding anions and cations are given in Table 1. The nature of the MOs are described by giving the symbols π , n etc. The different monoexcited configurations which contribute to some of the low frequency transitions are given in Table 2. The theoretical (after configuration interaction) and experimental results in different solvents for the singlet manifold along with the oscillator strengths and calculated degree of polarization are also given in Table 2. The agreement between the experimental and theoretical values of transition energies and other quantities seem to confirm that our assignments are correct.

The electron density calculations indicate that all the singlet excited states are of intramolecular charge

transfer type; the charge is transferred from the substituents to the ring. Thus the electron density on oxygen of the hydroxyl group and nitrogen of the amino group decreases, i.e. it becomes positive relative to the ground state. In other words the —OH and —NH₂ groups become more acidic in the excited states, a fact consistent with the experimental results^{17,18}. The decrease in electron density on oxygen of hydroxyl group and nitrogen of the amino group for various excited state is given in Table 3.

The absorption spectra of aminophenols, and of their anions and cations, recorded in different solvents are given in Table 2. It has been found on the basis of charge density calculations that the excited states are less polar than the ground state. Thus the excited state is relatively destabilised with respect to the ground state and hence there is a blue shift of the absorption bands with increasing polarity of the solvent. The spectra of aminophenol in the alkaline medium is due to aminophenolate ions, which show three bands. A comparison of the experimental and the theoretical results for aminophenates,

TABLE 1 — ENERGY AND APPROXIMATE FORM OF MO USED TO CONSTRUCT THE EXCITED STATE CONFIGURATIONS OF AMINOPHENOLS AMINOPHENATES AND THE CORRESPONDING CATIONS

| Molecular orbital | Energy of MO/eV | Type† | Energy of MO/eV | Type † | Energy of MO/eV | Type† |
|------------------------------------|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| <i>o</i>-AMINOPHENOL | | | | | | |
| 24 | 1.918 | π_r^* | 1.922 | π_r^* | 1.852 | π_r^* |
| 23 | -0.255 | $\pi^*_{C_2C_3C_5C_6}$ | -0.267 | $\pi^*_{C_1C_2C_4C_6}$ | -0.298 | π_r^* |
| 22 | -0.442 | π_r^* | -0.399 | π_r^* | -0.562 | $\pi^*_{C_1C_3C_4C_6}$ |
| 21 | -8.677 | π_{del} | -8.865 | π_{del} | -8.736 | π_{del} |
| 20 | -9.533 | π_{del} | -9.406 | π_{del} | -9.949 | $\pi_{C_1C_3C_4C_6}$ |
| 19 | -11.994 | σ | -11.954 | $\pi + \sigma_{del}$ | -11.906 | π_{del} |
| 18 | -12.312 | $\pi_{C_4C_5C_6N}$ | -12.014 | $\pi + \sigma_{del}$ | -12.020 | π_{del} |
| 17 | -12.592 | σ | -12.744 | σ | -13.067 | σ |
| <i>o</i>-AMINOPHENATE | | | | | | |
| 25 | 7.441 | σ^* | 7.444 | σ^* | 7.274 | σ^* |
| 24 | 6.078 | π_r^*O | 6.151 | π_r^*O | 5.976 | π_r^*O |
| 23 | 3.952 | π_r^*O | 3.999 | π_r^*O | 3.833 | π_r^*O |
| 22 | 3.447 | $\pi^*_{C_1C_2C_4C_6}$ | 3.439 | $\pi^*_{C_2C_3C_5C_6}$ | 3.186 | $\pi^*_{C_1C_3C_4C_6}$ |
| 21 | -3.528 | π_{del} | -3.726 | π_rO | -3.680 | π_rO |
| 20 | -4.903 | n_O | -4.913 | n_O | -4.875 | n_O |
| 19 | -5.541 | π_{del} | -5.514 | π_{del} | -6.239 | $\pi_{C_1C_2C_4C_6}$ |
| 18 | -7.485 | π_{del} | -7.245 | π_{del} | -6.481 | π_{del} |
| 17 | -8.183 | σ | -8.255 | σ | -8.307 | σ |
| <i>o</i>-AMINOPHENOL CATION | | | | | | |
| 24 | -1.709 | π_r^* | -1.704 | π_r^* | -1.705 | π_r^* |
| 23 | -3.903 | π_r^* | -3.872 | $\pi^*_{C_2C_3C_5C_6}$ | -3.969 | $\pi^*_{C_2C_3C_5C_6}$ |
| 22 | -4.331 | π_r^* | -4.367 | π_r^* | -4.252 | π_r^* |
| 21 | -12.797 | π_rO | -12.639 | π_rO | -12.732 | π_rO |
| 20 | -13.548 | π_r | -13.499 | $\pi_{C_1C_2C_4C_6}$ | -13.393 | $\pi_{C_2C_3C_5C_6}$ |
| 19 | -15.704 | σ | -15.592 | σ | -15.381 | σ |
| 18 | -16.794 | π_{del} | -15.456 | σ | -16.716 | π_{del} |
| <i>m</i>-AMINOPHENOL | | | | | | |
| 24 | 1.922 | π_r^* | 1.922 | π_r^* | 1.852 | π_r^* |
| 23 | -0.267 | $\pi^*_{C_1C_2C_4C_6}$ | -0.267 | $\pi^*_{C_1C_2C_4C_6}$ | -0.298 | π_r^* |
| 22 | -0.399 | π_r^* | -0.399 | π_r^* | -0.562 | $\pi^*_{C_1C_3C_4C_6}$ |
| 21 | -8.865 | π_{del} | -8.865 | π_{del} | -8.736 | π_{del} |
| 20 | -9.406 | π_{del} | -9.406 | π_{del} | -9.949 | $\pi_{C_1C_3C_4C_6}$ |
| 19 | -11.954 | $\pi + \sigma_{del}$ | -11.954 | $\pi + \sigma_{del}$ | -11.906 | π_{del} |
| 18 | -12.014 | $\pi + \sigma_{del}$ | -12.014 | $\pi + \sigma_{del}$ | -12.020 | π_{del} |
| 17 | -12.744 | σ | -12.744 | σ | -13.067 | σ |
| <i>m</i>-AMINOPHENATE | | | | | | |
| 25 | 7.444 | σ^* | 7.444 | σ^* | 7.274 | σ^* |
| 24 | 6.151 | π_r^*O | 6.151 | π_r^*O | 5.976 | π_r^*O |
| 23 | 3.999 | π_r^*O | 3.999 | π_r^*O | 3.833 | π_r^*O |
| 22 | 3.439 | $\pi^*_{C_2C_3C_5C_6}$ | 3.439 | $\pi^*_{C_2C_3C_5C_6}$ | 3.186 | $\pi^*_{C_1C_3C_4C_6}$ |
| 21 | -3.726 | π_rO | -3.726 | π_rO | -3.680 | π_rO |
| 20 | -4.913 | n_O | -4.913 | n_O | -4.875 | n_O |
| 19 | -5.514 | π_{del} | -5.514 | π_{del} | -6.239 | $\pi_{C_1C_2C_4C_6}$ |
| 18 | -7.245 | π_{del} | -7.245 | π_{del} | -6.481 | π_{del} |
| 17 | -8.255 | σ | -8.255 | σ | -8.307 | σ |
| <i>m</i>-AMINOPHENOL CATION | | | | | | |
| 24 | -1.704 | π_r^* | -1.704 | π_r^* | -1.705 | π_r^* |
| 23 | -3.872 | $\pi^*_{C_2C_3C_5C_6}$ | -3.872 | $\pi^*_{C_2C_3C_5C_6}$ | -3.969 | $\pi^*_{C_2C_3C_5C_6}$ |
| 22 | -4.367 | π_r^* | -4.367 | π_r^* | -4.252 | π_r^* |
| 21 | -12.639 | π_rO | -12.639 | π_rO | -12.732 | π_rO |
| 20 | -13.499 | π_r | -13.499 | $\pi_{C_1C_2C_4C_6}$ | -13.393 | $\pi_{C_2C_3C_5C_6}$ |
| 19 | -15.592 | σ | -15.592 | σ | -15.381 | σ |
| 18 | -15.456 | π_{del} | -15.456 | σ | -16.716 | π_{del} |
| <i>p</i>-AMINOPHENOL | | | | | | |
| 24 | 1.852 | π_r^* | 1.852 | π_r^* | 1.852 | π_r^* |
| 23 | -0.298 | π_r^* | -0.298 | π_r^* | -0.298 | π_r^* |
| 22 | -0.562 | $\pi^*_{C_1C_3C_4C_6}$ | -0.562 | π_r^* | -0.562 | $\pi^*_{C_1C_3C_4C_6}$ |
| 21 | -8.736 | π_{del} | -8.736 | π_{del} | -8.736 | π_{del} |
| 20 | -9.949 | $\pi_{C_1C_3C_4C_6}$ | -9.949 | π_{del} | -9.949 | $\pi_{C_1C_3C_4C_6}$ |
| 19 | -11.906 | π_{del} | -11.906 | $\pi + \sigma_{del}$ | -11.906 | π_{del} |
| 18 | -12.020 | π_{del} | -12.020 | $\pi + \sigma_{del}$ | -12.020 | π_{del} |
| 17 | -13.067 | σ | -13.067 | σ | -13.067 | σ |
| <i>p</i>-AMINOPHENATE | | | | | | |
| 25 | 7.274 | σ^* | 7.274 | σ^* | 7.274 | σ^* |
| 24 | 5.976 | π_r^*O | 5.976 | π_r^*O | 5.976 | π_r^*O |
| 23 | 3.833 | π_r^*O | 3.833 | π_r^*O | 3.833 | π_r^*O |
| 22 | 3.186 | $\pi^*_{C_1C_3C_4C_6}$ | 3.186 | $\pi^*_{C_2C_3C_5C_6}$ | 3.186 | $\pi^*_{C_1C_3C_4C_6}$ |
| 21 | -3.680 | π_rO | -3.680 | π_rO | -3.680 | π_rO |
| 20 | -4.875 | n_O | -4.875 | n_O | -4.875 | n_O |
| 19 | -6.239 | π_{del} | -6.239 | π_{del} | -6.239 | $\pi_{C_1C_2C_4C_6}$ |
| 18 | -6.481 | π_{del} | -6.481 | π_{del} | -6.481 | π_{del} |
| 17 | -8.307 | σ | -8.307 | σ | -8.307 | σ |
| <i>p</i>-AMINOPHENOL CATION | | | | | | |
| 24 | -1.705 | π_r^* | -1.705 | π_r^* | -1.705 | π_r^* |
| 23 | -3.969 | $\pi^*_{C_2C_3C_5C_6}$ | -3.969 | $\pi^*_{C_2C_3C_5C_6}$ | -3.969 | $\pi^*_{C_2C_3C_5C_6}$ |
| 22 | -4.252 | π_r^* | -4.252 | π_r^* | -4.252 | π_r^* |
| 21 | -12.732 | π_rO | -12.732 | π_rO | -12.732 | π_rO |
| 20 | -13.393 | $\pi_{C_2C_3C_5C_6}$ | -13.393 | $\pi_{C_1C_2C_4C_6}$ | -13.393 | $\pi_{C_2C_3C_5C_6}$ |
| 19 | -15.381 | σ | -15.381 | σ | -15.381 | σ |
| 18 | -16.716 | π_{del} | -16.716 | σ | -16.716 | π_{del} |

†Subscript r means that the orbital is localized on the benzene ring only; del means that the orbital is delocalized over the entire molecule and X_1, Y_1, Z_k .. etc. mean that the orbital is mainly delocalized over the atoms X_1, Y_1, Z_k .

TABLE 2 — ELECTRONIC SPECTRA OF AMINOPHENOLS, AMINOPHENATES AND AMINOPHENOL CATIONS

| Experimental | | Theoretical | | Type | Polarization $\theta^\dagger/\text{deg.}$ | Composition | |
|-----------------------------|--------------|------------------------|--------|------------|--|------------------------------|---------------|
| λ_{max} (nm) | f | λ_{max} | f | | | $\theta^\dagger/\text{deg.}$ | configuration |
| <i>o</i> -AMINOPHENOL | | | | | | | |
| 291 (Ethanol) | 0.0636 | 239.9(S_1) | 0.0217 | $\pi\pi^*$ | 267.5 | 69 | 21→22 |
| 286 (Water) | 0.0404 | | | | | 28 | 20→23 |
| 283 (Cyclohexane)† | — | | | | | | |
| 234 (Ethanol) | 0.1951 | 238.2(S_2) | 0.0785 | $\pi\pi^*$ | 342.4 | 83 | 21→23 |
| 231 (Water) | 0.1113 | | | | | 14 | 20→22 |
| 260 (Cyclohexane)† | — | | | | | | |
| 212 (Ethanol) | Intense band | 200.2(S_3) | 0.5148 | $\pi\pi^*$ | 269.8 | 29 | 21→22 |
| | | | | | | 67 | 20→23 |
| 203 (Water) | Intense band | 198.4(S_4) | 0.3306 | $\pi\pi^*$ | 186.6 | 14 | 21→23 |
| | | | | | | 83 | 20→22 |
| <i>m</i> -AMINOPHENOL | | | | | | | |
| 287 (Ethanol) | 0.0279 | 286.4(S_1) | 0.0095 | $\pi\pi^*$ | 331.3 | 61 | 21→22 |
| 286 (Water) | 0.0098 | | | | | 5 | 20→23 |
| 286 (Cyclohexane)† | — | | | | | 30 | 21→23 |
| 234 (Ethanol) | 0.1866 | 231.6(S_2) | 0.0593 | $\pi\pi^*$ | 263.8 | 34 | 21→22 |
| 233 (Water) | 0.1003 | | | | | 61 | 21→23 |
| 208 (Ethanol) | Intense band | 202.5(S_3) | 0.5469 | $\pi\pi^*$ | 329.0 | 72 | 20→23 |
| | | | | | | 23 | 20→22 |
| 202 (Water) | Intense band | 200.4(S_4) | 0.3356 | $\pi\pi^*$ | 55.1 | 21 | 20→23 |
| | | | | | | 74 | 20→22 |
| | | 192.6(S_5) | 0.0024 | $\pi\pi^*$ | 45.0 | 6 | 19→23 |
| | | | | | | 88 | 19→22 |
| <i>p</i> -AMINOPHENOL | | | | | | | |
| 302 (Ethanol) | 0.0276 | 289.3(S_1) | 0.0264 | $\pi\pi^*$ | 29.0 | 76 | 21→22 |
| 301 (Water) | 0.0249 | | | | | 23 | 20→23 |
| 312 (Cyclohexane)† | — | | | | | | |
| 234 (Ethanol) | 0.1693 | 234.6(S_2) | 0.1641 | $\pi\pi^*$ | 299.8 | 90 | 21→23 |
| 233 (Water) | 0.1244 | | | | | 7 | 18→22 |
| 210 (Ethanol) | 0.0540 | 192.5(S_3) | 0.3363 | $\pi\pi^*$ | 26.6 | 25 | 21→22 |
| | | | | | | 71 | 20→23 |
| 200 (Water) | Intense band | 191.6(S_4) | 0.0080 | $\pi\pi^*$ | 26.7 | 9 | 21→23 |
| | | | | | | 88 | 18→22 |
| | | 189.4(S_5) | 0.4512 | $\pi\pi^*$ | 116.2 | 94 | 20→22 |
| <i>o</i> -AMINOPHENATE | | | | | | | |
| 300 (Ethanol) | 0.0808 | 354.9(S_1) | 0.0009 | $n\pi^*$ | — | 92 | 20→23 |
| 298 (Water) | 0.0542 | 346.9(S_2) | 0.0656 | $\pi\pi^*$ | 314.4 | 72 | 21→22 |
| | | 284.6(S_3) | 0.0168 | $n\pi^*$ | 52.3 | 17 | 21→25 |
| | | | | | | 87 | 20→22 |
| | | | | | | 9 | 21→23 |
| 244 (Ethanol) | 0.1665 | 278.5(S_4) | 0.1746 | $\pi\pi^*$ | 50.0 | 83 | 21→23 |
| 245 (Water) | 0.0919 | | | | | 10 | 20→22 |
| 219 (Ethanol) | 0.2683 | 212.9(S_5) | 0.0965 | $\pi\pi^*$ | 20.9 | 25 | 21→22 |
| | | | | | | 45 | 21→25 |
| | | | | | | 20 | 17→22 |
| 214 (Water) | 0.1331 | 208.7(S_6) | 0.1537 | mixed | 278.8 | 34 | 20→24 |
| | | | | | | 44 | 21→24 |
| | | | | | | 20 | 17→22 |
| | | 202.6(S_7) | 0.3006 | $\pi\pi^*$ | 253.3 | 7 | 21→23 |
| | | | | | | 25 | 20→24 |
| | | | | | | 64 | 19→22 |
| <i>m</i> -AMINOPHENATE | | | | | | | |
| 294 (Ethanol) | 0.0411 | 355.9(S_1) | 0 | $n\pi^*$ | — | 92 | 20→23 |
| 293 (Water) | 0.0118 | 339.6(S_2) | 0.0485 | $\pi\pi^*$ | 278.0 | 69 | 21→22 |
| | | | | | | 15 | 21→25 |
| | | | | | | 12 | 17→22 |
| | | 277.7(S_3) | 0.0003 | $\pi\pi^*$ | — | 96 | 20→22 |
| 240 (Ethanol) | 0.1949 | 266.7(S_4) | 0.2083 | $\pi\pi^*$ | 2.7 | 92 | 21→23 |
| 242 (Water) | 0.0968 | 214.6(S_5) | 0.1159 | mixed | 221.9 | 29 | 21→22 |
| | | | | | | 33 | 21→25 |
| | | | | | | 30 | 17→22 |
| 222 (Ethanol) | 0.2376 | 210.4(S_6) | 0.3316 | mixed | 332.8 | 6 | 20→23 |
| 210 (Water) | Intense band | | | | | 53 | 20→24 |
| | | | | | | 29 | 19→23 |
| | | 196.1(S_7) | 0.0665 | mixed | 331.5 | 7 | 21→23 |
| | | | | | | 25 | 20→24 |
| | | | | | | 41 | 19→23 |
| | | | | | | 20 | 19→22 |

(Contd.)

TABLE 2 — (Contd.)

| Experimental | | Theoretical | | Type | Polarization θ _‡ /deg. | % Composition configuration | |
|------------------------------|--------|------------------------|--------|-------|--------------------------------------|--------------------------------|-------|
| λ _{max} (nm) | f | λ _{max} | f | | | | |
| <i>p</i> -AMINOPHENATE | | | | | | | |
| 314 (Ethanol) | 0.0427 | 354.4(S ₁) | 0.0551 | ππ* | 30.0 | 94 | 21→22 |
| 310 (Water) | 0.0933 | 326.1(S ₂) | 0 | ππ* | — | 98 | 20→23 |
| | | 289.7(S ₃) | 0 | ππ* | — | 74 | 20→22 |
| | | | | | | 13 | 19→22 |
| 245 (Ethanol) | 0.2302 | 275.7(S ₁) | 0.2634 | ππ* | 300.0 | 96 | 21→23 |
| 258 (Water) | 0.3074 | | | | | | |
| 217 (Ethanol) | 0.1072 | 216.1(S ₁) | 0.0014 | ππ* | 29.6 | 85 | 21→24 |
| 208 (Water) | 0.2216 | 208.0(S ₁) | 0.0662 | mixed | 120.0 | 11 | 19→23 |
| | | | | | | 26 | 20→22 |
| | | | | | | 35 | 19→22 |
| | | | | | | 30 | 17→22 |
| | | 190.4(S ₁) | 0.0232 | ππ* | 120.0 | 67 | 21→24 |
| <i>o</i> -AMINOPHENOL CATION | | | | | | | |
| 276 | 0.0318 | 276.6(S ₁) | 0.0282 | ππ* | 70.3 | 71 | 21→22 |
| 217 | 0.0789 | | | | | 27 | 19→22 |
| | | 221.8(S ₁) | 0.0407 | ππ* | 113.6 | 69 | 21→23 |
| | | | | | | 26 | 20→22 |
| | | | | | | 5 | 19→22 |
| 209 | 0.1400 | 195.1(S ₁) | 0.0002 | σπ* | — | 29 | 21→22 |
| | | | | | | 64 | 19→22 |
| | | 192.0(S ₁) | 0.5218 | ππ* | 136.9 | 29 | 21→23 |
| | | | | | | 67 | 20→22 |
| | | 188.3(S ₁) | 0.4664 | ππ* | 42.5 | 90 | 20→23 |
| | | | | | | 8 | 19→23 |
| <i>m</i> -AMINOPHENOL CATION | | | | | | | |
| 273 | 0.0680 | 281.1(S ₁) | 0.0261 | ππ* | 312.6 | 64 | 21→22 |
| | | | | | | 14 | 21→23 |
| | | | | | | 20 | 19→22 |
| 219 | 0.0786 | 228.4(S ₁) | 0.0655 | ππ* | 262.5 | 7 | 21→22 |
| | | | | | | 62 | 21→23 |
| | | | | | | 29 | 20→23 |
| 212 | 0.0882 | 195.2(S ₁) | 0.0269 | ππ* | 26.5 | 5 | 21→22 |
| | | | | | | 25 | 21→23 |
| | | | | | | 58 | 20→23 |
| | | 194.6(S ₁) | 0.5044 | σπ* | 28.1 | 23 | 21→22 |
| | | | | | | 72 | 19→22 |
| | | 187.9(S ₁) | 0.4431 | ππ* | 293.9 | 85 | 20→22 |
| | | | | | | 4 | 20→23 |
| <i>p</i> -AMINOPHENOL CATION | | | | | | | |
| 273 | 0.0214 | 273.6(S ₁) | 0.0017 | mixed | 267.0 | 53 | 21→23 |
| | | | | | | 42 | 19→22 |
| 220 | 0.0752 | 233.7(S ₁) | 0.1274 | ππ* | 0.0 | 86 | 21→22 |
| | | | | | | 12 | 19→23 |
| 210 | 0.0871 | 202.7(S ₁) | 0.0002 | mixed | — | 41 | 21→23 |
| | | | | | | 58 | 19→22 |
| | | 195.4(S ₁) | 0.4449 | ππ* | 270.0 | 96 | 20→22 |
| | | 190.9(S ₁) | 0.0003 | σπ* | — | 12 | 21→22 |
| | | | | | | 86 | 19→23 |
| | | 185.9(S ₁) | 0.5226 | ππ* | 180.0 | 98 | 20→23 |

†Due to poor solubility of aminophenols in cyclohexane the oscillator strengths have not been calculated and the λ_{max} values are obtained from excitation spectra.

‡Angle between transition vector, V and the Z-axis.

TABLE 3 — GROUND AND EXCITED STATE ELECTRON DENSITIES IN AMINOPHENOLS

| Atom | Ground state | 1st π→π* | 2nd π→π* | 3rd π→π* |
|-----------------------|--------------|----------|----------|----------|
| <i>o</i> -AMINOPHENOL | | | | |
| O | 6.279 | 6.163 | 6.169 | 6.189 |
| N | 5.238 | 5.109 | 5.097 | 6.169 |
| <i>m</i> -AMINOPHENOL | | | | |
| O | 6.226 | 6.183 | 6.189 | 6.185 |
| N | 5.236 | 5.120 | 5.118 | 5.193 |
| <i>p</i> -AMINOPHENOL | | | | |
| O | 6.258 | 6.207 | 6.203 | 6.252 |
| N | 5.234 | 5.113 | 5.106 | 5.203 |

reveals that the first experimental band corresponds to theoretical transitions S₀ to S₁, S₂ and S₃ and the second experimental band corresponds to the theoretical transition S₀→S₄ in all the aminophenates. The electron density calculations predict these bands to be of charge transfer type. The charge being transferred from —O⁻ (with some contribution from —NH₂ group) to the ring.

The next theoretical transitions S₀→S₅—S₇ seem to form the third experimental band. The agreement in these cases is not so good as for the neutral molecules. This may be attributed to the

TABLE 4 — EMISSION SPECTRA OF AMINOPHENOLS IN DIFFERENT SOLVENTS

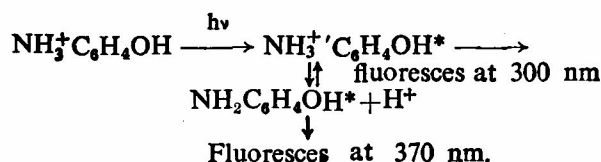
| Molecule | Fluorescence(nm) | | | | | | Phosphorescence(nm) | | |
|------------------------------|------------------|----------------|----------------|----------------|----------------|----------------|---------------------|----------------|----------------|
| | Cyclohexane | | Water | | Ethanol | | Ethanol | | EPA |
| | λ_{ex} | λ_{em} | λ_{ex} | λ_{em} | λ_{ex} | λ_{em} | λ_{ex} | λ_{em} | λ_{em} |
| <i>o</i> -Aminophenol | 283 | 330 | 286 | 338-344 | 291 | 336 | 291 | 440 | 424 |
| <i>o</i> -Aminophenolate | | | 298 | nil | 300 | nil | 300 | 420 | |
| <i>o</i> -Aminophenol cation | | | 275 | 296-302 | 279 | 296 | 279 | 430 | |
| <i>m</i> -Aminophenol | 290 | 320 | 286 | 331-334 | 287 | 333 | 287 | 425 | 410 |
| <i>m</i> -Aminophenolate | | | 293 | nil | 294 | nil | 294 | 425 | |
| <i>m</i> -Aminophenol cation | | | 273 | 296-300 | 274 | 298 | 274 | 420 | |
| <i>p</i> -Aminophenol | 270 | 330 | 301 | 367-374 | 302 | 364.5 | 302 | 470 | 420-430 |
| <i>p</i> -Aminophenolate | | | 310 | nil | 314 | nil | 314 | 470 | |
| <i>p</i> -Aminophenol cation | | | 275 | 300, 370 | 284 | 306, 364.5 | 284 | 420 | |

inefficient handling of the *n*-electrons in CNDO/S method as well as the assumption that the geometry of the anion is the same as that of the neutral molecules (Table 2). A comparison of theoretical and the experimental results for the aminophenol cations reveals that the first excited state S_1 in all the isomers has substantial contribution from the $\sigma \rightarrow \pi^*$ type of transition originating from $-\text{NH}_3^+$ group. The second absorption band is assigned to the next transition $S_0 \rightarrow S_2$ whereas the transitions $S_0 \rightarrow S_3 - S_5$ constitute the third absorption band.

The emission spectra (both fluorescence and phosphorescence) for the aminophenols in different solvent at different pH values are given in Table 4. Their fluorescence corresponds to the transition from $S_1 \rightarrow S_0$ which seems to be of slightly longer wavelength showing that the transition does not involve higher vibrational energy levels during absorption or emission. Phosphorescence is also of the type $\pi^* \rightarrow {}^3\pi$.

At high pH values none of the molecules exhibits fluorescence but phosphorescence is observed. Our theoretical calculations predict that the lowest excited state has the $n\pi^*$ character for the *ortho* and *meta*-aminophenates whereas, for the *para*-aminophenolate ion the first excited state is $\pi\pi^*$, but the energy difference between this state and the lowest excited $n\pi^*$ state is only 1602 cm^{-1} . One of the factors leading to the high efficiency of intersystem crossing to the triplet state in molecules with a $n\pi^*$ triplet state as the lowest is the persistence of one centered atomic spin orbit coupling caused by the favourable local symmetry conditions at the *n*-centres¹⁹. El-Sayed²⁰ pointed out that the $n\pi^*$ singlet and the $n\pi^*$ triplet belong to different spin orbital representations and cannot mix and therefore, the intersystem crossing rate should be high for ${}^1n\pi^* \rightarrow {}^3n\pi^*$ transition compared to the ${}^1n\pi^* \rightarrow {}^3n\pi^*$ transition.

At low pH values *o*- and *m*-aminophenols display a fluorescence at $\sim 300\text{nm}$ whereas *p*-aminophenol exhibit two fluorescence bands at 300 and 370 nm. This can be attributed to existence of $\text{NH}_3^+\text{C}_6\text{H}_4\text{OH}^*$ and $\text{NH}_2\text{C}_6\text{H}_4\text{OH}^*$ specie according to the reaction



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