Molecular Interaction between Piperidines & 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

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Ultraviolet-visible, IR and PMR studies on the electron donor-acceptor interaction between piperidines and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in chloroform have indicated the formation of mono- and di-substitution products. A probable path of the substitution reaction has been suggested and discussed.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is known as one of the most powerful organic n-acids, with an electron affinity of 2.0 eV on Briegleb's scale. In spite of this, relatively little attention has been focussed on the interaction of DDQ with electron donors. Recently we have studied the molecular interaction of various n-acids with piperidines as typical strong n-donors. The n-n character of the molecular complexes is dependent on the acceptor molecule and such electron-donor-acceptor (EDA) complexes involving strong components may lead to either complete electron transfer or to immediate substitution products. We have presently examined the molecular interaction of piperidine bases with DDQ in chloroform medium, employing UV, IR and PMR spectroscopic techniques.

Piperidine and its methyl derivatives were purified as reported earlier. Spectral grade chloroform (BDH) was used after purification. DDQ (Fluka) was recrystallised twice from a 1:1 chloroform-carbon tetrachloride. Other chemicals used were of high purity.

| Table 1 — Absorption Maxima of Interaction of Piperidines with DDQ |
|-----------------|-----------------|-----------------|
| Electron donor  | Absorption maxima (nm) of |
|                 | Purple red colour | Yellow colour   |
| Piperidine      | 513              | 418             |
| 4-Methylpiperidine | 504            | 412             |
| 3-Methylpiperidine | 500            | 405             |
| 3,5-Dimethylpiperidine | 502         | 406             |
| 2-Methylpiperidine   | 475            | 386             |
| 2,6-Dimethylpiperidine | 469          | 382             |

Carl Zeiss UV-vis Specord spectrophotometer with 1 cm matched cells. Perkin-Elmer 237 grating IR spectrophotometer and Perkin-Elmer R 32 NMR (90 MHz) spectrometer were used for recording the spectra.

The UV-visible spectra were recorded under three different conditions: (a) Donors and acceptor when mixed in equimolar concentrations gave red colour solutions, having \( \lambda_{\text{max}} \) around 500 nm (Table I); (b) there was no change in the absorption band when lower concentrations of the donors were employed; (c) at higher concentrations of the donors the purple red colour formed initially changed to yellow immediately and the solution exhibited \( \lambda_{\text{max}} \) in the region 400 nm (Table I).

In accordance with the EDA interactions of piperidines with other benzoquinones, a new broad absorption band corresponding to 1:1 charge transfer (CT) complex having \( \lambda_{\text{max}} \) around 750 nm was expected. But, no such band appeared in these cases, perhaps, due to the negligible percentage of CT in the ground state. Although, inner complex type intermediates can be proposed, they would be too unstable to be amenable for measurement.

The absorption maxima observed may not be due to the anion radical of DDQ, which is reported to have \( \lambda_{\text{max}} \) at 425 nm. The purple red colour is due to that of a substitution product, because the strong nucleophilic character of piperidine \((pK_a = 11.1)^15\) leads to substitution reaction. As attempts to isolate this product proved abortive an indirect method was used for its identification. The positive Feigl and Feigl's test for the liberation of HCN favours structure (I) and eliminates the other possible structure (II). This is in agreement with the known preferential substitution of cyanide over I, II chloride.
The yellow coloured compound formed at higher concentrations of the donor was isolated and characterised as 2-chloro-5-cyano-3,6-dipiperidino-1,4-benzoquinone (III) based on the elemental analyses. IR spectrum of the product showed the presence of νC≡N group (~2250 cm⁻¹) and absence of νN–H (~3200 cm⁻¹). The PMR spectrum of the product also indicated the absence of nitrogen-bonded proton of the donor. The observed resonance signals of the product (III) are compared with those reported for the products of other quinones (Table 2). A small difference in the resonance signals (0.07 ppm) of the α-protons of both the piperidine moieties of III is due to the difference in the influence of adjacent substituents on piperidine moieties of III.

Both the components of the EDA system being strong, the intermediate such as CT complex, inner complex or radical ions are not evidenced in the present study, probably due to the transitory existence of these intermediates under the experimental conditions employed. Immediate formation of III at equimolar concentrations of the donor and acceptor is favoured because of the high basicity of the donor. However, in the presence of excess of donor the monosubstitution product (λmax ~ 500 nm) transforms to a disubstitution product (λmax ~ 400 nm).

References