BASICITY AND REDOX-CHARACTER OF PYRROLO[3,2-b] PYRROLE AND ITS RELATED COMPOUNDS

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Although titled system possessing two condensed pyrrole ring is a fundamental heteroaromatic compound, the chemistry remains unexplored because of the synthetic barrier. Recently we developed the convenient synthetic procedure for pyrrolo[3,2-b]pyrrole using nitrene addition reaction. Now we wish to discuss the chemical and physical properties of 1,4-dihydropyrrolo[3,2-b]pyrrole (1) and its derivatives in comparison with those of pyrrole and indole.

The unsubstituted framework is unstable in atmosphere and in acidic media to result in a polymeric material with blue color. On the other hand, it is found that the 3,6-di-t-butyl derivative la gives golden plates, $dec 255-260\,^{\circ}C$ by the treatment with conc. HCl. The structure can be deduced to be a α -protonated species la and la are protonated by UV method in la 0 to give the value of 3.6. The basicity is comparable to typical aromatic amine such as dimethylaniline and it should be noted the large deviation from those of pyrrole (-3.8) and indole (-3.6). In addition, it is interesting that the N,N-dimethylation of la causes a decrease of basicity (la by la 1.7 in MeOH-la20(10:1)).

The oxidation potential of dihydropyrrolo[3,2-b]pyrrole was measured with cyclic voltammetry to be 0.48 V (vs SCE) for 1 and 0.41 V for 1a in $\mathrm{CH_3CN}$. These values are almost half of pyrrole and indole indicating the electon-rich 10π -aromatic character. These compounds produce a charge transfer complex with $\mathrm{CCl_4}$ which shows a typical absorption in the UV spectrum. These phenomena are reflecting the more electron-excess and more basic character of pyrrolopyrrole compared with pyrrole and indole. It might be possible to compose new redox-system using this anormal feature.