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

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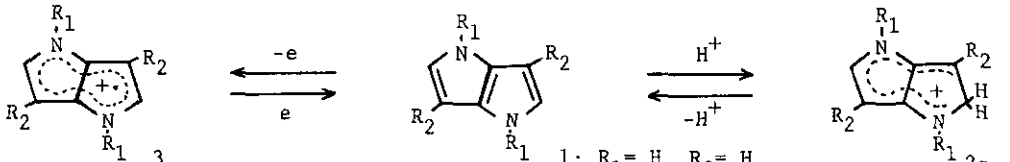
Although titled system possessing two condensed pyrrole ring is a fundamental heteroaromatic compound, the chemistry remains unexplored because of the synthetic barrier. Recently we developed the convenient synthetic procedure for pyrrolo[3,2-b]pyrrole using nitrene addition reaction. Now we wish to 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 **1a** gives golden plates, dec 255-260°C by the treatment with conc. HCl. The structure can be deduced to be a α-protonated species **2a**. The pKa of **2a** is determined by UV method in H_2O 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 **1** causes a decrease of basicity (**2b**: pKa= 1.7 in MeOH-H_2O(10:1)).



3
3a
3b

1: R_1= H, R_2= H
1a: R_1= H, R_2= t-Bu
1b: R_1= Me, R_2= t-Bu

2a
2b

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 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 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.