SHORT COMMUNICATIONS

The Electronic Structure of Carbazole in the Fluorescent State

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The nature of the electronic states of pyrrole, indole and carbazole seems to be not so well understood as those of benzenoid hydrocarbons, aza-aromatics and their derivatives, although there have been some theoretical studies(1).

We have studied various solvent effects on the absorption and fluorescence spectrum of carbazole, including the effect of hydrogen bonding in a nonpolar solvent and the effect of ionic dissociation in an aqueous alkaline solution(3,1b). We have also made some quantum mechanical studies of the electronic structure and spectra of this series of molecules by the composite system method(4) and have found a nice agreement with the experimental observations. For example, carbazole was regarded as composed of biphenyl and the $\rangle$N–H group. Wave functions and energies(5) for the ground state as well as for the excited states of planar biphenyl, which reproduce the observed spectra satisfactorily, were used. For the calculation of the lower excited states, it was sufficient(5) to take into consideration three occupied MO's, ϕ_4, ϕ_5, and ϕ_6, and three vacant MO's, ϕ_7, ϕ_8, and ϕ_9, among the twelve π-MO's of biphenyl. Three charge transfer (CT) configurations from nitrogen to ϕ_7, ϕ_8, and ϕ_9, were taken into consideration. The core resonance integral between nitrogen and the nearest neighbor carbon and the energy of the nitrogen orbital were assumed to be -2.0 and -10.25 eV.(6) respectively.

For the sake of simplicity, only the wave functions for the lowest and the second excited singlet state of carbazole are shown here. $^1\chi_{Nk}$ is the CT configuration, and ^{1}L's and ^{1}B's are locally excited states in biphenyl.

$$^1\Psi_1 = 0.1283\,\chi_0 + 0.7811\,^1L_b - 0.2575\,^1B_b - 0.5279\,^1\chi_{N7} + 0.1684\,^1\chi_{N9}$$

$$^1\Psi_2 = 0.9961\,^1L_a - 0.0473\,^1B_a + 0.0739\,^1\chi_{N8}$$

The oscillator strengths for these states of carbazole were calculated as: $f(\Psi_0 \rightarrow {}^1\Psi_1) = 0.13$: $f(\Psi_0 \rightarrow {}^1\Psi_2) = 1.02$. These two transitions correspond quite well to the observed band at 3.90 eV. with moderate intensity and the strong band at 4.27 eV. respectively. The form of $^1\Psi_1$ calculated here clearly shows that the very weak "hidden transition"(7) of biphenyl (^1L_b) is modified considerably in carbazole because of the mixing with $^1\chi_{N7}$ and also with ^1B_b. Both the replacement of NH hydrogen by alkyl group and hydrogen bonding of the $\rangle$N–H$\cdots$X type cause a large red shift of the 3.90 eV. band, but only a slight shift of the 4.27 eV. band. This fact can be explained quite well on the basis of the calculated results because the contribution from the CT configuration is very small in $^1\Psi_2$ compared with that in $^1\Psi_1$, where it is considerably large, and both the alkyl replacement and the hydrogen bonding lower the energy of the CT configuration and increase the core resonance integral between carbon and nitrogen.

The increase of the dipole moment in the fluorescent state,

$$\overrightarrow{\Delta\mu} = \langle {}^1\Psi_1 \mid \sum_i e_i \boldsymbol{r}_i \mid {}^1\Psi_1 \rangle - \langle \Psi_0 \mid \sum_i e_i \boldsymbol{r}_i \mid \Psi_0 \rangle,$$

was calculated to be $\sim 1.96\,D$. The value of $\overrightarrow{\Delta\mu}$ was determined experimentally by the method proposed by Lippert(8) and by Mataga(9), using the following equation and assuming $a \sim 4$A.

$$hc(\sigma_a{}^m - \sigma_f{}^m) \simeq \text{Const} + 2\left[\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1}\right] \cdot \frac{(\overrightarrow{\Delta\mu})^2}{a^3}$$

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1) For example, a) R. D. Brown and M. L. Heffernan, *Australian J. Chem.*, **12**, 319 (1959); b) H. Kokubun, Summary of the Symposium on the Electronic State, held by the Chem. Soc. Japan, Sept., 1959.

2) N. Mataga, Y. Torihashi and Y. Kaifu, *Z. physk. Chem. N. F.*, in press.

3) N. Mataga and Y. Torihashi, ibid., in press.

4) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); J. N. Murrell, ibid., **68**, 969 (1955).

5) S. Mataga, to be published.

6) The minus value of the observed I. P. of ammonia taken from K. Watanabe, *J. Chem. Phys.*, **22**, 1564 (1954).

7) A. Wenzel, *J. Chem. Phys.*, **21**, 403 (1953); H. Suzuki, This Bulletin, **32**, 1340 (1959).

8) E. Lippert, *Z. Naturforsch.*, **10A**, 541 (1955); *Z. Electrochem.*, **61**, 962 (1957).

9) N. Mataga et al., This Bulletin, **28**, 690 (1955); ibid., **29**, 465 (1956).

The experimental value was estimated to be $\sim 2.2\,D$, which agrees very well with the calculated results.

The $\overrightarrow{\Delta\mu}$ values of naphthylamines and naphthols calculated by the ordinary semiempirical ASMO method, with appropriate Hückel MO's delocalized over all cores in the molecule, have been found to be ca. 4∼5 times larger[10] than the observed values. In the present method, however, such a situation does not arise. This fact seems to indicate that the composite system method can give a more reliable charge distribution in the heteroaromatics when appropriate values of semiempirical parameters are chosen.

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[10] N. Mataga, to be published.