Note on the Unsymmetrical Form of Biphenyl in its First Excited State and the Ionic State

A. GOŁĘBIEWSKI and A. PARCZEWSKI

Department of Theoretical Chemistry, Jagiellonian University Cracow, Poland

(Z. Naturforsch. **26 a**, 180 [1971]; received 28 October 1970)

Recently we have elaborated a new, selfconsistent method of analysis of steric effects in organic conjugated systems [1]. The results of such an analysis for the ground state, the first excited state and the ionic state of biphenyl were published in this journal [2]. However, after completing the article on biphenyl it was found that a twisting of the two phenyl rings causes a shift of the ionization or the excitation to one of the two rings, the shift being complete for $\Theta = 90°$. Here we give some details on this peculiar behaviour.

In Fig. 1 we give the bond lengths and the net charge distribution for the biphenyl anion, as calculated for $\Theta = 90°$. However, the calculated barrier of rotation is quite small, 1.5 kcal/mole, a strong vibronic coupling being thus possible. In Fig. 2 we show the dependence of the bond lengths on the twisting angle Θ, the broken lines corresponding to the unsymmetrical form, the dotted lines to the symmetrical form. As seen from Fig. 2 the asymmetry is not important for $\Theta < 60°$. Therefore our basic conclusions, drawn formerly, remain unchanged.

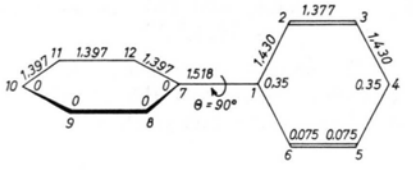

Fig. 1. Bond lengths and net charge distribution in the biphenyl anion for $\Theta = 90°$.

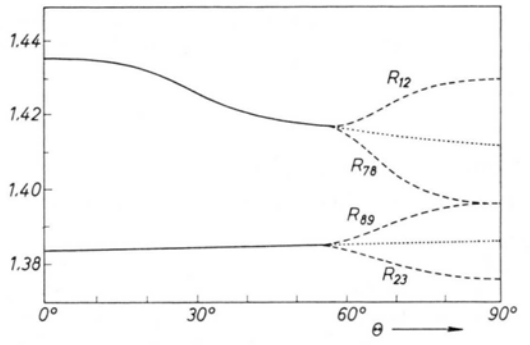

Fig. 2. Dependence of bond lengths on the twisting angle Θ in the biphenyl ion.

It is perhaps worthwhile to mention that the difference of bond lengths $R_{12} - R_{23} = 0.053$ Å which was calculated for $\Theta = 90°$ (when the conjugation of the two rings is broken) is in a nice agreement with the Colpa result (0.046 Å) which was estimated for the Jahn-Teller effect in the benzene positive ion [3].

A similar behaviour was observed in the case of the first excited state, within the framework of the self-consistent Hückel theory. Here the asymmetry is slightly higher, however, being significant up from $\Theta = 50°$. Also the barrier of rotation is in this case larger, being equal to 5.6 kcal/mole.

Reprints request to Dr. A. GOŁĘBIEWSKI, Department of Theoretical Chemistry, Jagiellonian University, Krupnicza 41, *Kraków*, Poland.

[1] A. GOŁĘBIEWSKI and A. PARCZEWSKI, Acta Phys. Polon. **A 37**, 879 [1970].

[2] A. GOŁĘBIEWSKI and A. PARCZEWSKI, Z. Naturforsch. **25 a**, 1710 [1970].

[3] C. A. COULSON and A. GOŁĘBIEWSKI, Mol. Phys. **5**, 71 [1962].

Verantwortlich für den Inhalt: A. KLEMM

Satz und Druck: Konrad Triltsch, Würzburg