## *Spatial Configurations and Ultraviolet Absorption Spectra of Some 2,2′-Bridged Biphenyl Derivatives*

By Hiroshi Suzuki

(Received July 19, 1956)

Previously, the present author calculated with certain simple assumptions the quantitative relations between the degree of deviation from coplanarity of molecular configuration and the ultraviolet absorption spectrum as well as the extent of conjugation for stilbene derivatives(1) and also for biphenyl-type compounds(2) by the molecular orbital method, and clarified the theory that the absorption maximum is shifted toward shorter wavelengths with increasing angle between the two benzene rings in the case of biphenyls, and between the benzene rings and the plane

TABLE

| Compound | Conjugation band* $\lambda_{max.}$ (Å) | $\varepsilon_{max.}$ | $\Delta E(\beta)$ | $\alpha$ | R. E. ($\beta$) | $\theta$ | $\theta$ (from model)* |
|---|---|---|---|---|---|---|---|
| 3, 4, 5, 6-Dibenzocyclohepta-3, 5-diene-1-carboxylic Acid | 2490 | 15300 | 1. 653 | 0. 550 | 0. 120 | 48. 4° | ca. 50° |
| Methyl 3, 4, 5, 6-dibenzocyclohepta-3, 5-diene-1-carboxylate | 2485 | 15500 | 1. 657 | 0. 543 | 0. 117 | 49. 0° | 〃 |
| 1-Hydroxymethyl-3, 4, 5, 6-dibenzocyclohepta-3, 5-diene | 2485 | 15400 | 1. 657 | 0. 543 | 0. 117 | 49. 0° | 〃 |
| Ethyl 4, 5, 6, 7-dibenzocycloocta-4, 6-diene-1, 1, 2, 2-tetracarboxylate | 2395 | 13100 | 1. 723 | 0. 432 | 0. 075 | 58. 0° | 60–65° (or 75–80°) |
| Methyl 4, 5, 6, 7-dibenzocycloocta-4, 6-diene-1, 2-dicarboxylate | 2365 | 12700 | 1. 747 | 0. 392 | 0. 062 | 61. 1° | 〃 |

* According to G.H. Beaven and others, loc. cit.

of the central ethylenic linkage in the case of stilbenes, and further, demonstrated the fact that the values of the angle of twist computed by this method from the observed positions of the absorption maxima agree satisfactorily well with those deduced from scale models or by other methods such as the electron diffraction analysis in almost all the examples cited in both the cases.

Applying the same method to some 2, 2′-bridged biphenyl derivatives with seven- and eight-membered homocyclic rings, whose absorption spectra in 96% ethanol solutions have recently been reported by G.H. Beaven and others3), the results summarized in the Table are obtained. The notation used here is the same as in the previous paper2): $\Delta E$ is the energy difference between the lowest vacant orbital and the highest occupied orbital, $\alpha$ is a parameter by which allowances are made for the situation that the value of the exchange integral for the 1–1′ bond varies with the angle of twist $\theta$ and the length of the bond, and R.E. is the extra-resonance energy, representing the extent of conjugation. Agreements between the values of the angle of twist computed from the absorption maxima and those deduced from scale models are fairly good also here.

*The College of General Education*
*The University of Tokyo*
*Tokyo*

---

1) H. Suzuki, This Bulletin, **25**, 145 (1952).

2) H. Suzuki, This Bulletin, **27**, 597 (1954).

3) G. H. Beaven, Gwendoline R. Bird, D. Muriel Hall, E. A. Johnson, Joan E. Ladbury, Mary S. Lesslie and E. E. Turner, *J. Chem. Soc.*, **1955**, 2708.