Theoret. chim. Acta (Berl.) 11, 452—454 (1968)

Relationes

A CNDO Study of Steric Effects in Biphenyl

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Received August 1, 1968

The conformation of biphenyl is studied by the CNDO method. A fixed length of the twisted bond allows no minimum for the total energy between the values 0° and 90° of the angle of twist.

Introduction

The determination of the angle of twist in biphenyl and related compounds has been the subject of a large number of studies using various methods [1, 2, 3, 4, 6, 7, 8, 9, 10, 20, 21, 23, 24, 25].

The aim of the present work is to investigate the influence of the angle of twist on the total energy and electronic properties of biphenyl.

Method and Parameters

Much of the progress in the study of unsaturated organic molecules has its origin in the MO calculations based on the π electron approximation. In the recent years, new methods were proposed which take into account all the valence-shell electrons. One of them, the extended Hückel method, has been very successfully applied by Hoffmann to a variety of organic chemical problems [5]. However, this method has a major drawback in that it neglects electron repulsion integrals completely.

Pople *et al.* [12, 13, 14, 15, 18] have developed the CNDO method which introduces the approximation of zero differential overlap into the SCF LCAO MO formalism of Roothaan [18] which simplifies the calculations enormously by eliminating all but one- and two-center repulsion integrals. The equations are therefore formally similar to those used in the highly successful Pariser-Parr-Pople SCF theory [11, 16].

The semiempirical parameters used in this work are Pople's usual ones. The geometries of the six-membered rings were approximated as regular hexagons. All rings bonds were taken as 1.40 Å and all carbon-hydrogen bonds as 1.10 Å. The twisted bond was assumed to be of constant length 1.5 Å as in the case of crystalline biphenyl [22] for all values of the angle of twist θ. The hydrogens were placed radially out of the rings they were on.

Results

In a previous paper [23] we estimated the angle of twist to be $\theta = 18°$ for biphenyl in the liquid state, from UV absorption spectra. More recently [25] we applied the extended Hückel method to biphenyl and we obtained a minimum value of the total electronic orbital energy for $\theta \simeq 66°$. This value is greater than the experimental equilibrium one which is $\theta = 42°$ for biphenyl in the vapour phase.

It appeared therefore of interest to complete the previous studies by a CNDO one. As may be seen in Table 1 the total energy E of biphenyl is a function of θ which has no minimum between 0° and 90°. We may however notice that the energy remains nearly constant between 70° and 90°.

Table 1. *Total energy of biphenyl as a function of* θ

θ (degrees)	0	30	60	70	80	90
$-E$ (a.u.)	92.7931	92.7977	92.8001	92.8004	92.8004	92.8005

Table 2. *Atomic valence electron densities in biphenyl*

Position	$\theta = 0°$		$\theta = 90°$	
	C	H	C	H
1	-0.020	—	-0.033	—
2, 6	$+0.008$	$+0.004$	$+0.013$	$+0.008$
3, 5	-0.012	$+0.008$	-0.013	$+0.008$
4	-0.006	$+0.008$	$+0.003$	$+0.008$

It is probably unrealistic to assume the constancy of the twisted bond for all values of θ. A small variation of this bond length might possibly give rise to a minimum value of E for $\theta < 90°$.

This may be the subject of further studies on biphenyl-type molecules.

The electronic charge densities of atoms for $\theta = 0°$ and $\theta = 90°$ are listed in Table 2.

The calculations were performed on a CDC 3600 computer, using the original CNDO/2 program written in Fortran IV by Segal and distributed by the QCPE organization [17].

References

1. Beaven, G. H.: Steric effects in conjugated systems, p. 22. London: Butterworths 1958.
2. Golebiewski, A., and A. Parczewski: Theoret. chim. Acta (Berl.) **7**, 171 (1967).
3. Gondo, Y.: J. chem. Physics **41**, 3928 (1964).
4. Grinter, R.: Molecular Physics **11**, 197 (1966).
5. Hoffmann, R.: J. chem. Physics **39**, 1397 (1963).
6. Iguchi, K.: J. physic. Soc. Japan **12**, 1250 (1957).
7. Jaffé, H. H., and O. Chalvet: J. Am. chem. Soc. **85**, 1561 (1963).
8. London, A.: J. chem. Physics **13**, 396 (1945).
9. Murrell, J. N.: J. chem. Soc. (London) **1956**, 3779.
10. —, and H. C. Longuet-Higgins: Proc. physic. Soc. (London) A**68**, 601 (1955).
11. Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466, 767 (1953).

12. Pople, J. A., D. P. Santry, and G. A. Segal: J. chem. Physics **43**, S 129 (1965).
13. —, and G. A. Segal: J. chem. Physics **43**, S 136 (1965).
14. — — J. chem. Physics **44**, 3289 (1966).
15. — D. L. Beveridge, and N. S. Ostlund: Int. J. Quant. Chem. IS, **1967**, 293.
16. — Trans. Faraday Soc. **49**, 1375 (1953).
17. *Quantum Chemistry Program Exchange.* Chemistry Department, Indiana University. Bloomington, Indiana 47401. USA.
18. Roothaan, C. C. J.: Rev. mod. Physics **23**, 69 (1951).
19. Santry, D. P., and G. A. Segal: J. chem. Physics **47**, 158 (1967).
20. Stewart, E. T.: J. chem. Soc. (London) **1958**, 4016.
21. Suzuki, H.: Electronic absorption spectra and geometry of organic molecules, p. 261. New York: Academic Press 1967.
22. *Tables of interatomic distances and configuration in molecules and ions.* London: The Chemical Society 1958.
23. Tinland, B.: Acta Physica Acad. Sci. Hung. **24** (4), (1968), in press.
24. — Theoret. chim. Acta (Berl.) **12**, in press (1968).
25. — J. molecular Struct. (under press).

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