Hindered Rotation in Biphenyl According to a Selfconsistent Steric Analysis

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A selfconsistent steric conformation analysis is applied to the ground state, first excited state and the ionic state of biphenyl in terms of the internal rotation angle. The calculated barrier of rotation through $\Theta=0^\circ$ is equal to 3.1 kcal/mole. In the case of the isolated anion the twisting angle equal to 26° was obtained. In the case of solutions the angle is 15—19°, the value following from an analysis of the EPR data published by Möbius. The electronic absorption spectrum is discussed in terms of the SCF CI method. The results are compared with other recent calculations.

1. Introduction

Biphenyl was a subject of many experimental and theoretical articles. X-ray results were obtained by HARGREAVES and RIZVI [1], ROBERTSON [2], and TROTTER [3], electron diffraction data by ALMENNINGEN and BASTIANSEN [4] and by BASTIANSEN and TRAETTEBERG [5]. A spectroscopic estimate of the rotation barrier in the ground state was given by WAGNER [6], basing partly on the experimental works published by LEWIS and KASHA [7] and HIROTA [8]. A different estimate of the barrier follows from the PMR studies of KURLAND and WISE [9], and MAYO and GOLDSTEIN [10]. EPR studies of the conformation of the ionic state were carried out by MÖBIUS in this journal [11].

The theoretical analysis was connected mainly with the structure of the molecule and with its UV spectrum. Preliminary results were obtained by ADRIAN [12], COULSON [13] and by SAMOILOV and DYATKINA [14]. GOODWIN and MORTON-BLAKE [15] evaluated the van der Waals (vdW) potential for the H...H pair, basing on the experimental value of the twisting angle, $\Theta = 42^\circ$. CHAPMAN and SCHAAD [16] derived the relation $R = R(\Theta)$, where R is the bond length of the central bond. However, the relation did not stand the test of time. DASHEVSKY and KITAJGORODSKY [17] applied a mechanical model to biphenyl. MILLER and MURRELL [18] discussed the structure of the planar molecule, applying a modified COULSON and HAIGH method with this purpose. The structure of the isolated molecule was also discussed by the present authors [19], basing on a modification of the COULSON and SENENT method [20] and the LONGUET-HIGGINS and SALEM method [21]. The present authors applied also a new selfconsistent steric analysis to the ground state biphenyl [22]. CNDO-type calculations were performed by TINLAND [23], leading to a large overestimate of the twisting angle. Most related to the present work

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seem to be the articles published by FISCHER-HJALMARS [24, 25] and by IMAMURA and HOFFMANN [26]. They are concerned with the dependence of the total energy on Θ. The PARISER, PARR and POPLE method was used with this purpose. The σ-bond energy was kept constant. Van der Waals interaction was included for the H...H pairs only.

The Θ angle was also estimated from an analysis of the spectral data. SUZUKI [27] applied the Hückel method with this purpose and TINLAND [28] (giving reference to oldest papers only) the variable β-approximation of the PPP method.

Older π-electronic calculations of the UV electronic spectrum were mainly based on a perturbation treatment of two phenyl rings [29–34]. SCF CI calculations, for one or more values of the Θ angle, were carried out by GONDO [35], GRINTER [36], the present authors [19] and later by TINLAND [28], IMAMURA and HOFFMANN [26]. Until 1967 our results [19] were in a best agreement with experiment. Tinland's result are rather close to ours. The results obtained by Imamura and Hoffmann, however, are quite different. They will be analyzed in the last section.

In spite of the many contributions some of the problems related to biphenyl are still open to questions. The potential curves, barriers for internal rotation, etc., have been often estimated with many oversimplifications. Mostly vdW interactions of the H...H type have been considered only, although interactions of H...C and C...C pairs might be significant also. The variation of valence angles and bond lengths, as well as out-of-plane shifts of hydrogen atoms, have been disregarded. More complete calculations dealt with the planar system only. For this reason we thought it worthwhile to make a more complete steric analysis, basing on a selfconsistent steric conformation method [22]. We also report our new SCF CI results which have been obtained by mixing all the singly excited states for the optimal ground state conformation. The purpose was to test our previous calculations for these additional assumptions.

2. Brief Outline of the Selfconsistent Steric Method

The selfconsistent steric method has been already described elsewhere [22]. We summarize, therefore, only the main assumptions.

The sum of the σ- and π-electronic energies was calculated in accordance with the LONGUET-HIGGINS and SALEM method [21], requiring, however, different conditions of selfconsistency:

$$\beta_i(r_i, \Theta_i) = \beta_i(r_i, 0) \cos\Theta_i = \beta_0 \exp[-x(r_i - 1.397)] \cos\Theta_i \qquad (1)$$

and

$$r_i = a - b\, p_i(\Theta_i) \cos\Theta_i + \frac{b}{2x\beta_i(r_i, 0)} \frac{dW}{dr_i} \qquad (2)$$

where $\beta_i(r_i, \Theta_i)$ is the resonance integral for the bond length equal to r_i and the angle of twist equal to Θ_i, W is the sum of all vdW interactions significant in the problem (Fig. 1), and a, b, β_0 and x

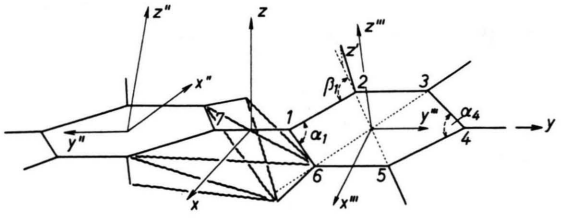

Fig. 1. Numbering of atoms in biphenyl and definition of independent coordinates α_1, α_2, β_1 and z'. Types of vdW interactions considered are indicated by wavy lines.

are empirical parameters: $a = 1.517$ Å, $b = 0.18$ Å, $\beta_0 = -1.403$ eV, $x = 4.1/$Å. Neglecting torsions and vdW interactions one would obtain the conditions put upon by Longuet-Higgins and Salem. The vdW interactions of the H...H type and the C...H type were calculated with the BARTELL formula [37] and those of the C...C type after DASHEVSKY and KITAJGORODSKY [17]. As the above theory does not consider the variation of energy due to the variation of independent valence angles α_1, α_4 and the out-of-plane distortion z' (Fig. 1), we have discussed it

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additionally with a modified COULSON and HAIGH method [38]. The optimal structure was then obtained iteratively, by minimization of the total energy. Eventually, the angle $\Theta_{17} = \Theta$ was kept fixed in these calculations.

3. Dependence of R_{17} on Θ

Two attempts are known to determine the dependence $R_{17} = R(\Theta)$ [16, 27]. However, none of them seems to behave properly in the whole region of Θ's. According to experiment, $R_{17} = 1.497 - 1.507$ Å in a planar molecule [1–3], $1.48 - 1.49$ Å for $\Theta = 42°$ (l. c. [4, 5]), 1.52 Å for $\Theta = 90°$, as found approximately for the hexaphenylbenzene molecule [39]. There is thus a minimum between 0° and 90°. Neither of the two atempts succeeded in obtaining such a minimum.

The dependence on $\Theta_{17} = \Theta$ of the various bond lengths in biphenyl, which follows from the present calculations, is given in Figs. 2 and 3. We see from Fig. 2 that R_{17} has a minimum equal to 1.494 Å

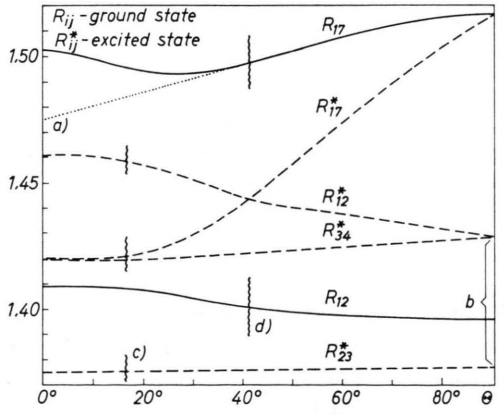

Fig. 2. Dependence of bond lengths on the internal rotation angle for the ground state and average first excited state. a) Extrapolation line for the case of no vdW interactions; b) difference of bond lengths due to the Jahn-Teller effect; c) position of the stable conformation of the excited state; d) position of the stable conformation of the ground state.

at about 30° in the case of the ground state and 1.420 Å at about 5° in the case of the center of gravity of the first excited state. It is interesting that also the R_{12} value depends strongly on the twisting angle. For $\Theta \to 90°$ we find that $R^*_{12} \to R^*_{34}$ and

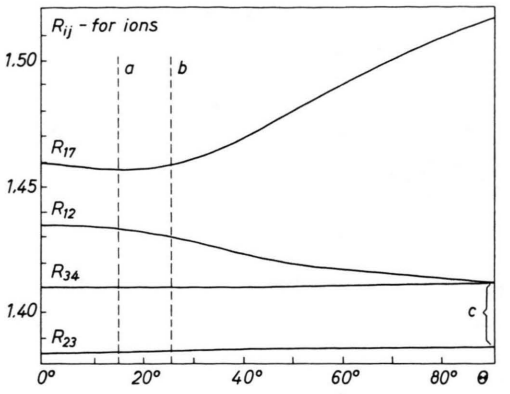

Fig. 3. Dependence of bond lengths on the internal rotation angle for the ± ion. a) Stable conformation in solutions; b) stable conformation in the gaseous phase; c) Jahn-Teller effect.

$R^*_{12} - R^*_{23} \to 0.05$ Å, the difference being caused by the Jahn-Teller effect. In Fig. 3 a similar relation is reproduced which has been obtained for the biphenyl ion. Minimum of R_{17} corresponds here to $\Theta = 15°$ and is equal to 1.457 Å. The Jahn-Teller effect amounts now to $1.412 - 1.386 = 0.026$ Å. Let us recall that the Jahn-Teller effect in $C_6H_6^+$ was estimated by Colpa with the PPP method [40]. He found that $\Delta R = 1.418 - 1.372 = 0.046$ Å. Thus we see that the agreement is satisfactory.

In order to compare the calculated and observed bond length R_{17} let us note that in accordance with Fig. 2 $R_{17}(0) = 1.503$ Å, $R_{17}(40° 21') = 1.498$ Å and $R_{17}(90°) = 1.518$ Å. Comparing these values with the experimental ones, $1.497 - 1.507$, $1.48 - 1.49$ and 1.52 we see that the agreement with experiment is satisfactory.

Let us recall that also the remaining bond lengths, the bond angles α_1, α_4, β_1 (Fig. 1) are reproduced rather well with this theory [22].

4. Potential Energy of Internal Rotation. Structure of the Ion

There are two barriers for internal rotation in biphenyl, corresponding to $\Theta = 0°$ and to $\Theta = 90°$. According to the PMR method [9, 10] the largest of them is expected to be small, equal to $0.2 - 1.0$ kcal per mole. However, the analysis of the phosphorescence spectrum and the quenching experiments leads

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to a different result [6]. The barrier of rotation through $\Theta = 0^\circ$ is said to be equal to 4 kcal/mole.

The spread of the calculated values is in general small, not exceeding 5 kcal/mole [12, 15, 17, 24, 25].

The results of the present calculation are shown in Fig. 4. The shape of the ground state curve is the same as that found by other authors. The internal rotation through $\Theta = 0^\circ$ exhibits a barrier of 3.1 kcal/mole what compares rather well with the spectroscopic value. Let us also note that the barriers found for the ground state are in a semiquantitative agreement with those which follow from the extended Hückel method [26]: 5.5 kcal/mole and 0.9 kcal/mole accordingly. The first excited state is predicted to be nearly planar, with $\Theta = 16^\circ 37'$. The dependence of E on Θ is stronger in the case of the excited state than in the case of the ground state. Let us recall, however, that the method does not make any difference between the singlet and triplet states, corresponding thus to a center of gravity of the two excited states.

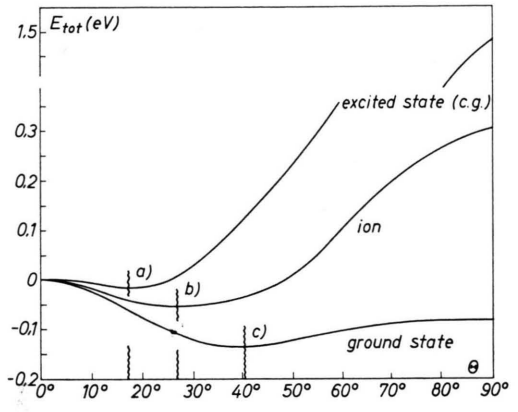

Fig. 4. Dependence of the total energy on Θ.

It might be also interesting to consider the contributions of the various types of energy to the total energy of the system. They follow from Table 1 and Fig. 5. Let us note that in the case of the ground state $E_\pi(\Theta)$ shows two minima, the first one being very flat (0.1 kcal/mole). It is also very gratifying, although somewhat surprising that the relation $W = W(\Theta)$ depicted in Fig. 5 is in an almost quantitative agreement with that which was found by GOODWIN and MORTON-BLAKE [15] with a much more simplified model.

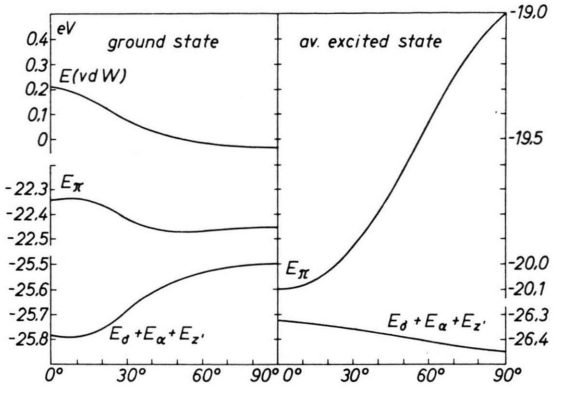

Fig. 5. Contribution of various types of interactions as a function of Θ.

Biphenyl anion and cation is predicted to have a twisted structure, with $\Theta = 26^\circ 13'$, at least in the isolated state. This angle is in a large disproportion to the value found by Möbius for the stably solvated biphenyl radical ion: $38 \pm 2^\circ$. However, the analysis of the EPR data which was carried out by Möbius requires a revision:

i) Interaction of the biphenyl molecule with the solvent is expected to cause a flattening of the molecule; in the case of the neutral molecule Θ is equal to 42° in the gaseous phase, $20 - 30^\circ$ in solutions and 0° in the solid state.

ii) The mobile bond order p_{17} is larger in the ionic state than in the case of the neutral molecule;

Contribution	Ground state		Av. excited state		Cation or anion	
	ΔE(I) kcal/mole	ΔE(II) kcal/mole	ΔE(I) kcal/mole	ΔE(II) kcal/mole	ΔE(I) kcal/mole	ΔE(II) kcal/mole
ΔE_π	+ 2.81	+ 0.25	− 1.41	+ 24.68	− 0.41	+ 9.00
ΔE_σ	− 4.82	+ 2.81	− 0.23	− 1.59	− 1.82	+ 3.00
ΔW	+ 4.11	− 1.45	+ 1.48	− 4.61	+ 2.61	− 3.23
ΔE_α	+ 0.99	− 0.05	+ 0.65	− 0.65	+ 0.92	− 0.28
$\Delta E_{z'}$	+ 0.02	− 0.02	+ 0.05	− 0.05	+ 0.05	− 0.05
ΔE_{tot}	+ 3.11	+ 1.54	+ 0.53	+ 17.79	+ 1.34	+ 8.44

Table 1. Contributions to the barriers of internal rotation in biphenyl and its ion.
$\Delta E(\mathrm{I}) = E(0^\circ) - E(\Theta)_{min}$, $\Delta E(\mathrm{II}) = E(90^\circ) - E(\Theta)_{min}$.

thus there is no reason to believe that the value of Θ is now larger than $20-30^\circ$.

iii) Let us draw the dependence of the ratio of spindensities ϱ_4 and ϱ_2 (Fig. 6). Experimentally, according to Möbius, $\varrho_4/\varrho_2 = 5.247/2.666 = 2.00 \pm 1\%$. As can be seen from the Figure, the spindensities which have been obtained with the selfconsistent steric conformation method lead to the range: $15^\circ \leqq \Theta \leqq 19^\circ$. The values suggested by Möbius were based on Hückel-type calculations (Fig. 6), neglecting the role of the steric hindrance and of the detailed structure of the ion.

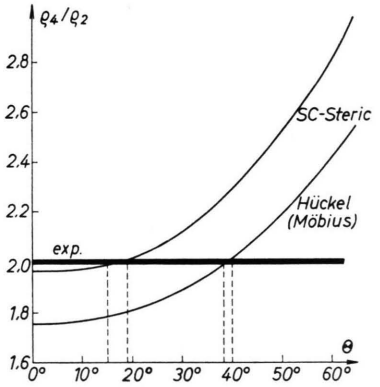

Fig. 6. Ratio of the spindensities ϱ_4 and ϱ_2 in the biphenyl ion.

5. Correlation Diagrams of π-electronic Orbital Energies and Densities

The dependence of the π-electronic orbital energies on Θ is reproduced in Figs. 7 and 8. Fig. 7 corresponds to the ground state conformation of the neutral molecule and Fig. 8 corresponds to the ion.

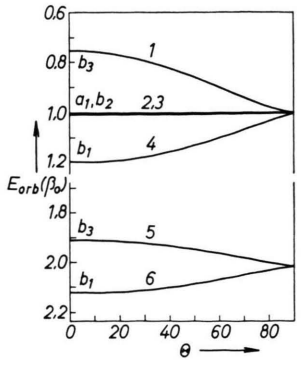

Fig. 7. Dependence of orbital energies on Θ for the ground state conformation. The energies of the excited states follow from the pairing theorem.

Let us note that for $\Theta = 90^\circ$ and for the case of the ionic state the orbital energies E_1, E_4 and E_2, E_3 are different. It is the result of the Jahn-Teller effect which is included in our method automatically.

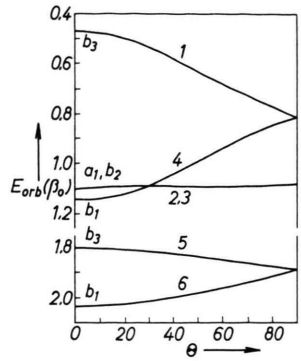

Fig. 8. Dependence of orbital energies on Θ for the biphenyl ion. The remaining six orbital energies follow from the pairing theorem.

The dependence of the π-electron density q_s ($s = 1, 2, 3, 4$) on Θ is shown in Fig. 9, the Figure referring to the biphenyl anion. There is an accumulation of charge in positions 2, 6, 8 and 12 causing an additional repulsion which has not been analyzed in this work. The repulsion energy is of the order of 1 kcal/mole and is not much sensitive to the variation of Θ.

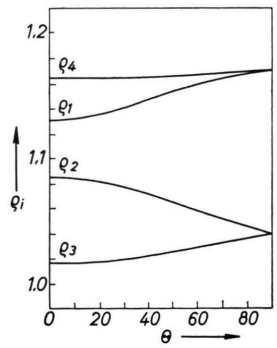

Fig. 9. Dependence of pi-electron densities on Θ for the biphenyl anion.

6. The Electronic Spectrum of a Neutral Biphenyl Molecule

As already noticed the limited CI calculation of the UV absorption spectrum [19] allowed us to interpret the experimental spectrum quite successfully. Since then, however, Imamura and Hoffmann published their results which had been obtained by mix-

Symmetry	Principal contributions (%)	$\Theta = 40°21'$ ΔE (eV)	f	$\Theta = 0°$ ΔE (eV)	f
$^1B_2^-$	$V_{12'}$ (37.9) $V_{21'}$ (37.9)	4.62	0	4.51	0
$^1B_1^-$	$V_{13'}$ (37.3) $V_{31'}$ (37.3)	4.63	0	4.55	0
$^1B_3^+$	$V_{11'}$ (96.2) $V_{33'}$ (0.9)	5.15	0.668 (y)	4.82	0.817 (y)
$^1A_1^+$	$V_{32'}$ (26.9) $V_{23'}$ (26.9)	6.08	0	6.07	0
$^1B_1^+$	$V_{31'}$ (49.6) $V_{13'}$ (49.6)	6.23	0.133 (z)	6.03	0
$^1A_1^-$	$V_{14'}$ (47.1) $V_{41'}$ (47.1)	6.29	0	6.20	0
$^1B_3^+$	$V_{22'}$ (51.1) $V_{33'}$ (43.0)	6.34	1.109 (y)	6.35	1.104 (y)
$^1B_2^+$	$V_{12'}$ (48.3) $V_{21'}$ (48.3)	6.41	0.726 (x)	6.29	0.890 (x)
$^1B_1^-$	$V_{43'}$ (35.9) $V_{34'}$ (35.9)	6.80	0	6.85	0
$^1B_2^-$	$V_{42'}$ (35.6) $V_{24'}$ (35.6)	6.81	0	6.86	0
$^1A_1^-$	$V_{23'}$ (49.9) $V_{32'}$ (49.9)	6.90	0	6.92	0
$^1B_3^+$	$V_{33'}$ (54.3) $V_{22'}$ (45.6)	6.90	0.003 (y)	6.93	0.006 (y)
$^1B_1^+$	$V_{24'}$ (49.0) $V_{42'}$ (49.0)	7.16	0.134 (z)	7.26	0
$^1A_1^+$	$V_{14'}$ (26.7) $V_{41'}$ (26.7)	7.20	0	7.19	0
$^1B_2^+$	$V_{34'}$ (47.6) $V_{43'}$ (47.6)	7.32	1.335 (x)	7.43	1.401 (x)
$^1B_3^+$	$V_{44'}$ (87.6) $V_{15'}$ (3.6)	7.46	0.499 (y)	7.70	0.428 (y)

Table 2. Calculated excitation energies and oscillator strengths for the twisted and planar biphenyl.

ing of all the singly excited states. Their results agree a little worse with experiment than ours. Thus we thought it important to study the CI effect within the same theoretical framework as previously [19]. The geometry of the molecule was assumed that which follows from the self consistent steric method [22]. Mataga-Nishimoto formula was used for Coulomb integrals, $\gamma_{ij} = 14.402(1.328 + R_{ij})^{-1}$. The resonance integrals were approximated by the exponential formula:

$\beta_{ij} = -2.318 \exp[-2.1888(R_{ij} - 1.397)] \cos \Theta_{ij}$.

Calculating γ_{ij} we neglected the correction factor for the twisting of orbitals [19]. This factor, although important in some cases, appeared to be negligible in this particular case.

The results of these SCF CI calculations are listed in Table 2. In column 1 we give the symmetry species of the excited state for $\Theta = 40° 21'$, in column 2 the principle two contributions, in column 3 the excitation energies and in column 4 the calculated oscillator strengths and polarization. In the last two columns the calculated spectroscopic data of the planar molecule are given. Occupied molecular orbitals are numbered downwards (1, 2, ...) and excited orbitals upwards (1′, 2′, ...).

The present calculations lead to results which are rather close to the previous ones [19]. For this reason we do not repeat the detailed discussion of the spectrum. There seems to be also no need to compare our results with those obtained by TINLAND [28] with the β-variable approximation for $\Theta = 0°$, 10°, 20° and 30°. However, we would like to compare our results with the results obtained by IMAMURA and HOFFMANN [26]. Looking at Fig. 10 one notes that our results are still better than theirs, particularly considering the oscillator strengths. In addition we note that the other authors seem not to have obtained several allowed transitions. It is somewhat surprising as they have also included all singly excited states. Besides, we do not understand the origin of the different from zero value of f for the lowest two states, which correspond apparently to transitions to minus states.

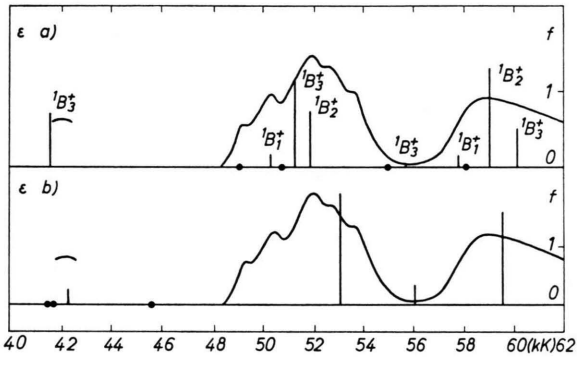

Fig. 10. A comparison of the calculated and observed spectrum of biphenyl in the gaseous phase. a) Present results, b) results obtained by IMAMURA and HOFFMANN.

Thus we would like to confirm the assignments made four years ago.

7. Final Comments

The selfconsistent steric analysis in its present form suffers some limitations. It includes all significant deformations of the molecular skeleton, even

in the case when the twisting angle Θ is kept constant. On the other hand, however, it deals with a one-electronic Hamiltonian. For this reason the method considers triplet and singlet excited states on the same basis. Besides, in the case of the excited state, one should better introduce a slightly different value of the resonance integral β_0.

It is a straightforward matter, in principle, to combine the method with the SCF CI method, without all these limitations. However, it would require a computer with a larger memory than that we could use.

Already after completing this work we have found that for large twistings ($\Theta \sim 90^\circ$) an asymmetric conformation of the excited state and the ionic state is more stable, with the excitation or charge, for example, being localized on one phenyl ring only. However, this effect requires still investigation. It does not seem to change the conclusions drawn in the present work.

The program was written in ODRA-ALGOL and can be sent on request.

Berechnung der Elektronendichte von Alkanen nach dem S-DIAG-Verfahren zur Interpretation chemischer Verschiebungen

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Mit dem nichtempirischen Verfahren S-DIAG werden unter Verwendung sphärischer Gauß-Funktionen die Elektronendichten an den Kohlenstoffkernen und an den Protonen einiger Alkane berechnet. Im Gegensatz zu semiempirischen Verfahren liefern die hier berechneten Elektronendichten im Gang vollkommene Übereinstimmung mit den gemessenen chemischen Verschiebungen.

Das Verfahren S-DIAG [1] unterscheidet sich von allen anderen quantenchemischen Verfahren zur Berechnung von Molekülen dadurch, daß es bei der Berechnung der Wellenfunktion auf keine Energievariation angewiesen ist. Diese vorteilhafte Eigenschaft gilt dann, wenn die nichtlinearen Parameter des Basissatzes bereits einmal an kleineren Teilsystemen des Moleküls durch Energievariation, die ebenfalls innerhalb des S-DIAG-Verfahrens vorgenommen werden kann, bestimmt worden sind.

Eine Gegenüberstellung verschiedener Verfahren soll dieses Vorgehen noch deutlicher machen. Bei der Berechnung eines Alkanmoleküls etwa nach der CNDO- oder EHMO-Methode werden die nichtlinearen Parameter der Kohlenstoff-Funktionen vom freien C-Atom übernommen, während die linearen Parameter durch Variation der Gesamtenergie des Moleküls berechnet werden. Bei der S-DIAG-Methode dagegen werden die nichtlinearen Parameter für Alkane am Äthan einmal durch Minimisierung der Gesamtenergie berechnet, so daß die Wellenfunktion für ein beliebiges Alkanmolekül dann nur noch von seiner vorgegebenen Geometrie abhängt, ohne daß die Gesamtenergie berechnet werden muß. Dadurch ist dieses Verfahren unter allen anderen das schnellste und bezüglich der Molekülgröße das geeignetste, wenn es darum geht, Elektronendichten oder Populationen zu berechnen.

Das Konzept der hier verwendeten Basisfunktionen, der reinen Gauß-Funktionen, ist schon seit langem bekannt [2]. Trotzdem sollen hier noch einmal einige wesentliche Merkmale, die die Darstellung der Elektronendichte betreffen, herausgestellt werden. Für diejenigen Verfahren, die als Basisfunktionen Slater-Funktionen verwenden, wie etwa CNDO- oder EHMO-Verfahren, bestehen Moleküle qualitativ gesagt aus einzelnen Atomen (LCAO-Bild). Bei der Verwendung reiner Gauß-Funktionen zeigt sich aber, daß es ein aus energetischen Gründen besseres Bild gibt. Mit Hilfe der FSGO-Darstellung (floating spherical Gaussian orbitals) erhält man nämlich das Ergebnis, daß ein Molekül hinsichtlich seiner Elektronenverteilung besser als aus Atomrümpfen und Bindungen bestehend aufgefaßt wird [3].

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[2] H. PREUSS, Z. Naturforsch. **11 a**, 823 [1956].
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