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Steric Effect in Biphenyl According to SC LCAO MO and Limited CI Methods

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The conformation of an isolated biphenyl molecule has been analyzed with the use of a combination of the Coulson and Senent and the SC LCAO MO methods. The predicted angle between the planes of the two benzene rings and all the predicted bond lengths are in very good agreement with experiment. Using the SC LCAO MO and limited CI methods the electronic spectrum has been reinterpreted; it has been shown that the recent interpretations given by Gondo and independently by Grinter need a few corrections.

Die Konformation des isolierten Biphenyls wurde mit Hilfe einer Kombination der Coulson-Senent- und der SC-LCAO-MO-Methode analysiert. Der berechnete Winkel zwischen den Benzolebenen und alle berechneten Bindungslängen stimmen sehr gut mit dem Experiment überein. Mit Hilfe der SC-LCAO-MO und der beschränkten CI-Methode wurde auch das Spektrum neuinterpretiert; es wurde gezeigt, daß die Interpretationen, die von Gondo und Grinter gegeben wurden, zum Teil korrigiert werden müssen.

La conformation d'une molécule isolée de biphényle a été analysée à l'aide d'une combinaison des méthodes de Coulson-Senent et des orbitales moléculaires SCF LCAO. L'angle prévu entre les plans des deux cycles benzéniques et toutes les longueurs de liaisons prédites sont en très bon accord avec l'expérience. En utilisant les méthodes SCF LCAO MO et IC limitée, le spectre électronique a été réinterprété; nous avons montré que les interprétations récentes données par Gondo et indépendamment par Grinter nécessitent quelques modifications.

Introduction

The steric effect in overcrowded molecules has been the subject of several papers [*1, 5, 9, 10, 12, 17, 31, 35*]. Of closest interest to us, however, is the paper by Coulson and Senent [*11*] in which out-of-plane coordinates have been introduced which allow one to neglect with a surprisingly good approximation the interaction force constants [*7, 11*]. With this approach a good deal of information for several overcrowded hydrocarbons has been obtained [*5, 8, 10*]. In all these calculations a hard sphere model for non-bonded hydrogen atoms has been used, an assumption which was criticized later by Coulson and Haigh [*9*]. However, their arguments seem to be of smaller importance in the case of a calculation of the geometry of a molecule like biphenyl; in an isolated molecule like this there do not exist any forces which could distinctly reduce the van der Waals distance between non-bonded hydrogen atoms. Therefore, discussing the twisting of benzene rings in biphenyl we have decided to use the original approach, taking $R_{\mathrm{H} \ldots \mathrm{H}} = 2.40$ Å. In one detail, however, we have decided to modify Coulson and

SENENT's method. The change of the energy of the bond $r - s$, due to twisting, has been assumed to be equal to the change of the appropriate π-electron bond energy, $2p_{rs}\,\beta_{rs}\,(\cos\Theta_{rs} - 1)$.

The purpose of this work was not only to explain the observed bond lengths and the angle between the two rings in biphenyl. It was found [*14*, *15*, *30*] that results obtained with the SC LCAO MO method correlate much better with experimental data than it was possible in the case of the standard Hückel method. However, just in the case of biphenyl a larger deviation was observed than usually. One could well expect that SC LCAO MO calculations for a properly twisted biphenyl would yield better results.

Whatsoever, no one-electron theory can yield a completely satisfactory interpretation of the UV spectrum. Semiempirical calculations involving a two-electronic hamiltonian have been carried out for biphenyl by LONGUET-HIGGINS and MURRELL [*23*], STEWART [*32*], IGUCHI [*19*], GONDO [*16*] and GRINTER [*18*]. GONDO has shown that the accuracy of all the earlier calculations [*19*, *23*, *32*] was very poor. He himself was using an extension of the Pariser and Parr method [*28*, *27*], with a somewhat arbitrary interpolation formula for Coulomb integrals of the type $(\sigma\sigma\,|\,\pi\pi)$ and $(\pi\pi\,|\,\bar{\pi}\bar{\pi})$. His calculations were based on simple symmetry orbitals and the limited configuration interaction method. However, he discussed transitions as high as 8.60 eV which lie only 1.3 eV or less lower than the lowest doubly excited state according to his estimation. For this reason we expected his basis set to be rather unsuitable for these calculations. Certainly, a definitely better set would consist of SCF MO's [*29*]. We know from our experience that not much the worse set consists of the SC LCAO MO's. Therefore we repeated the limited CI calculations, basing on our SC LCAO orbitals. We have used, however, a partly different approach from GONDO's; we have used the Mataga-Nishimoto formula for the Coulomb integral [*24*], corrected, however, for twisting of the $2p_z$-orbitals. It will be seen that the agreement with experiment will be improved significantly in this way.

In the course of completion of this article for publishing we came upon a new paper published by GRINTER [*18*], in which CI calculations for the twisted (45° and 90°) biphenyl are reported. These calculations were based on Hückel-type orbitals and a configuration interaction with all singly excited states. Coulomb integrals for non-neighbours were estimated basing on the charged-sphere approximation. For neighbours a Pariser-Parr type interpolation formula was used, corrected for the twisting effect. The resonance integral β_{rs} was assumed to be proportional to the overlap integral. This might be a weak point of his theory, because zero differential overlap is assumed elsewhere. Zero differential overlap, however, is based on orthogonalized atomic orbitals, and these are localized much stronger than the original atomic orbitals. — It will be seen that also GRINTER's results are inferior to ours, even qualitatively.

Fusion of SC LCAO MO and Coulson and Senent's methods

The application of the SC LCAO MO method to planar aromatic and conjugated hydrocarbons has been described elsewhere [*14*]. Therefore we recapitulate only the notation and basic assumptions. We assume no overlap of atomic orbitals,

$S_{ij} = 0$ for $i \neq j$, equality of all Coulomb integrals α_i for Carbon atoms. We consider resonance integrals only between nearest neighbours, assuming the exponential form established by Gołębiewski and Nowakowski [*14*]:

$$\beta_{ij} = \beta_0 \exp\left(-4.0 \cdot \Delta R_{ij}\right) \tag{1}$$

where $\Delta R_{ij} = R_{ij} - 1.397$ Å and β_0 is the resonance integral for benzene. We require the calculated mobile bond orders p_{ij} to satisfy the linear equations:

$$R_{ij} = 1.517 - 0.180\, p_{ij}\,. \tag{2}$$

The calculations are carried out iteratively starting with Hückel orbitals until selfconsistency is achieved.

In biphenyl the central bond is twisted. Let's denote the appropriate angle by Θ. For this bond we have modified the assumption (1), taking

$$\beta_{ij}^{\Theta} = \beta_{ij} \cos \Theta_{ij}\,. \tag{3}$$

The angle Θ could be taken either from experiment or from some theoretical speculations. We have chosen the second way, requiring selfconsistency in the following sense.

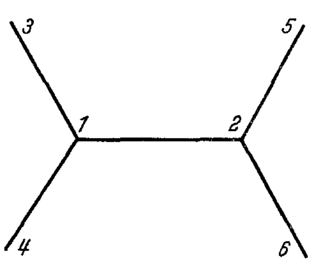

Fig. 1

Let's assume that all the bond angles in biphenyl are equal to 120°. According to Coulson and Senent [*10, 11*] we can define coordinates which apart from certain scale factors are equivalent to:

a_1 = distance of atom 1 from the plane of its three neighbours (Fig. 1);

b_{12} = angle between the projections on to a plane perpendicular to 1 – 2 of two vectors, one of which is perpendicular to the plane 3 – 1 – 4 and the other to the planes 2 – 5 – 6 (Fig. 1).

Then

$$a_1 = A_{41}(z_4 - z_1) + A_{31}(z_3 - z_1) + A_{21}(z_2 - z_1) \tag{4}$$

$$b_{12} = A_{31}(z_3 - z_1) - A_{41}(z_4 - z_1) - A_{52}(z_5 - z_2) + A_{62}(z_6 - z_2) \tag{5}$$

where

$$A_{ij} = 1.40/R_{ij}$$

and

$$\Theta_{12} = -\left(1.40\sqrt{3}\right)^{-1} b_{12}\,. \tag{6}$$

Let's denote the force constants corresponding to coordinates a_i and b_{ij} by K_i^a and K_{ij}^b respectively. They certainly differ from molecule to molecule and in general even within the molecule. For ethylene $K^b = 0.0947 \cdot 10^5$ dyne/cm, for benzene $K^b = 0.0569 \cdot 10^5$ dyne/cm and $K^a = 0.1254 \cdot 10^5$ dyne/cm*. Clearly the K^a constant is relatively insensitive and therefore in all the calculations for biphenyl the benzenic value has been taken. As regards the K_{ij}^b force constants, they should be given by the π-electron theory:

$$p_{ij}\,|\beta_{ij}| \cdot \Theta_{ij}^2 = \tfrac{1}{2} K_{ij}^b\, b_{ij}^2\,. \tag{7}$$

In the case of the Hückel method, however, this formula gives a poor estimation of K_{ij}^b, the relation between the experimental values of K_{ij}^b and the mobile bond orders p_{ij} being rather

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* Coulson and Senent's values of K_{ethylene}^b, K_{benzene}^b and K_{benzene}^a differ from these values; their ethylenic value corresponds to the (less reasonable) choice: $A_{31} = A_{41} = A_{52} = A_{62} = 1$, the same as in benzene. As regards our benzenic values, they have been chosen by a least squares procedure to reproduce in a best possible way Shimanouchi's force constants [*34a*] in terms of two constants, K^a and K^b.

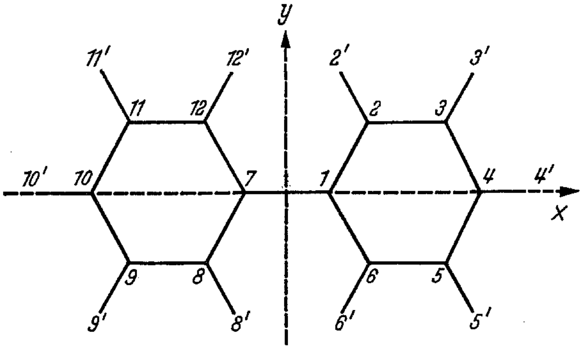

Fig. 2. Indices of atomic positions in biphenyl

non-linear. Therefore a graphical interpolation curve has been used in this case. Owing to the limited number of experimental values of K^b_{ij} the estimated values of K^b_{ij}'s of biphenyl are somewhat arbitrary. In the case of the SC LCAO MO method, on the other hand, relation (7) is quite satisfactory, yielding $\beta_0 = -1.403$ eV or equivalently, for small torsions,

$$K^b_{ij} = 0.0768 \cdot 10^5 \, p_{ij} \frac{\beta_{ij}}{\beta_0} \, . \tag{8}$$

The procedure was then as follows. Starting with SC LCAO molecular orbitals for the planar biphenyl the bond order p_{17} (Fig. 2), and hence the bond length R_{17} and the resonance integral β_{17} have been calculated. In the next step the deformation energy

$$V = 2p_{17}\beta_{17}(\cos\Theta_{17} - 1) + \tfrac{1}{2} K^b_{\text{benzene}} \sum{}' b^2_{ij} + \tfrac{1}{2} K^a_{\text{benzene}} \sum a^2_i \tag{9}$$

has been minimized, where the first sum runs over all bonds $i - j$ in biphenyl except the central bond, $1 - 7$, the second sum runs over all Carbon atoms and the distance between the hydrogen atoms $2' - 12'$ and $6' - 8'$ is kept constant (2.40 Å). Taking into account the angle Θ_{17}, found in this way, and all the bond lengths R_{ij} of this iteration a set of new resonance integrals has been calculated with the use of Eqs. (1) to (3). Then, solving the secular problem, new bond orders p_{ij} and hence also new bond lengths have been calculated. A subsequent minimalization of Eq. (9) lead then to a corrected value of the twisting angle, Θ_{17}. This procedure was repeated several times, to obtain selfconsistency.

The procedure within the Hückel approximation was slightly different. The first term in Eq. (9) was approximated by the harmonic term $\frac{1}{2} K^b_{17} b^2_{17}$, where K^b_{17} was found graphically as already explained. For obvious reasons this procedure is much less accurate than the preceding one.

Results of the SC LCAO MO Method

The calculated twisting of the benzene rings in biphenyl and all the calculated bond lengths are given in Tab. 1. The experimental value of Θ_{17} is 42° [*2*]. The bond length R_{17} in the isolated molecule is equal to 1.48 Å, the remaining C — C bonds being equal to 1.40 Å [*2*]. We note that almost the same values are predicted by the SC LCAO MO method.

Previous structural calculations of biphenyl were not so successful. Adrian [*1*], using a soft model of hydrogen atoms, predicted the twisting to lie within the range 20° — 30°. Samoilov and Dyatkina [*31*] suggested the value $\Theta_{17} = 30°$.

Only Suzuki [*35*] has obtained the proper range, 40° – 43°. He considered, however the angle as a parameter chosen to fit the calculated *p*-band to the experimental one. It was then not a direct calculation of the structure. Besides, no predictions of bond lengths have been made.

It is known that in crystal biphenyl is planar [*36*], and the central bond is equal to 1.507 Å. This value, however, cannot be compared with the value 1.463 Å from Tab. 1, because in the planar case no steric forces have been taken into account.

Interesting is also a comparison of predicted and observed transition energies for the *p* and *β* bands. Both, HMO and SC LCAO MO theories underestimate the transition energies in the case of the planar model, both yield much better results for the twisted one. From the two theories, however, the SC LCAO MO theory gives again a better agreement with experiment.

In the case of the charge transfer band in solution the agreement with experiment is not so good. Here, the calculations carried out for the planar model give better results, the accuracy being the same for the SC LCAO MO theory and the Hückel theory.

In the case of the first ionization potential, *I*, the difference between the predicted and observed value is rather large, if the twisted model is taken into account. May be the reason is that in the ionized state a strong change of the

Table 1. *Predicted and observed properties of biphenyl*

Property	Experimental value	Planar model		Twisted model	
		HMO	SC LCAO MO	HMO	SC LCAO MO
Θ_{17}	$42^{\circ h}$	—	—	41 – 43°	41° 50′
R_{17} (Å)	1.48^{h}	1.450	1.463	1.466	1.479
R_{12} (Å)	1.40^{h}	1.406	1.404	1.402	1.400
R_{23} (Å)	1.40^{h}	1.395	1.395	1.395	1.396
R_{34} (Å)	1.40^{h}	1.398	1.398	1.398	1.397
p_{17}	—	0.370	0.299	0.286	0.212
p band (in kK)	42.1^{a} 40.3^{b}	37.3	37.2	39.8	40.6
β band (in kK)	51.9^{c} 49.7^{d} 49.2^{e}	48.0	48.9	49.5	50.8
C.T. band (kK)	20.0^{f}	20.7	19.3	22.4	21.3
I (in eV)	8.27^{g}	—	8.36	—	8.65

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[a] absorption maximum in vapour [*35*, *25*]

[b] absorption maximum in solution [*35*]

[c] absorption maximum in vapour [*4*]

[d] absorption maximum in solution [*35*]

[e] absorption onset in vapour [*4*]

[f] absorption maximum of the charge transfer band of the π-complex with tetracyanoethylene [*26*]

[g] taken from Ref. [*33*]

[h] according to electron diffraction [*2*]

Table 2. SC LCAO MO *energies and orbitals for* $\Theta_{17} = 41^\circ\ 50'$

Orbital energy (in β_0)	Symmetry	c_1	c_2	c_3	c_4
2.10875	b_1	0.37160	0.29527	0.25449	0.24086
1.92478	b_3	0.22173	0.27622	0.31142	0.32292
1.17203	b_1	0.40613	0.13028	−0.24790	−0.42215
1.00344	a_1	0	0.35355	0.35355	0
1.00344	b_2	0	0.35355	0.35355	0
0.81810	b_3	0.38446	0.26371	−0.16371	−0.39938

structure takes place (indeed, p_{17} is then equal to 0.07). On the other hand the observed value of I is said to correspond to a $0 \to 0$ transition.

We recall that all the predicted properties in Tab. 1 (except Θ_{17}) follow from correlation curves which were so successful in the case of many other alternant conjugated hydrocarbons [*14, 15, 30*].

The self consistent orbital energies and LCAO coefficients of molecular orbitals, obtained with the SC LCAO MO method for $\Theta_{17} = 41^\circ\ 50'$, are given in Tab. 2. In the table only non-equivalent LCAO coefficients are given, the other ones following from symmetry properties. According to our notation a_1 represents a totally symmetric orbital in D_2, b_1 represents an orbital symmetric in C_z, b_2-symmetric in C_x, b_3-symmetric in C_y, where C_x, C_y and C_z are rotations by 180° around the x axis, y axis and z axis respectively (Fig. 2).

Limited Configuration Interaction Method for Twisted Biphenyl

As already stated we have used a straightforward modification of the Pariser and Parr method. Let us outline our approach in short.

The enumeration of Carbon atoms in biphenyl is that given in Fig. 2. The indices of bonding molecular orbitals run in the order 1, 2, . ., 6 from the least bonding to the most bonding one. The antibonding molecular orbitals are enumerated by 1′, 2′, . ., 6′ in the order of increasing energy. Molecular orbitals 2 and 3, and similarly 2′ and 3′ are accidently degenerate. To carry out the configuration interaction we need LCAO coefficients of appropriate molecular orbitals. For Hückel orbitals they are given in Dictionaries [*14*]. The coefficients for planar biphenyl have been taken from earlier computations (unpublished results of Ref. [*34*]). SC LCAO coefficients for the twisted biphenyl are given in Tab. 2.

In all the calculations we have made use of a zero differential overlap. The penetration integrals have been neglected. All Coulomb integrals have been calculated with the use of the Mataga-Nishimoto formula [*24*]:

$$\gamma_{ij} = 14.402\ (1.328 + R_{ij})^{-1}\ \mathrm{eV} \tag{10}$$

where R_{ij} is the distance between atoms i and j in Å. However, we have corrected this formula for the non-planarity effect. With this purpose we have taken the ratio of the corrected and uncorrected Mataga-Nishimoto integral to be the same as follows from the charged sphere model [*28*]:

$$(\gamma_{ij})_{\mathrm{corr.}} = \frac{14.402}{1.328 + R_{ij}} \left(\frac{2}{R_{ij}} + \frac{2}{R_{ij}^2 + 4a^2} \right)^{-1} \times$$
$$\times \sum_{k=1}^{2} \sum_{l=1}^{2} \{ R_{ij}^2 + a^2 [\boldsymbol{h}_i + (-1)^k \boldsymbol{h}_j]^2 + (-1)^l\, 2a\, R_{ij}\, \boldsymbol{e}_{ij} \cdot [\boldsymbol{h}_i + (-1)^k \boldsymbol{h}_j] \}^{-1/2} \tag{11}$$

where a is the radius of the charged spheres, $\boldsymbol{e}_{ij}$ is a unit vector directed from atom i to atom j and $\boldsymbol{h}_i$ is a unit vector perpendicular to the ring plane which includes the atom i. For a distance larger than 4 Å and a desired accuracy of not less than third decimal place Eq. (11) takes the following form:

$$(\gamma_{ij})_{\text{corr.}} = \frac{14.402}{1.328 + R_{ij}} \left\{1 + \frac{1.5\,(a/R_{ij})^2\,[(\boldsymbol{e}_{ij}\cdot\boldsymbol{h}_i)^2 + (\boldsymbol{e}_{ij}\cdot\boldsymbol{h}_j)^2]}{1 - a/R_{ij}{}^2}\right\}. \tag{12}$$

This asymptotic form allows one to evaluate the radius a; if the correction factor has to be the same as for Slater-type orbitals, then $a = 0.56$ Å.

For the resonance integral β_{ij} we have assumed the exponential form

$$\beta_{ij} = -2.3697 \exp\left[-2.1888\,(R_{ij} - 1.397)\right] \cos\Theta_{ij}\ \text{eV}. \tag{13}$$

The parameters in this formula have been fitted by a comparison of observed and calculated transition energies in ethylene (with CI with the important doubly excited state) and in benzene (without CI).

All the bond angles were assumed to be equal to 120°. For the bondlengths inside the rings we took 1.40 Å, for the long central bond the value which was found theoretically (1.45 Å for the Hückel method, 1.463 for SC LCAO MO method and a planar system, 1.480 for CS LCAO MO method and the twisted system).

We have mixed all configurations which lie not higher than $|2.9\,\beta_0| \sim 6.87$ eV from the ground state.

The oscillator strengths have been calculated in a standard way [*13*].

Let us remind that the limited CI method based on Mataga-Nishimoto's formula has been known to be very useful. For example, Koutecky et al. applied this method successfully to 20 benzenoid hydrocarbons [*21*, *22*] and 45 non-alternant hydrocarbons [*20*]. Therefore the method seems to be rather reliable in principle. However, they used a constant value of the resonance integral −2.318 eV, and Hückel-type molecular orbitals. Clearly for this reason their results were less satisfactory in cases, in which a large variation of bond lengths had to be expected.

The results of our calculations, carried out for three different cases, are given in Tab. 3. The symmetry notation is the same as Gondo's [*16*], but different from that used by Grinter [*18*] (Grinter has not taken into account the + and − notation, useful for alternant hydrocarbons). In column 2 the zeroth order wave function is given, were $V_{ij'}$ means a singlet wave function in which one of the electrons of the ground state, occupying the i-th bonding orbital, is promoted to the j'-th antibonding orbital. In the next column the polarization of the transitions is given. In the three remaining columns we give the calculated transition energies in eV and oscillator strengths in brackets: a) for the planar molecule and Hückel-type basis; b) for the planar molecule and the SC LCAO MO basis; c) for the twisted molecule $\Theta_{17} = 41°\,20'$ and the SC LCAO MO basis.

Very instructive is a comparison with experiment, shown in Fig. 3. Position and $\varepsilon_{\max}$ of the conjugation band is taken from Suzuki's work [*35*]: $\Delta E = 42\,100$ cm^{-1}, $\varepsilon_{\max} = 19\,000$ in vapour. The experimental curve from 46 kK upwards is an enlargement of the spectrum published by Carr and Stuecklen for vapour [*4*]. These authors do not give the intensity scale. However, Suzuki quotes the transition energies and extinctions for three bands measured in 95% ethanol: 40.3 kK ($\varepsilon_{\max} = 18\,000$), 49.0 kK ($\varepsilon_{\max} = 42\,000$) and 49.7 kK ($\varepsilon_{\max} = 32\,000$). These data

Table 3. *Calculated transition energies and oscillator strengths according to the limited* CI *method*[a]

Final state	Zeroth order wave function	Polarization	Planar case		Twisted case
			HMO basis	SC LCAO MO	SC LCAO MO
${}^1B_2^-$	$V_{12}' - V_{21}'$	—	4.64 (0)	4.66 (0)	4.71 (0)
${}^1B_1^-$	$V_{13}' - V_{31}'$	—	4.70 (0)	4.78 (0)	4.73 (0)
${}^1B_3^+$	V_{11}'	$\parallel$	5.04 (1.08)	5.11 (0.90)	5.21 (0.71)
${}^1A_1^+$	$V_{23}' + V_{32}'$	—	not included		6.12 (0)
${}^1B_1^+$	$V_{13}' + V_{31}'$	$\perp$	6.12 (0)	6.16 (0)	6.27 (0.15)
${}^1B_3^+$	$V_{22}' + V_{33}'$	$\parallel$	6.44 (1.42)	6.45 (1.40)	6.40 (1.20)
${}^1B_2^+$	$V_{12}' + V_{21}'$	$\perp$	6.42 (0.94)	6.44 (0.97)	6.46 (0.82)
${}^1A_1^-$	$V_{14}' - V_{41}'$	—	not included		6.54 (0)
${}^1A_1^-$	$V_{23}' - V_{32}'$	—	not included		6.95 (0)
${}^1B_3^+$	$V_{22}' + V_{33}'$	$\parallel$	6.95 (0.02)	6.94 (0.04)	6.95 (0.004)
${}^1B_1^-$	$V_{24}' - V_{42}'$	—	7.02 (0)	6.98 (0)	6.96 (0)
${}^1B_2^-$	$V_{34}' - V_{43}'$	—	7.05 (0)	6.98 (0)	6.97 (0)
${}^1A_1^+$	$V_{14}' + V_{41}'$	—	not included		7.27 (0)
${}^1B_1^+$	$V_{24}' + V_{42}'$	$\perp$	7.36 (0)	7.28 (0)	7.28 (0.13)
${}^1B_2^+$	$V_{34}' + V_{43}'$	$\perp$	7.17 (1.26)	7.44 (1.32)	7.42 (1.21)
${}^1B_3^+$	V_{44}'	$\parallel$	7.96 (0.07)	7.78 (0.15)	7.58 (0.43)
${}^1B_3^+$	$V_{25}' + V_{52}'$	$\parallel$	not included		8.71 —

[a] Transition energies are given in eV; the oscillator strengths are given in brackets.

served us as a connection between the two separate experimental works on vapours; we have assumed the same proportionality of intensities in vapour and in the solution. The calculated oscillator strengths are drawn in Fig. 3 in an arbitrary scale; the scale was matched to fit the calculated oscillator strength of one of the transitions to the experimental peak. The position of all the calculated transitions, both allowed and forbidden, are given also below the spectrum. We note that due to vibration borrowing also the forbidden transitions are observed usually in the spectrum.

We see from Fig. 3a that the agreement with experiment obtained by GONDO is relatively poor. The intensity ratios are not bad, but band 1 is too low by about $1\frac{1}{2}$ kK and the band complex 2 to 6 has a maximum higher than expected by about 6 kK. Besides, it seems rather unlikely that the finestructure of this very broad and intensive band complex is entirely due to vibration excitation. However, according to GONDO, only one allowed and one forbidden transition fall into this region.

GRINTER's results [*18*] are in some respects better than GONDO's, in other worse (Fig. 3b). The calculated position of band 1 is too high by about 1.6 kK. The band complex 2 to 6 is reproduced by two strongly allowed transitions and 2 to 3 forbidden ones. Neithertheless the reproduction of the shape of this band complex is not satisfactory. Very poor are his results for band 7; there falls only one forbidden transition into this range, according to his calculations.

Our results are definitely better (Fig. 3c). It follows that practically all peaks in the range from 41 to 62 kK can be explained by purely electronic transitions and the calculated intensity ratios mirror nicely the observed shapes. *Band 1* coincides almost exactly with the calculated ${}^1A_1^- \to {}^1B_3^+$ transition. The most intensive, *band 4*, coincides almost exactly with the calculated ${}^1A_1^- \to {}^1B_3^+$ transition. *Band 5* can be assigned as ${}^1A_1^- \to {}^1B_2^+$ transition, the calculated position

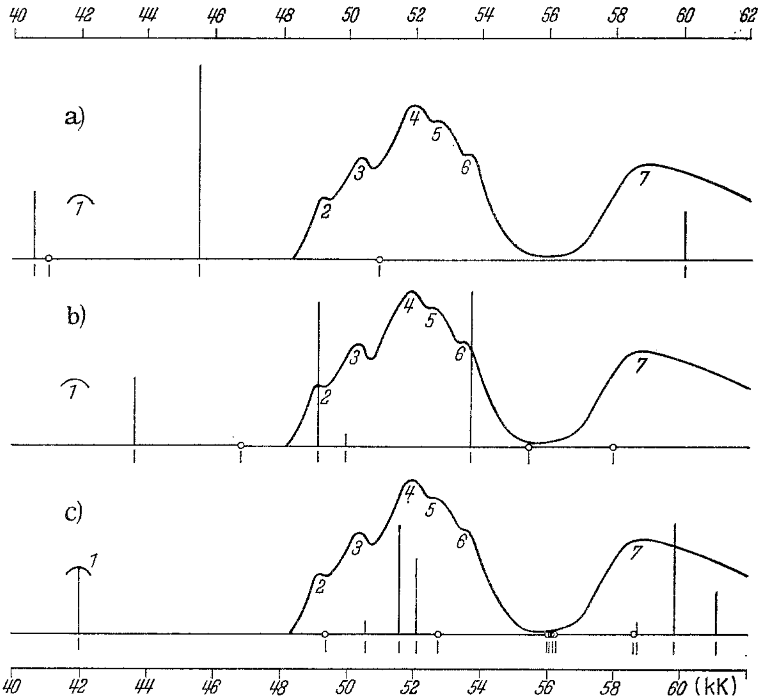

Fig. 3. Comparison of observed and calculated electronic spectrum of biphenyl: a) according to GONDO's calculations; b) according to GRINTER's calculations; c) according to present calculations

being too low by only 0.5 to 0.6 kK, but the intensity ratio being approximately the proper one. Third in intensity in this band complex is certainly *band 3*, both according to experiment (after correction for overlap of neighbouring bands) and theory; the predicted position is too high by about 0.2 to 0.3 kK only. *Band 2* of a relatively low intensity seems to correspond, according to these calculations, to a forbidden transition ${}^1A_1^- \rightarrow {}^1A_1^+$, which coincides almost exactly with the observed maximum. Less satisfactorily explained is *maximum No. 6*. There are three possibilities: a) there is a forbidden transition predicted by 0.8 kK lower than this maximum; however, it is hardly to believe that vibration borrowing in the case of a ${}^1A_1^- \rightarrow {}^1A_1^-$ transition could explain the observed intensity of this band; b) vibration excitation; c) there is a weak allowed transition ${}^1A_1^- \rightarrow {}^1B_3^+$, lying however too high by 2.3 kK; it is likely that configuration interaction with doubly excited configurations would shift this band towards lower frequencies and cause a gain of intensity. Indeed, such a possibility follows from a comparison made for the *band 7*. Although also in this case the shape of this broad band is nicely reproduced by our calculations, the calculated maximum is too high by about 1.1 to 1.2 kK. Obviously these highly excited states will mix much more with the doubly excited states than the preceding ones. There are still three other forbidden transitions which fall in the region around 56 kK; all they are (—) → (—) transitions and therefore vibration borrowing should be of a smaller importance. Neithertheless even in this range the observed intensity does not fall down to zero.

We do not claim that our results are final. It is, however, hardly to believe that much a better agreement which experiment could be achieved within the framework of a semiempirical π-electron theory. We wish, however, to add two final remarks. i) the use of SC LCAO MO basis is almost as good as of SCF LCAO MO basis; the configuration interaction in biphenyl caused a shift of the ground state by as little as 0.01 eV; ii) from the semiempirical approaches to overcrowded hydrocarbons: Longuet-Higgins and Murrell's [*23*], Stewart's [*32*], Iguchi's [*19*], Gondo's [*16*], Grinter's [*18*] and ours, our approach seems to be the most suitable one.

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