

A SELFCONSISTENT CONFORMATIONAL ANALYSIS OF CONJUGATED AND AROMATIC MOLECULES WITH A STERIC HINDRANCE

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A new, selfconsistent conformation analysis is developed for conjugated and aromatic molecules with a steric hindrance. The method is a generalization and combination of the SC LCAO MO and the Coulson, Senent and Haigh methods. The optimal choice of the van der Waals interactions for the pairs H...H, H...C and C...C is discussed, taking biphenyl as a reference compound.

1. Introduction

Determination of the structure of a molecule is one of the principle tasks of quantum chemistry. In this article we shall deal with a narrow part of this general problem; we will consider organic conjugated and aromatic systems which cannot be strictly planar because of a steric hindrance.

No *ab initio* calculations are known for the systems in question and semiempirical methods are used, as a rule. By far the most of them are based on purely harmonic forces which counteract the deformation from the idealized form and on van der Waals forces which behave in the opposite way (Westheimer, Mayer 1946; Westheimer 1947; Hill 1946, 1948a, b; Hendrickson 1961, 1962, 1964; Wiberg 1965; Jacob *et al.* 1967; Allinger *et al.* 1967; Kitajgorodsky 1961; Kitajgorodsky, Dashevsky 1967a, b; Coulson and Senent 1955a, b; Coulson and Haigh 1963 and others). More recently also the extended Hückel method has been used with this purpose in mind (Hoffmann 1963, 1964a, b, c, 1966a, b; Hoffmann *et al.* 1968, 1969; Van Dine and Hoffmann 1968; Adam *et al.* 1968), as well as the CNDO method (Pople *et al.* 1965a, b, 1966; Tinland 1968) and the semiempirical SCF CI method (Parr 1963; Beveridge and Jaffe 1965; Wettermark and Schor 1967; Imamura and Hoffmann 1968; Tinland 1968 a, b).

All these methods show merits and demerits. Mechanical models are simple, but they work properly in the case of small deformations only. Among them the Coulson, Senent (1955 a, b) method is to be recommended, particularly in the form extended by Coulson and Haigh (1963). Occasionally the pure mechanical model has been used for molecules with

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a large deformation like that in biphenyl (Dashevsky and Kitajgorodsky 1967). However, extensions of this kind give rather a rough estimate of the real structure and the physical information gained is usually scarce. The extended Hückel and CNDO methods, on the other hand, are very laborious. Besides, their findings are not always adequate. An example of this is Tinland's analysis of biphenyl by the CNDO method (1968). He has shown that a minimum of energy is obtained for a twisting angle equal to 90° , what compares rather poorly with the experimental value, 42° .

In what follows we develop a new approach. Basically it is a modification and combination of both the Coulson and Haigh method (1963) and the Longuet-Higgins and Salem method (1959). Semiempirical parameters in our approach will be optimized for the particular case of biphenyl.

2. Brief outline of Longuet-Higgins and Salem's theory

Let q_t be the π -electronic population at atom t , p_i the mobile bond order for bond i , α_t the Coulomb integral for atom t and β_i the resonance integral for the bond i . Neglecting overlap integrals over $2p_\pi$ -orbitals and all resonance integrals except for next neighbours, and assuming additivity of energies of σ -bonds, one obtains what follows:

$$E_{\text{tot}} = \text{const} + \sum e_i(r_i) + 2 \sum p_i \beta_i + \sum q_t \alpha_t \quad (1)$$

where r_i is the bond length of bond i and e_i is its σ -electronic energy. The value of p_i and q_t follow from the appropriate eigenvalue equation and depend thus on the α_t 's and β_i 's. However, yet another relation between these quantities is postulated. It is assumed that

$$\beta_i = \beta_{0i} \exp[-x(r_i - 1.397)] \quad (2)$$

where

$$r_i = a - bp_i^2, \quad (3)$$

r_i is measured in Ångströms, and β_{0i} , a and b depend only on the nature of the atoms bonded by bond i .

Following the ideas of Wheland and Mann (1949) one could similarly put

$$\alpha_t = \alpha_{t0} + \omega(1 - q_t) \quad (4)$$

where α_{t0} depends only on the nature of the atom t .

A selfconsistency of all these equations is obtained using an iterative procedure, the method being called the SC LCAO MO method for this reason (Gołębiewski and Nowakowski 1964). It has been shown that with these conditions the σ -electronic energy of the bond i follows from Eq. (5):

$$e_i(r_i) = 2 \left(\frac{1}{bx} - P_i \right) \beta_i \quad (5)$$

where P_i follows from Eq. (3) after replacing p_i by P_i .

Restricting the discussion to hydrocarbons let us note that several sets of parameters a , b and x have been used in this context. Two of them deserve special attention. Boyd and

Singer (1966) suggest the following values: $a = 1.524$, $b = 0.194$, $x = 2.835$. Nowakowski and one of us (1964), on the other hand, suggest the following set: $a = 1.517$, $b = 0.180$, $x = 4.1$. The first set gives the best reproduction of the experimental bond lengths in naphthalene and anthracene. The second set gives the best reproduction of the bond lengths in ethylene, benzene and graphite (Coulson and Gołębiewski 1961) and a good reproduction of many other physical properties of a large class of alternant hydrocarbons (Gołębiewski and Nowakowski 1964). In what follows we assume the second set.

3. Brief outline of Coulson, Senent and Haigh's theory

Let us consider the fragment of a conjugated or aromatic system shown in Fig. 1, with the bond angles all equal approximately to $2\pi/3$. According to Coulson, Senent and Haigh,

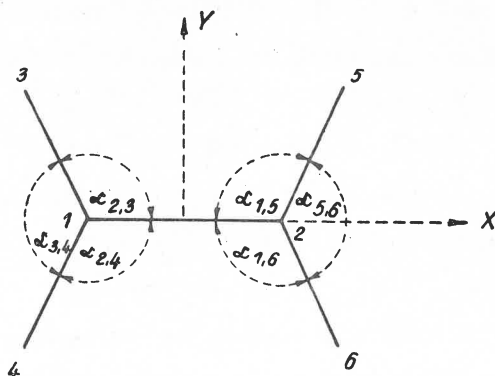


Fig. 1. A fragment of a conjugated system

its deformation can be described by in-plane coordinates, say $q_8 = \Delta\alpha_{2,3}$, $q_2 = \Delta\alpha_{3,4}$, ..., $q_7 = \Delta r_{1,2}$, $q_8 = \Delta r_{1,3}$, etc., and by out-of-plane coordinates, say

$$a_1 = 1.40 [(z_4 - z_1)/r_{1,4} + (z_3 - z_1)/r_{1,3} + (z_2 - z_1)/r_{1,2}] \quad (6)$$

$$b_{12} = 1.40 [(z_3 - z_1)/r_{1,3} + (z_6 - z_2)/r_{2,6} - (z_4 - z_1)/r_{4,1} - (z_5 - z_2)/r_{5,2}] \quad (7)$$

and similarly a_2 , where, apart from a factor, a_1 is the distance of atom 1 from the plane defined by its next neighbours and b_{12} is the twisting angle of the central bond.

Let us define a row vector of all the in-plane coordinates, \mathbf{q} , and similarly the vectors \mathbf{a} , \mathbf{b} and \mathbf{z} . Let $W(R_i)$ be the sum of van der Waals interactions which cause the deformation. They minimize then the total energy,

$$E_{\text{tot}} = \text{const} + \frac{1}{2} \mathbf{a} \mathbf{K}_a \mathbf{a}^T + \frac{1}{2} \mathbf{b} \mathbf{K}_b \mathbf{b}^T + \frac{1}{2} \mathbf{q} \mathbf{K}_q \mathbf{q}^T + W(R_i) \quad (8)$$

or, equivalently,

$$E_{\text{tot}} = \text{const} + \frac{1}{2} \mathbf{z} \mathbf{K}_z \mathbf{z}^T + \frac{1}{2} \mathbf{q} \mathbf{K}_q \mathbf{q}^T + W(R_i). \quad (9)$$

If $\mathbf{a} = z\mathbf{A}$ and $\mathbf{a} = z\mathbf{B}$, then

$$\mathbf{K}_z = \mathbf{A}\mathbf{K}_a\mathbf{A}^T + \mathbf{B}\mathbf{K}_b\mathbf{B}^T. \quad (10)$$

Here, \mathbf{K}_a , \mathbf{K}_b and \mathbf{K}_z represent the force constant matrices. According to these authors it suffices to consider the matrices \mathbf{K}_a and \mathbf{K}_b as diagonal, as well as the \mathbf{K}_q matrix. Let us recall that, at least for the case of benzene, the off diagonal elements of the \mathbf{K}_a and \mathbf{K}_b matrices are few percents of the diagonal elements (Coulson and Gołębiewski 1960). In the case of the \mathbf{K}_q matrix the off diagonal elements may be some 18% of the diagonal ones (Whiffen 1955).

The following values of the force constants can be recommended in this method:

i) for in-plane deformations within the benzenoid rings (Coulson and Haigh 1963):

$$\left. \begin{aligned} K(\sphericalangle \text{C}-\text{C}-\text{C}) &= 1.4504 \times 10^{-11} \text{ erg/rad}^2 \\ K(\sphericalangle \text{C}-\text{C}-\text{H}) &= 0.9903 \times 10^{-11} \text{ erg/rad}^2 \end{aligned} \right\} \quad (11)$$

ii) for in-plane deformations within the chains (Westheimer 1956):

$$\left. \begin{aligned} K(\sphericalangle \text{C}-\text{C}-\text{C}) &= 0.833 \times 10^{-11} \text{ erg/rad}^2 \\ K(\sphericalangle \text{C}-\text{C}-\text{H}) &= 0.567 \times 10^{-11} \text{ erg/rad}^2 \\ K(\sphericalangle \text{H}-\text{C}-\text{H}) &= 0.333 \times 10^{-11} \text{ erg/rad}^2 \end{aligned} \right\} \quad (12)$$

iii) for out-of-plane deformations of hydrocarbons (Gołębiewski and Parczewski 1967):

$$\begin{aligned} K^a &= 0.1254 \times 10^5 \text{ dyne/cm} \\ K^b &= 0.0947 \times 10^5 \text{ dyne/cm (for benzenoid bonds).} \end{aligned} \quad (13)$$

We do not cite the values of remaining force constants as they are considered differently in our approach.

4. Outline of the self consistent conformation analysis

Let \mathbf{r} be the row vector of bond lengths, $\Delta\alpha$ the row vector of $\Delta\alpha_i$'s, \mathbf{a} of all a_i 's, \mathbf{b} of those b_{ij} 's which are expected to be small and Θ of those twisting angles which can be large. Let $W = \sum W_i(R_i)$ be the sum of vdW interactions which are expected to influence the structure significantly. We use thus a central field model for vdW interactions, putting $R_i = R_i(\Delta\alpha, \mathbf{a}, \mathbf{b}, \Theta, \Delta\mathbf{r})$. We use a harmonic model to calculate the energy associated with the vectors $\Delta\alpha$, \mathbf{a} and \mathbf{b} , and the explicit SC LCAO MO method in calculating the influence of Θ and $\Delta\mathbf{r}$. Thus we minimize the total energy:

$$\begin{aligned} E_{\text{tot}} = \text{const} &+ \frac{1}{2} \Delta\alpha \mathbf{K}_a \Delta\alpha^T + \frac{1}{2} \mathbf{a} \mathbf{K}_a \mathbf{a}^T + \frac{1}{2} \mathbf{b} \mathbf{K}_b \mathbf{b}^T + W + \\ &+ E_\sigma(\mathbf{r}, \Theta)_{\text{SC}} - E_\pi(\mathbf{r}, \mathbf{O})_{\text{SC}} + E_\sigma(\mathbf{r}, \Theta)_{\text{SC}} - E_\sigma(\mathbf{r}, \mathbf{O})_{\text{SC}} \end{aligned} \quad (14)$$

where $E_\sigma(\mathbf{r}, \Theta)_{\text{SC}}$ is the σ -electronic energy for the twisted case calculated with the use of Eq. (5), $E_\sigma(\mathbf{r}, \mathbf{O})_{\text{SC}}$ has a similar meaning for the planar case, and $E_\pi(\mathbf{r}, \Theta)_{\text{SC}}$ and $E_\pi(\mathbf{r}, \mathbf{O})_{\text{SC}}$ are the appropriate π -electronic energies which follow from the SC LCAO MO method.

Let us specify the various terms of Eq. (14) in details. Calculating $E_{\pi}(\mathbf{r}, \boldsymbol{\Theta})_{\text{SC}}$ and $E_{\sigma}(\mathbf{r}, \boldsymbol{\Theta})_{\text{SC}}$ with the SC LCAO MO method we include a twisting factor of the resonance integrals, putting

$$\beta_i^1(r_i, \Theta_i) = \beta_i(r_i, 0) \cos \Theta_i = \beta_0 \exp[-x(r_i - 1.397)] \cos \Theta_i \quad (15)$$

where, for hydrocarbons, $x = 4.1/\text{\AA}$, $\beta_0 = -1.403$ eV (Gołębiewski, Parczewski 1967). With this value of β_0 the delocalization energy of benzene, according to the SC LCAO MO method, amounts to 28 kcal/mole. It compares reasonably well with the experimental value 36 kcal/mole, despite the fact that β_0 was estimated from the vibration analysis of benzene.

The selfconsistency requirement of the SC LCAO MO method, which follows from Eq. (3), is replaced now by Eq. (16):

$$r_i = a - bp_i(\boldsymbol{\Theta}) \cos \Theta_i + \frac{b}{2x\beta_i(r_i, 0)} \sum_j \frac{dW(R_j)}{dR_j} \frac{\partial R_j}{\partial r_i} \quad (16)$$

where the parameters a , b are approximately the same as previously provided the vdW interactions of the meta type, like 1-5 in Fig. 1, are neglected.

Indeed, we obtain within the SC LCAO MO scheme the following expression for the total energy:

$$E_{\text{tot}} = \text{const} + \frac{2}{b} \sum_j \left(\frac{1}{x} - a + r_j \right) \beta_j(r_j, 0) + 2 \sum_j p_j(\boldsymbol{\Theta}) \beta_j(r_j, 0) \cos \Theta_j + \sum_j W_s(R_j). \quad (17)$$

However, for the equilibrium,

$$\frac{\partial E_{\text{tot}}}{\partial r_i} = 0. \quad (18)$$

Substituting Eq. (17) into Eq. (18) we obtain the condition (16).

Certainly the influence of the $\sum W_s$ term in Eq. (16) decreases rapidly with an increase of the R_j 's. On the other hand, the original relation (3) seems to work satisfactorily in the case of planar systems despite the different neighbourhoods of the given bonds (ethylene, benzene, graphite, etc.). This behaviour could be understood if, for the most significant contributions from the vdW interactions (like 1-5 in Fig. 1), the effect would not depend on the nature of the neighbouring atoms:

$$\left(\frac{dW(\text{C...H})}{dR_{\text{CH}}} \right)_{2.1\text{\AA}} \approx \left(\frac{dW(\text{C...C})}{dR_{\text{CC}}} \right)_{2.4\text{\AA}} \quad (19)$$

Considering the vdW interactions of atoms 3-5 and 4-6 and their unrestricted influence on r_{12} (Fig. 1) we obtain, using potentials given in Eq. (20-22), a change of $\Delta r_{12} = 0.0007$ \AA for the case of H...H interactions and slightly less than 0.005 \AA for the C...C case. Thus using the same values of a , b as in Eq. (3) for simplicity we overestimate, in some cases, the role of vdW interactions by not more than 0.005 \AA. A more accurate technique would be to use different values of a , depending on the neighbourhood of the bond.

In a strict treatment one should consider the vdW interactions for all pairs of atoms except perhaps those of the meta type. This would be an unnecessary burden, however, at least for large molecules. In the present treatment we consider only those interactions, which are expected to influence the structure significantly. In the case of biphenyl, for example, we consider the interactions which are indicated by a wavy line in Fig. 2. These

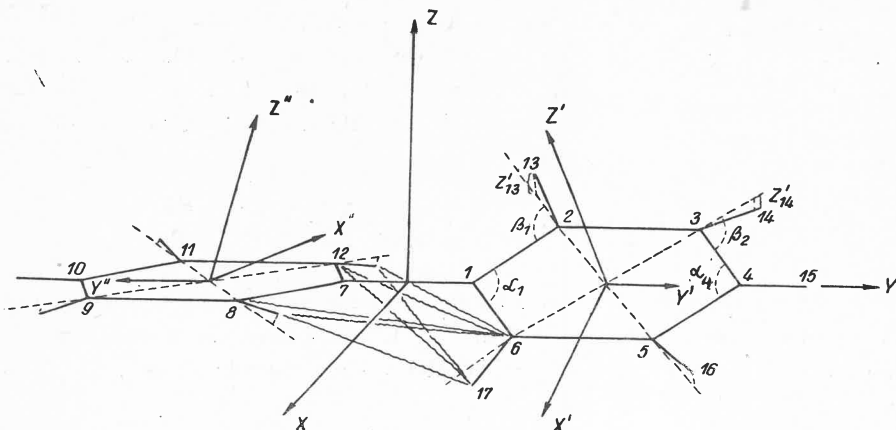


Fig. 2. Numbering of atoms, definition of independent coordinates and local Cartesian coordinate systems, types of vdW interactions which have been considered explicitly in the case of biphenyl

interactions are expected to change the twisting angle $\Theta_{1,7}$ and the central bond length $r_{1,7}$ rather distinctly, although the estimated bond length $r_{1,7}$ may be too large by about 0.005 Å.

The choice of the van der Waals potentials is postponed to the next section.

In order to calculate $W_i(R_i)$ and $\frac{\partial R_i}{\partial r_s}$ the relation $R_i = R_i(\Delta\alpha, r, a, b, \Theta)$ must be known. This is a simple trigonometric task if local Cartesian coordinates are used. Let us consider biphenyl, for example, introducing three local coordinate systems (Fig. 2). We assume, for simplicity, that both carbonic rings are planar, so that $z'_1 = z'_2 = z'_3 = z'_4 = z'_5 = z'_6 = 0$ and similarly for the other ring. Additionally we assume that $z'_{14} = z'_{16} = 0$, $z_1 = z_4 = z_{15} = x_1 = x_4 = x_{15} = 0$, $\sphericalangle 1, 2, H \approx \sphericalangle 1, 2, 13$, $\sphericalangle 4, 3, H \approx \sphericalangle 4, 3, 14$, etc., $\beta_2 = \pi - \frac{1}{2}\alpha_3$, and similarly for all equivalent positions. For all C-H bonds we assume a constant bond length, 1.08 Å. We have then the following independent coordinates: $r_{1,7}$, $r_{1,2}$, $r_{2,3}$, $r_{3,4}$, α_1 , α_4 , β_1 , $\Theta_{1,7}$ and z'_{13} . Let us pass now to Fig. 3. Analyzing all triangles in this figure we obtain the Cartesian coordinates x' , y' , z' of any atom in question. It suffices then to rotate the coordinate system x' , y' , z' around the y axis by $-\frac{1}{2}\Theta_{1,7}$ and to shift it along the y axis by $-\frac{1}{2}(r_{1,7} + r_{1,4})$.

The a_i - and b_{ij} -type coordinates which appear in the force field are expressed by out-of-plane z -coordinates like in Eqs (6) and (7). However, in contrast to Coulson and Senent,

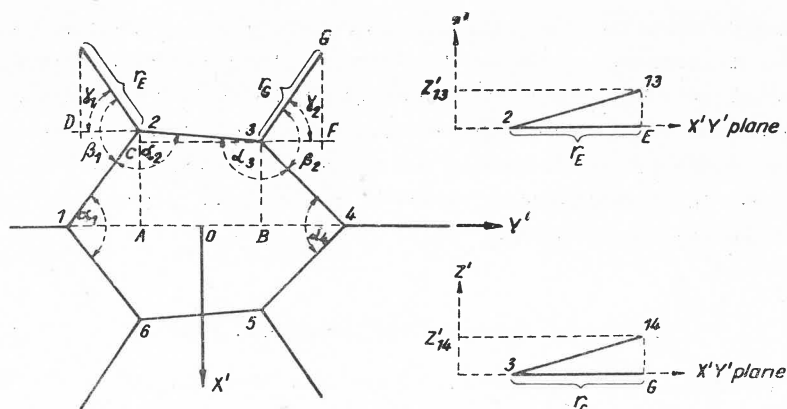
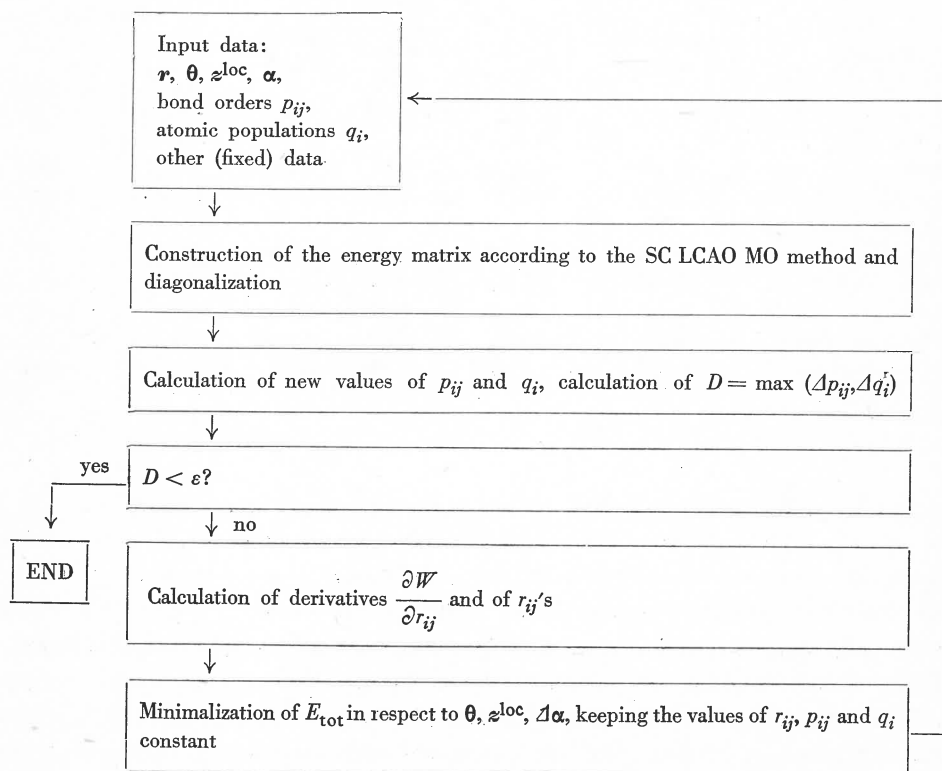


Fig. 3. A detailed diagram of a phenyl ring of biphenyl

we use a local coordinate system for this purpose, chosen in such a way that all z 's are small. In the case of biphenyl, for example, we express $a_1, a_2, b_{1,2}, b_{2,3}$ in terms of z'_i -values.

Thus $a_1 = 0, a_2 = \frac{1.40}{1.08} z'_{13}$ etc.

The floating chart of our program which has been written in Algol-60 is given by the following diagram:



The program allows us to keep the value of a given Θ_{ij} angle constant. It can be used, therefore, for an estimation of rotation barriers and related problems. It can be also used for ions and excited states within the framework of the SC LCAO MO theory.

The division of all twists into small and large ones, into b_{ij} -type and Θ_{ij} -type, is arbitrary, of course. For small twists we can consider them within the harmonic force field only. On the other hand, we can consider them all within the SC LCAO MO scheme. For small twisting angles both variants are equivalent.

5. Optimal choice of vdW potentials. Biphenyl

There is a large variety of semiempirical formulae known for the van der Waals interaction between the carbon and hydrogen atoms. In order to make a proper choice for the selfconsistent conformation analysis (SC CA) we have decided to test their utility for the case of biphenyl.

Certainly the main effect in biphenyl comes from H...H interactions. Restricting the discussion to these interactions (Fig. 2) we obtain the ground state properties listed in Table I.

The rôle of $W(H...H)$ interactions

TABLE I

Potential	$W(1.8 \text{ \AA})$ (eV)	$\left(\frac{dW}{dR}\right)_{1.8\text{\AA}}$ (eV/\AA)	$R(W_{\min})$ (\AA)	$W(\min)$ (eV)	Biphenyl	
					$\Theta_{1,7}$	$r_{1,7}$ (in \AA)
Hill (1946)	0.034	-0.245	2.42	-0.002	16°12'	1.474
Barton (1948)	0.032	-0.221	2.40	-0.005	16°23'	1.474
Kitajgorodsky, Dashevsky (1967a, b)	0.056	-0.385	2.46	-0.004	21°46'	1.477
Kitajgorodsky (1961)	0.106	-0.620	2.46	-0.003	27°45'	1.482
Bartell (1960)	0.122	-0.545	2.98	-0.001	31°00'	1.484
Pauncz-Ginsburg (1960)	0.263	-0.793	4.36	-0.000	46°01'	1.497
Mason, Kreevoy (1955)	0.527	-1.588	> 4	—	58°01'	1.506
Experiment	—	—	—	—	42°	1.48—1.49

The remaining vdW interactions (Fig. 2) will certainly modify these results, causing an increase of $\Theta_{1,7}$ and $r_{1,7}$. We see therefore, that the second Kitajgorodsky's and Bartell's approximations seem to be best suited in our case. Hill's and Barton's potentials are definitely too soft, while the remaining potentials are definitely too hard.

In the next step we have analyzed the effect of all vdW interactions indicated in Fig. 2, considering various combinations of the Bartell (1960) and Kitajgorodsky (1961) potential $W(H...H)$ with those known for C...C and C...H pairs (Bartell 1960, Eliel *et al.* 1965, Dashevsky and Kitajgorodsky 1967b). The best agreement with the experimental ground state

properties of biphenyl (both, isolated and in the solid state) was obtained for the following set:

$$W(H\dots H) = 285.90 \exp(-4.08R) - 2.134/R^6 \text{ (eV)} \quad (20)$$

$$W(C\dots H) = 1939.4 \exp(-2.04R)/R^6 - 5.4179/R^6 \text{ (eV)} \quad (21)$$

$$W(C\dots C) = 1635.3 \exp(-3.52R) - 20.561/R^6 \text{ (eV)}. \quad (22)$$

Formulae (20) and (21) have been suggested by Bartell (1960) and formula (22) by Dashevsky and Kitajgorodsky (1967b). We would like to add that this set of vdW potentials also satisfies the selfconsistency requirement (19).

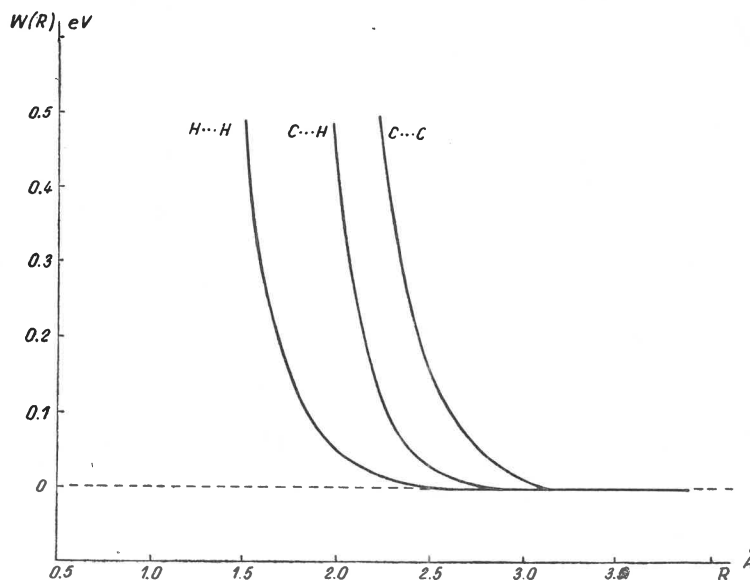


Fig. 4. Dependence of the van der Waals interactions $W(H\dots H)$, $W(C\dots H)$ and $W(C\dots C)$ on distance R

The dependence of these potentials on the distance R is illustrated in Fig. 4. A comparison of calculated and observed properties of biphenyl with this potential set is given in Table II. The experimental data for the isolated state are taken from the article written by Almenningen and Bastiansen (1958) and that for the crystal — from Robertson's papers (1961a, b).

We see from Table II that the agreement with experiment is quite satisfactory. In the case of the isolated state the calculated $\theta_{1,7}$ angle, all the calculated bond lengths and all the remaining bond angles are close to the experimental ones. A comparison of the calculated structure for the constrained planar case with that observed in a crystal is certainly less grounded. Nevertheless, not only does the central bond length again agree quite well with experiment. Also the deformations of the benzene rings are now expectedly larger and well comparable with those observed except for the angle β_1 . However, β_1 is defined by the position of a hydrogen atom, which by the X-ray method can be measured only very approxi-

Calculated and observed ground state properties of biphenyl

Property	Isolated molecule		Planar molecule (in crystal)	
	Calc.	Obs.	Calc.	Obs.
$\Theta_{1,7}$	40°21'	~42°	0°	0°
$r_{1,7}$	1.498	1.48—1.49	1.503	1.497
$r_{1,2}$	1.402	~1.40	1.409	1.397
$r_{2,3}$	1.396	~1.40	1.395	1.387
$r_{3,4}$	1.397	~1.40	1.398	1.379
β_1	120°19'	~120°	121°47'	118°48'
β_2	120°00'	—	119°55'	—
α_1	119°35'	~120°	118°20'	117°20'
α_2	120°17'	~120°	120°55'	121°10'
α_3	119°59'	~120°	120°10'	120°30'
α_4	119°54'	~120°	119°31'	119°20'
z'_{13}	0.01	—	0	0.017

mately. One way or the other, the decrease of β_1 below the ideal value, 120°, is physically unrealistic, at least as long as interactions with other molecules are neglected. This abnormal value of β_1 was also pointed out by Miller and Murrell (1967).

We would like to point out that our theory predicts a longer bond length $r_{1,7}$ for the planar case than for the twisted one. The calculated difference, 0.005 Å, compares well with the experimental value, 0.007 Å. To our knowledge this is the first analysis which predicts this behaviour properly. The absolute values of $r_{1,7}$ are slightly too high in both cases. However, a correction of the a parameter by 0.005 Å (see Section 4) would make the agreement quantitative.

6. Final remarks

It is hoped that the selfconsistent steric analysis of the conjugated and aromatic systems will yield valuable information in all the cases where the steric hindrance might be large. We have applied the method to extended calculations on biphenyl, butadiene and stilbene, discussing ground states, excited states, ionic states, rotation barriers, *etc.* We are in the course of preparation of these results for publishing. They will be published in the nearest future.

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