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# CONJUGATION AND NON-BONDED INTERACTION*

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**Abstract**—The effect of conjugation and non-bonded interaction has been calculated for carbon $sp^2$–$sp^2$ single bonds of different molecular conformations. It is found that the experimental results cannot be satisfactorily understood from a consideration of either concept alone. Only the combined effect leads to consistency with all experimental evidence.

## 1. INTRODUCTION

AS IS well known the theoretical study of molecular structure is based on the Schrödinger wave equation. At present it is, however, impossible to find a fairly accurate solution to this equation for any organic molecule, perhaps with one or two exceptions (e.g. HCN). In the theoretical study of molecules it is therefore necessary to make drastic simplifications. It is also found to be useful to introduce more or less well-defined concepts for the discussion and classification of molecular properties. Some of these concepts, e.g. resonance, are based on computational approximations, others on chemical experience and intuition.

On account of the approximate nature of all such concepts it does not seem to be meaningful to ask whether a certain concept is *correct* or not. The question to ask is whether a concept is *useful* or not, whether it can be used for the classification of a large or a small amount of experimental evidence. One concept which has recently been subject to rather vivid discussions is the concept of conjugation, see e.g. Dewar and Schmeising.[1] The present article will give some arguments in favour of this debated concept, but will also indicate the usefulness of such a concept as non-bonded interaction. The conclusions will be based on the results of some calculations on butadiene and biphenyl.

A report of the preliminary results has previously been given.[2]

From experiments it is well known that the most stable conformation of butadiene is the planar *trans*-form. The conformation of biphenyl is found to be planar in crystals[3] but non-planar in the gas phase.[4] It has been suggested by Bastiansen *et al.*[5] that non-bonded interaction between hydrogen atoms is the cause of both the planarity of butadiene and the non-planarity of biphenyl. The present investigation aims at a study of this proposal. Accordingly, non-bonded interaction has been calculated.

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[1] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959).

[2] I. Fischer-Hjalmars, *Tetrahedron* **17**, 235 (1962).

[3] J. Trotter, *Acta Cryst.* **14**, 1135 (1961).

[4] A. Almenningen and O. Bastiansen, *Kgl. Norske Vid. Selsk. Skr.* No. 4 (1958).

[5] O. Bastiansen and M. Traetteberg, *Tetrahedron* **17**, 147 (1962).

Since the present author felt that conjugation should be a more reasonable explanation of the planarity of butadiene, this latter effect has also been calculated for both molecules.

## 2. CALCULATION OF NON-BONDED INTERACTION

Non-bonded interaction is usually assumed to be the origin of the potential for rotation around a single bond. Moreover, the repulsive part of this interaction, usually called steric hindrance, is generally recognized as an important factor for the determination of molecular conformation. For the prediction of molecular structure it would therefore be very useful to have a reliable and comparatively easy way of calculating the non-bonded interaction, especially since this interaction also has a strong bearing upon the properties of liquids. It seems, however, to be very difficult to find an acceptable mathematical formulation for this kind of potential.

Several suggestions have been made about the form of the interaction potential. The most well-known is perhaps the Lennard–Jones 6,12-potential:

$$V = Ar^{-12} - Br^{-6}, \tag{1}$$

where $A$ and $B$ are positive constants. Thus the first term of (1) describes the repulsion, when the atoms are approaching each other, and the second term describes the attraction, which is dominating at larger distances. Other suggested potentials usually maintain the $r^{-6}$ description of the attraction, although the choice of $B$ is made differently, but modify the repulsive part, making it more flexible by the introduction of an exponential function. Some suggested potential are as follows: Modified Buckingham[6] ($r' = r + 0{\cdot}742$):

$$V(\mathrm{H, H}) = 6{\cdot}686 \,.\, 10^4 \exp(-r'/0{\cdot}238) - 1{\cdot}791 \,.\, 10^2(r')^{-6}, \tag{2}$$

Hill[7]:

$$V(\mathrm{H, H}) = 3{\cdot}481 \,.\, 10^4 \exp(-r/0{\cdot}177) - 0{\cdot}1807 \,.\, 10^2 r^{-6}, \tag{3}$$

Mason and Kreevoy[8]:

$$V(\mathrm{H, H}) = 0{\cdot}372 \,.\, 10^4 \exp(-r/0{\cdot}326) - 0{\cdot}895 \,.\, 10^2 r^{-6}, \tag{4}$$

Bartell[9]:

$$V(\mathrm{H, H}) = 0{\cdot}659 \,.\, 10^4 \exp(-r/0{\cdot}245) - 0{\cdot}492 \,.\, 10^2 r^{-6}, \tag{5}$$

Haigh[10]:

$$V(\mathrm{H, H}) = 0{\cdot}684 \,.\, 10^4 \exp(-r/0{\cdot}234) - 0{\cdot}811 \,.\, 10^2 r^{-6}. \tag{6}$$

In (2)–(6) the numerical values of the coefficients refer to interaction between two non-bonded hydrogen atoms and $r$ is the distance between the atoms. To facilitate a comparison the potential functions are in some cases expressed in another form than

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[6] E. A. Mason and W. E. Rice, *J. Chem. Phys.* **22**, 522 (1954).

[7] T. L. Hill, *J. Chem. Phys.* **16**, 399 (1948).

[8] E. A. Mason and M. M. Kreevoy, *J. Amer. Chem. Soc.* **77**, 5808 (1955).

[9] L. S. Bartell, *J. Chem. Phys.* **32**, 827 (1960).

[10] C. W. Haigh, private communication; cf. C. A. Coulson and C. W. Haigh, *Tetrahedron*, in press. A detailed discussion of several interaction potentials is given by these authors. It first appeared in preprint after the present study was completed.

that in the original publication. All numerical values are adjusted to give length in Å units and energy in kcal/mole.

The general appearance of the potentials (2)–(6) is shown in Fig. 1. It is immediately seen that (4) is by far the "hardest" potential. Next comes (5), since the attractive part is considerably weaker here than in e.g. (6). It is also seen that some functions, which formally look rather different, e.g. (2) and (3), give almost the same effective potential in the region considered, whereas others which are formally rather similar, e.g. (5) and (6), differ considerably in the region of interest.

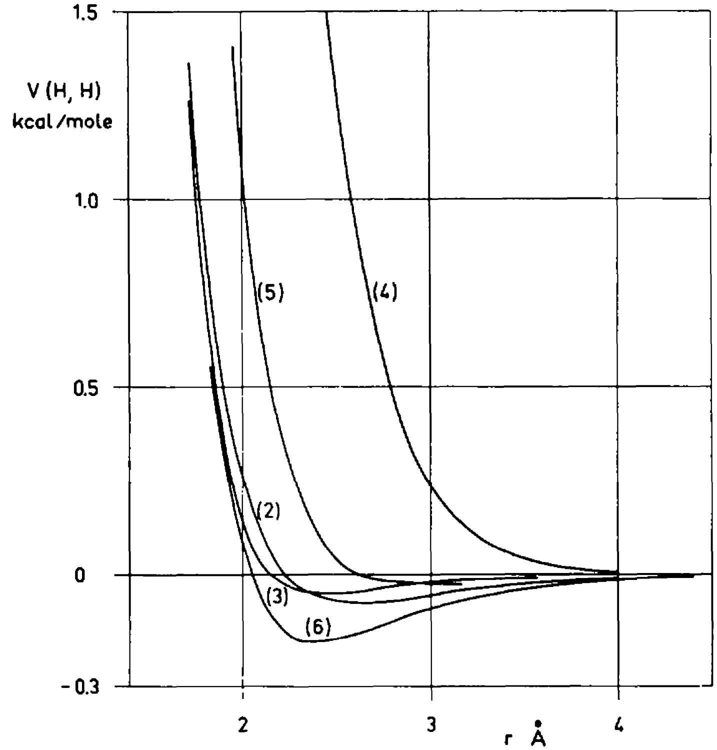

Fig. 1. Non-bonded interaction $V(H, H)$ between two hydrogen atoms as a function of the interatomic distance r. The different curves refer to the different potentials, given in the text with the same formula numbers.

Since (4) is almost completely dominated by the repulsive part, this potential will not be considered in the present study, which is especially concerned with the attractive part of the potential.

A complete treatment of the non-bonded interaction must, of course, also include the interaction between two carbon atoms, $V(C, C)$, and between one carbon and one hydrogen atom, $V(C, H)$. These potentials have not been so extensively studied in the literature as $V(H, H)$, since they will in most cases be of secondary importance. The potentials adopted in the present study, are those suggested by Bartell[9]:

$$V(C, C) = 2{\cdot}994 \,.\, 10^5 r^{-12} - 3{\cdot}253 \,.\, 10^2 r^{-6}, \qquad (7)$$

$$V(C, H) = 1{\cdot}2496 \,.\, 10^2 r^{-6} \{358 \exp(-r/0{\cdot}490) - 1\}. \qquad (8)$$

In the application to butadiene and biphenyl the following atomic distances have been assumed:

$$\text{Butadiene}^{11}\text{:}\ r(C_1C_2) = 1{\cdot}337\ \text{Å},\ r(C_2C_3) = 1{\cdot}483\ \text{Å},$$
$$r(CH) = 1{\cdot}082\ \text{Å}.$$

Biphenyl[4]: $r(CC) = 1{\cdot}397$ Å in the rings, $r(CC) = 1{\cdot}490$ Å between the rings, $r(CH) = 1{\cdot}082$ Å.

A new determination by X-ray diffraction of the bond lengths in biphenyl in crystals has recently been published.[3] This very careful determination shows that the assumption of regular hexagons should be slightly modified. According to this determination the bond lengths of the phenyl rings vary between 1·372 Å and 1·416 Å. The distance between the rings is according to this determination 1·507 Å. It has, however, been checked that such variations in bond lengths will have a negligible effect on the properties calculated in the present investigation and will have no influence on the conclusions.

## 3. CALCULATION OF CONJUGATION ENERGY

The two molecules studied in the present investigation both have the general formula *R–R*, where *R* is an unsaturated radical. The conjugation energy, due to the interaction between the two radicals, can be calculated by perturbation treatment as has been done e.g. by Longuet-Higgins and Murrell.[12] However, since the present study is concerned with the combined effect of conjugation and non-bonded interaction, it was considered advisable to make the calculation of the conjugation energy as accurate as was compatible with a feasible amount of numerical work. Accordingly, a molecular orbital $\pi$-electron approximation, applied to the system as a whole, has been adopted.

A previous study by the present author[13] has demonstrated the superiority of the Pariser–Parr–Pople method over the Hückel method also when considering ground state properties. Moreover, computer programmes applicable to $\pi$-electron systems even larger than that of biphenyl have recently been developed. Therefore, the computational method, described elsewhere,[13] has also been used in the present investigation, although some minor modifications have been introduced. A detailed discussion of the semiempirical approach adopted here will be presented in a separate paper.[14]

The one-electron integrals of the core part of the $\pi$-electron Hamiltonian in the atomic orbital representation are:

$$\int \chi_\mu^*(\mathrm{i}) \mathrm{H}^{\mathrm{core}} \chi_\mu(\mathrm{i})\, d\tau_i = \langle\mu|H^{\mathrm{core}}|\mu\rangle = W_\mu + \sum_{\mu\neq\nu} \langle\mu|U_\nu|\mu\rangle, \tag{9}$$

where

$$W_\mu = \langle\mu|T + U_\mu|\mu\rangle, \tag{10}$$

and

$$\beta_{\mu\nu} = \int \chi_\mu^*(\mathrm{i})\, H^{\mathrm{core}} \chi_\nu(\mathrm{i})\, d\tau_i = \langle\mu|H^{\mathrm{core}}|\nu\rangle. \tag{11}$$

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[11] A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.* **12,** 1221 (1958).

[12] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.* A **68,** 601 (1955).

[13] I. Fischer-Hjalmars, *Arkiv Fysik* **21,** 123 (1962).

[14] I. Fischer-Hjalmars, to be published.

In (9)–(11) $\chi_\mu$ and $\chi_\nu$ are atomic orbitals of the 2p$\pi$-type centred at atoms $\mu$ and $\nu$ respectively.

On account of the formal neglect of differential overlap, which is always assumed in this approximation, only one type of two-electron integrals will be different from zero, i.e. the Coulomb integrals:

$$(\mu\mu \mid \nu\nu) = \int \chi_\mu^*(\mathrm{i})\, \chi_\nu^*(j) r_{ij}^{-1} \chi_\mu(i)\chi_\nu(j)\, d\tau_i\, d\tau_j. \tag{12}$$

These integrals represent the electrostatic repulsion between the electrons $i$ and $j$, in orbitals centred at atoms $\mu$ and $\nu$ respectively. A special case of (12) is one-centre integrals $(\mu\mu \mid \mu\mu)$.

Moreover, since each centre contributes one $\pi$-electron, the two-centre potential integrals of (9) are:

$$\langle \mu | U_\nu | \mu \rangle = -(\mu\mu \mid \nu\nu),$$

when the penetration terms are neglected.

The parameter $W_\mu$, defined by (10), is assumed to be the same for all atoms $\mu$ because of the fact that only pure hydrocarbons are considered. The value of the parameter $W_\mathrm{C}$ has been determined from the ionization potential of ethylene:

$$-IP(\mathrm{C_2H_4}) = W_\mathrm{C} + \beta_\mathrm{CC} + \tfrac{1}{2}\,[(\mu\mu \mid \mu\mu) - (\mu\mu \mid \nu\nu)] = -10{\cdot}515 \text{ eV}.$$

Using the values of $\beta_\mathrm{CC}$ and $(\mu\mu \mid \nu\nu)$ given below, the value $W_\mathrm{C} = -9{\cdot}086$ eV has been obtained.

The integrals $\beta_{\mu\nu}$, defined by (11), have been computed from the formula given in ref. 13:

$$-\beta_{\mu\nu} = S_{\mu\nu}\{k_1[(\mu\mu \mid \mu\mu) + (\nu\nu \mid \nu\nu)] + k_2(\mu\mu \mid \nu\nu)\}, \tag{13}$$

where

$$S_{\mu\nu} = \int \chi_\mu^* \chi_\nu\, d\tau. \tag{14}$$

The constants $k_1$ and $k_2$ have been determined by fitting (13) for two representative compounds. The compounds benzene and ethylene have been chosen, the $\beta$-values obtained from the spectra of these molecules being

$$\beta(r = 1{\cdot}397 \text{ Å}) = -2{\cdot}390 \text{ eV and } \beta(r = 1{\cdot}337 \text{ Å}) = -3{\cdot}028 \text{ eV}$$

respectively. Inserting the numerical values in (13), the formula is found to be:

$$-\beta_{\mu\nu} = S_{\mu\nu}\{-2{\cdot}034327\, (\mu\mu \mid \mu\mu) + 6{\cdot}766857\, (\mu\mu \mid \nu\nu)\} \text{ a.u.} \tag{15}$$

It is seen that (15) can easily be applied also to cases when the symmetry axes of the 2p$\pi$-orbitals $\chi_\mu$ and $\chi_\nu$ are not parallel.

For the calculation of the two-electron, one-centre integral the formula given in ref. 13:

$$(\mu\mu \mid \mu\mu) = F_0 + 4F_2, \tag{16}$$

has been used. Using spectroscopic data to calculate $F_0$ and $F_2$ the value $(\mu\mu \mid \mu\mu) =$ 11·810 eV has been found.

For internuclear distances shorter than 2·6 Å the integrals $(\mu\mu \mid \nu\nu)$ of (12) have been computed from the extrapolation formula:

$$(\mu\mu \mid \nu\nu) = 11{\cdot}810 - 3{\cdot}068340r^2 + 1{\cdot}119503r^3 - 0{\cdot}121838r^4, \tag{17}$$

where the coefficients have been determined by a least square fitting to values obtained by the uniformly charged sphere approximation of Parr[15] in the region 2·6 Å–3·4 Å. For internuclear distances larger than 2·6 Å the values were calculated from Parr's formula using the value $Z_{\text{eff}} = 3{\cdot}12$.

The iterative solution of the self-consistent-field equations was performed automatically on an IBM 7090 computer. The programme used for this computation has been made by Professor R. K. Nesbet, Boston, and most kindly put at our disposal. The iterations went on until eight significant figures in the coefficients had been obtained. Eigenvalues, eigenvectors, gross atomic populations, bond orders and the matrix elements of $H^{\text{core}}$ in the molecular orbital representation were automatically printed out by the computer.

To obtain the conjugation energy, the $\pi$-electron energy has been computed from the formula

$$E_\pi = \sum_{k=1}^{n} \{\varepsilon_k + \langle k|H^{\text{core}}|k\rangle\}, \tag{18}$$

where $\varepsilon_k$ are the eigenvalues of the self-consistent Hartee–Fock operator and $\langle k|H^{\text{core}}|k\rangle$ the matrix elements in the molecular orbital representation. The sum should be taken over all the $n$ doubly occupied molecular orbitals ($2n$ electrons).

The energy, which is of importance in the present connection, is the sum of $E_\pi$ and the repulsion between the positively charged core atoms of the system:

$$E = E_\pi + E_{\text{repuls}} = E_\pi + \sum_{i>j} 1/R_{ij}. \tag{19}$$

It should be noted that both $E_\pi$ and the last sum in (19) have different values for the different molecular conformations, considered below. $E$ of (19) is therefore a function $E(\vartheta)$ of the angle $\vartheta$ between the planes of the two radicals $R$ of the molecule $R$–$R$.

The conjugation energy $E_{\text{conj}}$ is finally obtained from the difference between $E(\vartheta)$ of (19) for the conformation of interest and $E(\vartheta)$ of (19) for a conformation without any conjugation, i.e. the one with the two radicals $R$ in perpendicular planes:

$$E_{\text{conj}}(\vartheta) = E(\vartheta) - E(90^\circ). \tag{20}$$

## 4. RESULTS

With the above-mentioned assumptions both non-bonded interaction and conjugation energy have been calculated as a function of the angle of rotation around the central single bond. Energy as a function of twist angle has previously been calculated by Adrain[16] for several molecules containing phenyl groups. His method of calculation differs from the present one in several respects.

(i) The separation of the total energy in two parts is carried out differently.

(ii) Only the repulsive part of the non-bonded interaction is considered by Adrian. His potential lies between the potentials (4) and (5) of the present paper, cf. Fig. 1.

(iii) Adrian estimates the conjugation (resonance) energy by a simplified valence bond method.

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[15] R. G. Parr, *J. Chem. Phys.* **20**, 1499 (1952).

[16] F. J. Adrian, *J. Chem. Phys.* **28**, 608 (1958).

Since biphenyl is the only molecule, studied by both methods, a comparison of the numerical results has to be restricted to this case (see below).

The values obtained according to the present investigation for the non-bonded interaction in butadiene are reproduced in Table 1. It is seen that the different $V$(H, H) formulas (1)–(6) give rather similar interaction energies. As a consequence, only the extreme cases (5) and (6) will be discussed in the following. According to (5) the non-bonded interaction $V$(H, H) has a minimum in the perpendicular case. This result is also found for the combined effect of $V$(H, H) + $V$(C, C) + $V$(C, H) in both cases (5) and (6). Obviously, the non-bonded interaction alone cannot explain the well-established experimental results concerning the conformation of the ground state of butadiene.

TABLE 1. NON-BONDED INTERACTION ENERGY (KCAL/MOLE) IN BUTADIENE

| Potential | Interaction energy | | |
|---|---|---|---|
| | $\vartheta = 0$<br>*trans* | $\vartheta = 90°$ | $\vartheta = 180°$<br>*cis* |
| $V$(H, H) from (1) | −0·144 | −0·178 | +1·314 |
| $V$(H, H) from (2) | −0·139 | −0·188 | +1·202 |
| $V$(H, H) from (3) | −0·100 | −0·076 | +1·179 |
| $V$(H, H) from (5) | +0·075 | −0·169 | +3·651 |
| $V$(H, H) from (6) | −0·350 | −0·305 | +1·041 |
| $V$(C, C) from (7) | −0·084 | −0·063 | +0·547 |
| $V$(C, H) from (8) | +0·207 | −0·248 | +1·352 |
| $V$(C, C,) from (7)+<br>$V$(C, H) from (8)+<br>$V$(H, H) from (5) | +0·198 | −0·481 | +5·550 |
| $V$(C, C) from (7)+<br>$V$(C, H) from (8)+<br>$V$(H, H) from (6) | −0·227 | −0·616 | +2·939 |

In Table 2 the values obtained from the calculation of the conjugation energy of butadiene are collected. Moreover, some results are given from previous calculations of $E_{\text{conj}}$ by Longuet-Higgins *et al.*[12] and by Moser.[17] Although very different methods of calculation have been used, the agreement between the different theoretical computations is satisfactory. It is seen that the *trans* and the *cis* conformations are separated by a comparatively large potential hill. According to the previous perturbation calculation[12] the *cis* and the *trans* conformations should be about equally populated, but according to the present calculation the population at room temperature ($kT = 0{\cdot}5922$ kcal/mole) of the *cis* state should be 1 : 100 compared to the *trans* state. This latter result looks more reasonable, since only the *trans*-form has been found in electron diffraction experiments.

Table 3 shows the combined effect of non-bonded interaction and conjugation for butadiene. Different cases are shown including different kinds of non-bonded

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[17] C. M. Moser, *J. Chem. Soc.* 3455 (1954).

interaction, but all cases have the same general appearance. The *trans* state and the *cis* state are separated by a potential hill, but the *trans* state is in all cases well below the *cis* state, the most favourable population of the latter being 1:1000. Thus, conjugation combined with any reasonable non-bonded interaction potential leads to a correct prediction of the conformation of butadiene.

The values of Table 3 should also be compared with experimental values of conjugation energy. From experiments the difference in hydration energy of butadiene and of two isolated double bonds is found to be 3·7 kcal/mole. For comparison with the theoretical value of the combined effect, the steric hindrance for rotation around the CC bond in butane must be added to the hydration value. This hindrance has been estimated to about 2 kcal/mole. The experimental value of $[E_{\text{conj}} + V]$ is thus about 6 kcal/mole, which is in reasonable agreement with the theoretical value 10 kcal/mole, obtained in the present investigation.

TABLE 2. CONJUGATION ENERGY (A.U.) OF BUTADIENE

| Energy kind | $\vartheta = 0$ *trans* | $\vartheta = 90°$ | $\vartheta = 180°$ *cis* |
|---|---|---|---|
| $E_\pi$ from (18) | −3·104576 | −3·104778 | −3·142912 |
| $E_{\text{repuls}}$ from (19) | +1·727792 | +1·745067 | +1·770545 |
| $E$ from (19) | −1·376783 | −1·359711 | −1·372367 |
| $E_{\text{conj}}$ from (20) | −0·017072 | 0 | −0·012656 |
| $E_{\text{conj}}$ from ref. 12 | −0·0143 | | −0·0151 |
| $E_{\text{conj}}$ from ref. 17: | | | |
| 3 conf | −0·0143 | | — |
| 12 conf | −0·0283 | | — |

TABLE 3. COMBINED EFFECT OF NON-BONDED INTERACTION AND CONJUGATION FOR BUTADIENE
Energy values in kcal/mole.

| Energy kind | $\vartheta = 0$ *trans* | $\vartheta = 90°$ | $\vartheta = 180°$ *cis* |
|---|---|---|---|
| $[V(\text{H, H}) \text{ from } (5)] + \text{E}_{\text{conj}}$ | −10·639 | −0·169 | −4·292 |
| $[V(\text{H, H}) \text{ from } (6)] + \text{E}_{\text{conj}}$ | −11·064 | −0·305 | −6·902 |
| $V(\text{C, C}) + V(\text{C, H}) + (V(\text{H, H}) \text{ from } (5)) + \text{E}_{\text{conj}}$ | −10·516 | −0·481 | −2·393 |
| $V(\text{C, C}) + V(\text{C, H}) + (V(\text{H, H}) \text{ from } (6)) + \text{E}_{\text{conj}}$ | −10·941 | −0·616 | −5·004 |

The calculated values of non-bonded interaction in biphenyl are collected in Table 4. All the different potentials lead to rather similar results, i.e. the lowest energy is obtained for the perpendicular, or almost perpendicular conformation. Accordingly, the experimental results[3,4] cannot be understood from consideration of non-bonded interaction alone. The present results are in agreement with the result obtained in Adrian's investigation[16] that the repulsive, non-bonded interaction (steric) energy (most closely corresponding to the present $V(\text{H, H})$) has a maximum of 4 kcal/mole at $\vartheta = 0°$ and a minimum (0 kcal/mole) at $\vartheta = 90°$.

Table 5 lists the results of the conjugation energy calculations in the case of biphenyl. It should be noted that the values of $E_{\text{conj}}$, found from the complete calculation according to (18)–(20), are remarkably well reproduced by the simple formula:

$$E_{\text{conj}}(\vartheta) \approx E_{\text{conj}}\,(0^\circ)\cos^2\vartheta. \tag{21}$$

This result differs from the twist function ($\sim\cos^4\vartheta$) of Adrian.[16] However, both calculations give the prediction that the planar conformation should be the most stable, a prediction which of course is obtained from any general consideration, based on conjugation energy alone.

TABLE 4. NON-BONDED INTERACTION ENERGY (KCAL/MOLE) IN BIPHENYL

| Potential | Interaction energy | | | |
|---|---|---|---|---|
| | $\vartheta = 0$ | $\vartheta = 30^\circ$ | $\vartheta = 60^\circ$ | $\vartheta = 90^\circ$ |
| $V$(H, H) from (2) | +1·746 | +0·200 | −0·140 | −0·113 |
| $V$(H, H) from (3) | +1·495 | +0·025 | −0·072 | −0·037 |
| $V$(H, H) from (5) | +5·471 | +1·212 | −0·081 | −0·087 |
| $V$(H, H) from (6) | +1·493 | −0·186 | −0·278 | −0·159 |
| $V$(C, C) from (7) | +0·508 | +0·220 | −0·189 | −0·324 |
| $V$(C, H) from (8) | +2·307 | +0·698 | −0·291 | −0·422 |
| $V_{\text{tot}}$ = (C, C) + $V$(C, H) + $V$(H, H) from (5) | +8·286 | +2·130 | −0·561 | −0·655 |
| $V_{\text{tot}}$ = (C, C) + $V$(C, H) + $V$(H, H) from (6) | +4·038 | +0·731 | −0·758 | −0·727 |

TABLE 5. CONJUGATION ENERGY (A.U.) OF BIPHENYL

| Energy kind | $\vartheta = 0$ | $\vartheta = 30^\circ$ | $\vartheta = 60^\circ$ | $\vartheta = 90^\circ$ |
|---|---|---|---|---|
| $E_\pi$ from (18) | −16·605601 | −16·597026 | −16·579874 | −16·571336 |
| $E_{\text{repuls}}$ from (19) | +13·057585 | +13·051431 | +13·039137 | +13·033237 |
| $E$ from (19) | −3·548016 | −3·545595 | −3·540737 | −3·538099 |
| $E_{\text{conj}}$ from (20) | −0·009917 | −0·007496 | −0·002638 | 0 |
| $E_{\text{conj}}$ from ref. 12 | −0·0062 | | | |

TABLE 6. COMBINED EFFECT OF NON-BONDED INTERACTION AND CONJUGATION FOR BIPHENYL
Energy values in kcal/mole

| Energy kind | $\vartheta = 0$ | $\vartheta = 30^\circ$ | $\vartheta = 60^\circ$ | $\vartheta = 90^\circ$ |
|---|---|---|---|---|
| [$V$(H, H) from (5)] + $E_{\text{conj}}$ | −0·752 | −3·492 | −1·736 | −0·087 |
| [$V$(H, H) from (6)] + $E_{\text{conj}}$ | −4·730 | −4·890 | −1·933 | −0·159 |
| $V$(C, C) + $V$(C, H) + [$V$(H, H) from (5)] + $E_{\text{conj}}$ | +2·063 | −2·574 | −2·216 | −0·655 |
| $V$(C, C) + $V$(C, H) + [$V$(H, H) from (6)] + $E_{\text{conj}}$ | −1·915 | −3·972 | −2·413 | −0·727 |

The result of combining non-bonded interaction and conjugation for biphenyl is shown in Table 6. According to both calculations (5) and (6) the total energy has

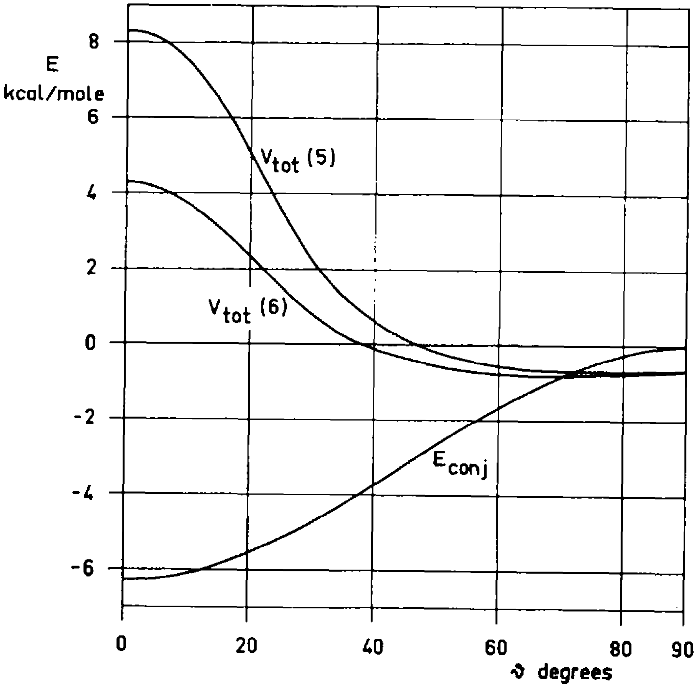

FIG. 2. Different kinds of interaction in biphenyl as functions of the twist angle $\vartheta$ around the single bond. $V_{tot}$ is the total non-bonded interaction and $E_{conj}$ is the $\pi$-electronic conjugation energy.

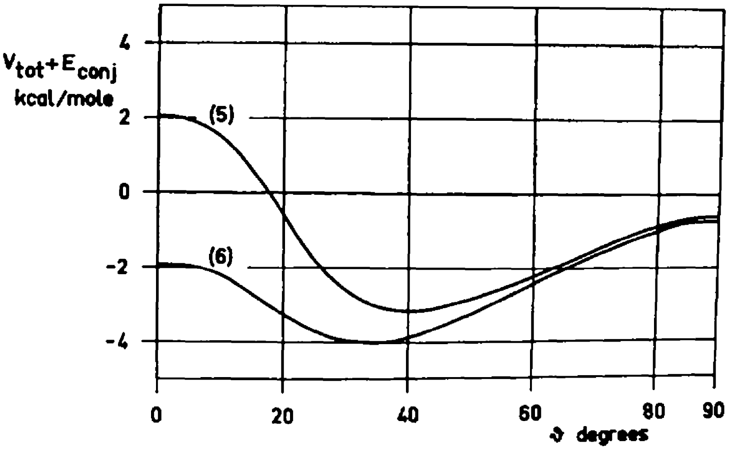

FIG. 3. Combined effect of non-bonded interaction and conjugation energy for biphenyl as a function of the angle of twist $\vartheta$.

a pronounced minimum close to $\vartheta = 40°$. It may be noticed that even the neglect of $V$(C, C) and $V$(C, H), which of course is a poorer approximation, only shifts the minimizing twist angle to a slightly lower value, although in the case of $\{[V(\mathrm{H, H})$ from (6)] $+ E_{\mathrm{conj}}\}$ the potential hill at $\vartheta = 0°$ is so flat that any angle between 0° and 40° should be accessible.

According to Adrian[16] the sum of the conjugation energy and the steric energy is only slightly dependent on the value of the twist angle, the energy variation over the whole angular range being less than 0·5 kcal/mole with a very flat minimum around $\vartheta = 25°$. Although his calculations have a correct general trend, they do not lead to a sufficiently hindered rotation around the central bond in biphenyl.

According to the present investigation the combined effect of conjugation and non-bonded interactions seems to give a good explanation of experiments. From electron diffraction studies of the gas phase[4] the equilibrium value of $\vartheta$ is found to be 41·6° in excellent agreement with the present result. Furthermore, the calculated potential barrier against rotation is sufficiently high (2–4 kcal/mole) to explain the preference of an angle close to 40°. Moreover, since this barrier has about the same magnitude as the rotational barrier in ethane, it is easily understood why hydration experiments do not indicate any extra stabilization of the molecule owing to conjugation between the two rings.

On the other hand, the planar conformation found in crystals can also be understood. In this case the *inter*-molecular interaction should be comparable to the *intra*-molecular potential $V_{\mathrm{tot}}$ (Table 4). Since a planar conformation should give more favourable packing conditions than a twisted one, and since the barrier against planarity is only a fraction of $V_{\mathrm{tot}}$ it is reasonable that the planar conformation should be found in the solid state.

In conclusion it should be stressed that the conformations of butadiene and biphenyl cannot be satisfactorily understood from a consideration of either non-bonded interaction on conjugation alone. Only the combined effect leads to a satisfactory consistency with all experimental evidence. Apparently, both these concepts are useful for the discussion of molecular properties. It may be said that a discussion of the conformations of only two molecules gives a meagre evidence for the necessity of two different concepts. The obvious answer to this remark is of course that an immensity of observations in organic chemistry can be at least qualitatively systematized more easily by accepting than by rejecting the concepts in question. The two cases which have been subject to the above detailed theoretical treatment have been chosen only because they permitted a detailed performance of the calculations.

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