Chapter-IV

Study of Inter-Ring Twist in Biphenyl Derivatives
IV-Study of Inter-Ring Twist of Biphenyl Derivatives

4.1 The PCILO Method

*Perturbative Configuration Interaction Over Localized Orbitals* is the general framework of the PCILO method. The originality of the PCILO method proper resides in the particular choice of the localized orbitals [1]: in the perturbative scheme developed so far nothing imposes a requirement of start with the SCF molecular orbitals (or their localized equivalents) for building the zeroth–order determinant. The sole restriction is that of using an orthonormal set of orbitals. On the other hand, best convergence is to be expected from the use of occupied and virtual orbitals localized in the same spatial region: hence the idea of using a set of bond orbitals and their antibonding counterparts defined *a priori* on the chemical bonds. (Such orbitals are distinct from the localized SCF on the orbitals which are not fully localized over the bonds but have tails in other parts of the molecules. Nevertheless, the similarity is sufficient to ensure a reasonable zeroth-order approximation).

A PCILO procedure using this idea can be developed in an *ab-initio* fashion [2]. However, the method usually called PCILO designates an all-valence electrons version of the method which introduces the following simplifications: (1) the use of the full ZDO hypothesis, (2) the adoption of the CNDO/2 integral approximations, both for the coulomb integrals and for the core matrix elements.

The starting molecular orbitals are built as bond orbitals and lone-pair orbitals according to the picture provided by the chemical formula, as two–by-two combinations of suitable atomic hybrids:

\[ i = \alpha \chi_1 + \beta \chi_2 \quad \ldots (4.1) \]

An antibonding orbital is made to correspond to each bond orbital:

\[ i^* = -\beta \chi_1 + \alpha \chi_2 \quad \ldots (4.2) \]

(for the lone-pair \( \chi_2 \) is rejected to infinity; \( \beta \) and \( i^* = 0 \)).

The appropriate hybrids are constructed from the usual Slater atomic orbitals so as to ensure maximum overlap on the chemical bonds and orthogonality between bonds by a procedure due to Del Re [3].
The ZDO condition has the considerable advantage of making the starting set of bond orbitals automatically orthogonal. The zeroth-order ground-state determinant is built over all the i’s and all possible “excited” determinants are built using the i∗’s. This and the total Hamiltonian define entirely both the E_k and necessary perturbation matrix elements V_{ok} according to the formulas of Chapter II. The advantage of using bond orbitals is both simply computation of the elements and to allow a simple physical interpretation of the various terms [4].

Thus the second-order correction to the energy comprises (a) single excitations \( i \rightarrow i^{\ast} \) (polarization term) or \( i \rightarrow j^{\ast} \) (delocalized term); (b) double excitations reduced by ZDO to \( ii \rightarrow i^{\ast}i^{\ast} \) (intrabond “corrections”), \( ij \rightarrow i^{\ast}j^{\ast} \) (interbond “correction”).

Third order terms involve interaction between the previous configurations, namely: single excitations with double excitations and double excitations with double excitations. The first combinations is made of polarization and/or delocalization corrections; the second and third involve again “correlation”.

An important point must be noted so as to keep clear the relation between PCILO and other procedures: in the PCILO method the starting orbitals not being self-consistent, the single excitation terms do not cancel out as in a conventional CI over an SCF determinant. The SCF level lies somewhere in the neighborhood of the “zeroth-order + single excitations corrections” level without being identical to it (see Table 4.1 for an example). The further addition of the double excitations term in PCILO thus corresponds roughly to what would be obtained by adding double excitations by perturbation to a SCF determinant, but again is not identical to it.

In practice, the currently available PCILO program goes to the third-order in the energy. The second-order correction is a summation over only negative terms and is large; thus it descends below the correct energy that would be obtained by full CI; the third-order correlation energy corrections are appreciably smaller. The result in a global positive contribution, thus bringing the energy closer to the exact value. Table 4.1 reproduces, as an example, the energy output for the formaldehyde molecule. In that case the CNDO/2 SCF energy is -16838 kcal/mole. CI performed on this starting point lowers this value by 57 kcal/mole [5]. Third-order PCILO value is 42 kcal/mole below the SCF level, thus yielding over 70% of the correction energy.
Table 4.1
A Typical PCILO Computer Output: Case of Formaldehyde*

<table>
<thead>
<tr>
<th>Term</th>
<th>Energies (kcal /mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy of the fully localized determinant</td>
<td>-0.16799055E 05</td>
</tr>
<tr>
<td>Polarization Energy</td>
<td>-0.28453348E-03</td>
</tr>
<tr>
<td>Delocalization Energy</td>
<td>-0.29723450E 02</td>
</tr>
<tr>
<td>Intrabond Correlation Energy</td>
<td>-0.33245941E 02</td>
</tr>
<tr>
<td>Interbond Correlation</td>
<td>-0.30136505E 02</td>
</tr>
<tr>
<td>Second-Order Energy</td>
<td>-0.93106171E 02</td>
</tr>
<tr>
<td>Total Energy after the Second-Order</td>
<td>-0.16892160E 05</td>
</tr>
<tr>
<td>One-Bond Correlation-Polarization-Interaction</td>
<td>-0.44230334E-02</td>
</tr>
<tr>
<td>Polarization-Polarization Interaction</td>
<td>-0.69539863E-04</td>
</tr>
<tr>
<td>Polarization-Delocalization Interaction</td>
<td>-0.89407538E-02</td>
</tr>
<tr>
<td>Polarization-2-Bond Correlation Interaction</td>
<td>-0.23979165E-02</td>
</tr>
<tr>
<td>Delocalization-2-Bond Correlation Interaction</td>
<td>-0.20620240E-01</td>
</tr>
<tr>
<td>One-Bond Correlation-1-Bond Correlation Interaction</td>
<td>0.13736535E 02</td>
</tr>
<tr>
<td>Delocalization-Delocalization Interaction</td>
<td>-0.62138920E 01</td>
</tr>
<tr>
<td>Two-Bond Correlation-2-Bond Correlation Interaction</td>
<td>0.49700222E 01</td>
</tr>
<tr>
<td>Third-Order Energy Correlation</td>
<td>0.12484096E 02</td>
</tr>
<tr>
<td>Total Energy after the Third-Order</td>
<td>-0.16879676E 05</td>
</tr>
<tr>
<td>The Perturbation Process has Required</td>
<td>0 MN 0 8 12</td>
</tr>
</tbody>
</table>

*All the contributions involving polarization are made very small by an optimization of the bond polarities at the zeroth order.

4.2 The Biphenyl Problem

Biphenyl has always been considered important since it forms a class of molecules showing liquid crystallinity. The inter-ring dihedral angle of biphenyl and its derivatives had been a subject of intense study for more than past 30 years. Gas phase studies with biphenyl [6] have clearly indicated the inter-ring twist $\sim 40^\circ$, crystallographic studies with unsubstituted [7] and some of its derivatives eg. 4, 4'-diflouro biphenyl [8], 4, 4'-dihydroxy biphenyl [9] has found that two rings are almost in the same plane. Further, at low temperature (22K), biphenyl shows $\sim 10^\circ$ twist between phenyl ring [10]. Similar variation ($14^\circ$ to $27^\circ$) is observed in the case of $p$-terphenyl [11] and $p$-quarter phenyl [12]. Other derivatives of biphenyl exhibit variety of inter-ring twist angles majority lying in the range $30^\circ$ - $60^\circ$. Table 4.2 gives a brief account of observed
inter-ring angle in crystals of some derivatives. The most significant question had been related to the apparent degrees of $40^\circ$ in the inter-ring dihedral angle upon crystallization.

A natural expectation from the molecular of biphenyl is repulsion between ortho hydrogens of the two rings resulting into the inter-ring twist. The observed planarity of biphenyl in crystal can be understood in terms of the tendency of layer formation due to large stacking forces between the phenyl ring in the absence of strong polar groups as substituents. Polar groups also have their stabilizing effect due to increased inter-molecular interactions. But the variety of twist angles observed with substitution of polar groups at different position i.e., ortho, meta and para suggests that relative strength of twisting force and planarization force have something more to reveal. For example, 4,4’-dichloro biphenyl shows a twist of $36^0 – 42^0$ while 4,4’-diamino-3,3’-dichloro derivative shows only $21^0$ twist and 4,4’-difluoro biphenyl is planar. What actually determines the inter-ring angle is therefore still an open question. Theoretical attempts to predict an inter-planar twist angle have so far not met significant success. A few theoretical attempts have been made earlier [13, 14] to predict the inter-ring twist angle, but they have met only a partial success.

**Table 4.2**

Inter-ring twist angles observed in biphenyl derivatives

<table>
<thead>
<tr>
<th>Biphenyl Derivative</th>
<th>Inter-ring Twist</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2’,4,4’,5,5’-Hexachloro biphenyl</td>
<td>58$^0$</td>
<td>Singh, Pederson, and Mckenmy (1986) [13]</td>
</tr>
<tr>
<td>2,2’-Dichloro biphenyl</td>
<td>58$^0$</td>
<td>Mckenmy, Gottschalk, and Pederson (1983) [14]</td>
</tr>
<tr>
<td>4,4’-Dichloro biphenyl</td>
<td>36$^0$ to 42$^0$</td>
<td>Brock, Kuo, and Levi (1978) [19]</td>
</tr>
<tr>
<td>4,4’-Dibromo biphenyl</td>
<td>36$^0$ to 42$^0$</td>
<td>Lui and William (1975) [20]</td>
</tr>
<tr>
<td>4-Nitro biphenyl</td>
<td>33$^0$</td>
<td>Casolan, Gavegatti (1973) [21]</td>
</tr>
<tr>
<td>4,4’-Dinitro biphenyl</td>
<td>33$^0$</td>
<td>Boonstra (1973) [22]</td>
</tr>
<tr>
<td>4-Acetyl-2’-Nitro biphenyl</td>
<td>45.9$^0$</td>
<td>Sutherland, Hogg, and William (1974) [23]</td>
</tr>
<tr>
<td>4-Acetyl-2’-Chloro biphenyl</td>
<td>49.2$^0$</td>
<td>Sutherland and Hoy (1968) [24]</td>
</tr>
<tr>
<td>4-Bromo biphenyl</td>
<td>54.7$^0$</td>
<td>Brock (1980) [25]</td>
</tr>
<tr>
<td>4-Acetyl-2’-Nitro biphenyl Amine</td>
<td>57.1$^0$</td>
<td>Sutherland (1986) [26]</td>
</tr>
<tr>
<td>2’-Iodo-4-biphenyl Carboxylic Acid</td>
<td>51.3$^0$</td>
<td>Sutherland (1976) [21]</td>
</tr>
<tr>
<td>4-Acetyl-2’-Fluro biphenyl</td>
<td>50.5$^0$</td>
<td>Young, Tollin, and Sutherland (1968) [28]</td>
</tr>
</tbody>
</table>

It was therefore decided to take up a systematic study of molecular structure of biphenyl in terms of variation in the twist angle on theoretical basis. In this chapter a detailed report of the investigation carried out using various theoretical techniques has been presented.

4.3 Method of Calculation

Since a large number of structural data for biphenyl is available from crystallographic studies of biphenyl derivatives; it is interesting to estimate the electron delocalization on parts of biphenyl ring under different conditions. Figure 4.1 shows the bond lengths of three representative molecules of different twist angle range. It is noteworthy that inside the ring, bond distance of the order of 1.34\text{Å} can be considered as consisting strongly interacting \(\pi\) orbitals while the range 1.4 \text{Å} can be treated as with weakly interacting \(\pi\) orbital pairs. Thus for practical purposes alternatively increasing and decreasing bond distance around ring can be treated as forming partially localized \(\pi\) orbitals whereas continuously increasing or decreasing bond length in a sequence suggests either the \(\pi\) orbitals are non-interacting or diffused over the entire range.

The available molecular orbital methods, in general do not provide adequate method for estimation of delocalization over a large range. Instead calculation with non-interacting \(\pi\) orbitals is relatively easy to perform. We have therefore taken the molecule as either with totally localized \(\pi\) orbitals or partial delocalization over certain bonds and estimated the minimum energy configuration under the selected configuration.

To construct the idealized biphenyl molecule, C-C bond length inside a ring taken as 1.4 \text{Å} while that between rings as 1.5 \text{Å}. Various MO methods [15-24] such as CNDO/2, MNDO, PCIL0 etc., have been employed.

Computations have been carried out using the MO programs obtained from TIFR, Mumbai, India. All the programs have been suitably modified by the investigator to run on a PC.
4.4 Results and Discussion I: Biphenyl

(a) SCF Studies:

Approximate SCF methods perform calculations with all valence electrons and have no special consideration for partial π electron delocalization. Conformational studies with CNDO/2 or MNDO method provide similar results i.e., indicate preference for inter-ring twist angle ± 90°.

(b) PCILO method

As stated earlier, this method is capable of handling π electron delocalization explicitly. It is much suitable for such problems. Detailed calculations have been performed using this technique. Further, in case of substituted molecules, structures such as

![Diagram](image1)

may not be treated as identical, hence these cases have been treated separately. The global and local minima in each case have been listed in Table 4.3. All the conformational search have been performed at the interval of 30°.

Table 4.3 summarizes the results obtained through PCILO calculations. The various configurations studies may be divided into three groups as mentioned below.
Table 4.3
Conformational minima obtained using PCILO method

<table>
<thead>
<tr>
<th></th>
<th>Structure</th>
<th>$E_{min}$</th>
<th>Minima</th>
<th>Energy Min.</th>
</tr>
</thead>
</table>
| A 1 | ![Structure](A1.png) | -49365.12 | +90  
-90 | 0.00  
0.00 |
| B 2 | ![Structure](B2.png) | -55803.56 | 60  
180-60  
180+60  
-60 | 0.00  
1.30  
0.06  
1.98 |
| C 3 | ![Structure](C3.png) | -58265.00 | 180+30  
180  
180+30 | 4.72  
0.00  
4.21 |
| 4 | ![Structure](C4.png) | -58302.16 | 0  
+30  
-30  
180 | 0.00  
2.25  
1.85  
4.95 |

(A) Totally unconjugated $\pi$ electrons in both the rings. This would mean that all $\pi$ orbitals in biphenyl ring are equivalent i.e., they have no preference to form a pair to make a specific partially localized $\pi$ orbitals. Instead, they can be fully delocalized over the entire ring (or remain localized on their atomic centres). The situation is similar to that considered by SCF method. Hence an identical result, i.e., preference towards $\pm 90^\circ$ twist has been obtained although the corresponding energy value is much higher than other configurations discussed in subsequent groups.

(B) One ring is fully conjugated to form three partially localized $\pi$ orbitals while the other is fully conjugated: It may be observed that all the forms of configuration in this group may be generated from one another by symmetry transformation by unsubstituted biphenyl. However, the clearly indicated preference for such configuration is in favour of inter-ring twist $60^\circ$. Energetically these configurations are preferred over group (A) or group (C) configurations.
(C) Biphenyl ring with six clear partially localized π orbitals i.e, π bonds fully conjugated to form pairs.

This group may be further analyzed into two sub groups. Configuration (3) has partially localized π orbitals attached to the inter-ring bridge in cis form while trans in configuration (4), they are in trans form. The preference is slightly towards trans form although in both the cases the molecule can readily assume the planar structure are inter-ring twist ± 30° with slight expense of energy.

An examination of these results in the light of experimentally observed twist angles (Table 4.2) shows that the configurations shown in group (A) are energetically unacceptable and have no experimental evidence. Experimentally observed twist angles are largely in the range 30° – 60° which is very supported by these calculations. However, the results in group (B) have also indicated planar configuration as a preferred one at lower energy. Hence planarity of unsubstituted biphenyl or some of its derivatives in crystals may be understood. Also it is understandable why in vapour phase (i.e. at increased energy) these molecules show inter-ring twist ~ 40°.

It must be mentioned here that in substituted molecules the configuration may possess an intermediate structure within these four cases, in other words, there may be a random combination of partially localized π orbitals. But since group (B) & (C) are at two extremes, a random combination is expected to prefer a value within the range (30° – 60°) only and in some cases a planar configuration.

These investigations clearly suggest that the intra molecular hydrogen-hydrogen repulsions are not the sole factor to determine the inter-ring twist. The interaction between π orbitals inside a ring has effective control over the inter-ring twist.

**Table 4.4**

<table>
<thead>
<tr>
<th>Biphenyl Derivative</th>
<th>Inter-ring Twist</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Acetyl-2’-Flurobiphenyl</td>
<td>129.0° 180-51°</td>
<td>Sutherland (1976) [27]</td>
</tr>
<tr>
<td>4’-Nitro-2-biphenyl amine</td>
<td>235.7° 180+55.7°</td>
<td>Sutherland and Ali (1986) [26]</td>
</tr>
<tr>
<td>4-Acetyl-2’-Chlorobiphenyl</td>
<td>229.2° 180+49.2°</td>
<td>Sutherland and Hoy (1968) [24]</td>
</tr>
<tr>
<td>4,4’-Dinitro-3,3’-Dimethyl biphenyl</td>
<td>319.0° (-41°)</td>
<td>Chawadhary (1968) [29]</td>
</tr>
</tbody>
</table>
It was therefore felt necessary to test these findings by taking up actual case studies.

Table 4.4 presents the systems on which the computations have been carried out. An attempt has been made to examine whether the criterion derived from the study of unsubstituted biphenyl ring is able to predict inter-ring twist with reasonably good accuracy. Here we have differed from the usual PCILO method in the selection of partially localized $\pi$ orbitals on the biphenyl ring. The criterion followed is as under:

(i) A bond on the biphenyl ring is presumed to have partially localized $\pi$ orbitals if the bonds on the both sides have greater bond length than the next adjacent ones.

(ii) If a sequence of bonds on the ring possesses continuously decreasing bond lengths and terminating to a sufficiently short bond length, even the shortest bond need not be treated to have partially localized $\pi$ orbitals.

(iii) A single bond on the ring is approximately equal to $1.4\text{Å}$ while partially localized $\pi$ orbitals is close to $1.35\text{Å}$ although, this may not be treated as a very strict criterion.

It is to be noted that all the selection criteria mentioned above should assign a partial double bond character for which molecular orbital methods, in general, do not include any specific procedure (not even PCILO). Thus these criteria are of ad-hoc nature and are not a result of any kind of theoretical justification.

Geometry of each molecule has been taken from literature [2-4]. Energy calculations have been carried out by inter-ring dihedral angle firstly at an interval of $30^\circ$. After reaching the minimum further refinements have been carried out at the accuracy of $5^\circ$ and there after of $1^\circ$.

4.5 Results and Discussion II: Case Studies

Geometries of the studied molecules have been shown in Figure 4.1 (a, b, c, d) along with their bond lengths. Results are discussed for each molecule separately.

(a) 4-acteyl-2’-fluro biphenyl

Inspection of bond lengths on the biphenyl ring recommends only one partially localized $\pi$ orbital between atom 1 and 2 as shown in Figure 4.1 (a). Figure 4.2 shows the variation of energy with inter-ring twist angle. It may be observed that the minima are at $180^\circ \pm 30^\circ$ and that at $150^\circ$ having the lowest energy value. The energy barrier is very
Figure 4.1(a): 4-acetyl-2'-Fluro biphenyl
Figure 4.1 (b): 4’-Nitro-2-biphenyl amine
Figure 4.1 (c): 4-Acetyl-2’-Chloro biphenyl
Figure 4.1 (d): 4, 4’-Diamino-3, 3’-Dimethyl biphenyl
Figure 4.2: Variation of conformational energy with respect to inter-ring twist angle for 4-acetylene-2'-fluorobiphenyl. The minimum energy conformation is treated as at zero.
high since a minor change in twist angle alters the energy in thousands (kcal/mole). The molecule shows a preference for nearly planar conformation. On further refinement of energy value near 150°, it was observed that at 129° the molecule shows a deep minimum which is surprisingly in exact agreement with the value reported by crystallographers [27].

(b) 4'-nitro-2-biphenyl amine

Bond lengths show in the Figure 4.1 (b) exhibit a totally unlocalized π distribution for the ring attached with nitro group while that with amino group shows a partial localization at bond between 7 and 12. Variation of energy with respect to twist angle (Figure 4.3) shows four minima located at 60°, 120°, 240° & 300° where 240° corresponds to the lowest energy configuration. On further refinement of conformation near 240° at lower intervals, it was observed that a wide minimum exhibit at 233°-236°, the lowest being at 235° which is in agreement with the crystallographers reported value 235.7°.

(c) 4-acetyl-2'-chlorobiphenyl

It seems difficult to assign partially localized π orbitals to any of the bonds of this molecule (Figure 4.1 (c)) through the criteria mentioned earlier. However, it may be noticed that the average bond length of this molecule is larger than other derivatives. Further, bond 3-4, 7-8, and 10-11 satisfy criteria partially. Results have been reported for the best combination i.e. a double bond at 3-4 and rest two as single bonds. The energy versus twist angle curve (Figure 4.4) shows a clear minimum at 240°. On further refinement it was observed that the minimum energy region is fairly wide ranging from 225° to 250°, agreeing with the crystallographically observed value.

(d) 4, 4'-diamino-3, 3'-dimethyl biphenyl:

This molecule contains four bonds of length 1.35Å - 1.36Å, each having the two bonds of length greater than 1.4 Å on both side (Figure 4.1(d)). Energy variation curve (Figure 4.5) shows that inter-ring twist is quite flexible for the entire 0°-360° range the energy difference is within 10 kcal/mole. The lowest energy point is at 150° but their exists a number of other minima where in the molecule can easily be trapped. Since the crystallographically observed twist is 319°, it seemed proper to refine the minimum at 330°, which lowered the energy value further by 2.76 kcal/mole. Thus, the
Figure 4.3: Variation of conformational energy with respect to inter-ring twist angle for 4’- Nitro-2-biphenyl amine.
Figure 4.4: Variation of conformation energy with respect to inter-ring twist angle for 4-acetyl-2' Chlorobiphenyl.
Figure 4.5: Variation of conformation energy of 4,4’-Diamino-3,3’-Dimethyl biphenyl with respect to inter-ring twist angle.
crystallographically observed conformation is identified as a local minimum and obviously not the most probable one.
References:


