TOWARD POLAR 1,4-DIPHENYLBUTADIENE MATERIALS

A Thesis presented to the Faculty of the Graduate School
University of Missouri-Columbia

In Partial Fulfillment
Of the Requirements for the Degree

Master of Science

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by
YONGQIANG SUI

Dr. Rainer Glaser, Thesis Supervisor

DECEMBER 2004

The undersigned, appointed by the Dean of the Graduate School,

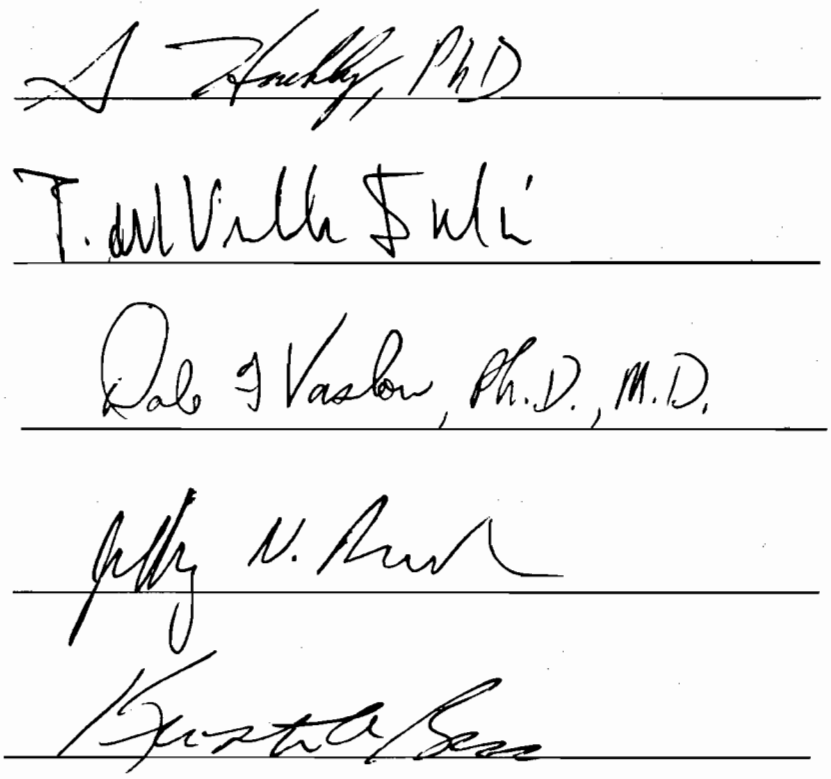
have examined the thesis entitled.

FAST OPTICAL SIGNAL DETECTED IN THE PREFRONTAL LOBE WITH NEAR-INFRARED SPCETROSCOPY DURING SLEEP

Presented by Jun Zhao

A Candidate for the degree of Master of Arts

And hereby certify that in their opinion it is worthy of acceptance.



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TOWARD POLAR 1,4-DIPHENYLBUTADIENE MATERIALS

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James Glass.

Jill Pflum

Mona Chandrasekhar

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TOWARD POLAR 1,4-DIPHENYLBUTADIENE MATERIALS

Yongqiang Sui

Dr. Rainer Glaser, Thesis Supervisor

ABSTRACT

The fast response time of π-electrons makes organic materials increasing interesting as highly anisotropic materials. We are especially interested in dipole parallel-aligned crystals because of the much higher chromophore density as compared to polymers. Our group achieved several near-perfectly and perfectly dipole parallel-aligned crystals of acetophenone azines, and two assumptions to guide the design. One is that arene-arene T-contacts work as lateral synthons and help to align polar molecules, and, secondly, the azine spacer functions as a conjugation stopper and provides quadrupolarity. To deeply analyze and support these suppositions, the intramolecular features and intermolecular bonding of 1,4-diphenylbutadiene and its derivatives have now been studied.

In Chapter 1, we illustrate the difficulty of achieving dipole parallel-aligned crystals, the solution to the problem, and the research in our group. In Chapter 2, (E,E)-1,4-diphenyl-1,3-butadiene is analyzed by computations in gas phase, dissections in its two polymorphs, and comparisons of the crystal structure of benzene, in Chapter 3, Unsymmetrical syntheses of *(E,E)*-2,5-diphenyl-2,4-hexadienes are discussed.

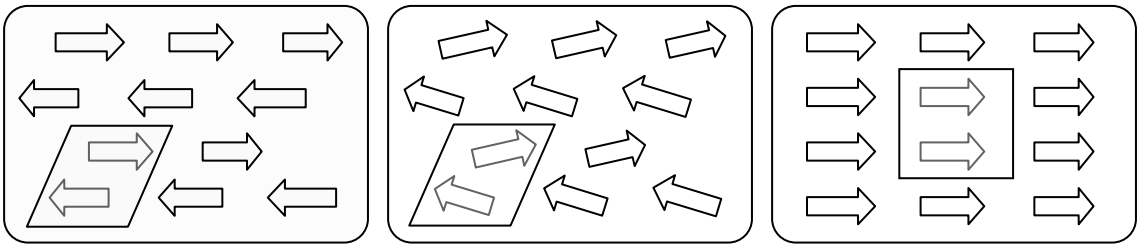
The last chapter of the thesis is concerned with an entirely different topic, namely the challenges of preparing college students for science communication. In Chapter 4, the design and development of a webtool is described to support the *Chemistry Is in the News* project.

CHAPTER 1. Organic Crystalline NLO Materials

1.1 Introduction

Nonlinear optical (NLO) materials have become increasingly more important to telecommunication, optical computing and lasers. Lately, organic NLO materials receiving increased more attention because of the characteristics of the materials i.e.: ultra-fast response time, lower electric constants, and easier processability, relative to traditional inorganic solids.[1-7,19-23] The macroscopic dipole moments are important to achieve many optical and electrical properties in organic NLO materials. The realization of macroscopic dipole moments for use in nonlinear optics has largely been achieved through liquid crystals,[8,9] poled polymers,[10,11] and the inclusion of NLO active chromophores into natural or synthetic zeolites.[12,13] These approaches listed above for the design of polar order are limited by their disadvantages. The use of liquid crystals suffers that the overall polarity is small because only a small excess of the molecules having their dipole moments aligned in a parallel fashion. The whole dipole moments of poled polymers and inclusion compounds are also low because of small chromophore densities, and the NLO activities of poled polymer will decline and disappear without external electric fields. Thus, the NLO crystals[14-18] with high polarity is the final goal in the design of polar materials.

Scheme 1-1 describes what primarily occurs when polar molecules aggregate in the solid phase.[19] Scheme 1-1a shows what most often occurs in a crystal lattice. The dipole moment of the crystal is zero because the molecules cancel their dipole moments. Some molecules have been crystallized with partial cancellation of the crystalline (Scheme 1-1b), the total dipole moment is very small. The ideal case is shown in Scheme 1-1c, in which complete reinforcement of molecular dipole moments is achieved.



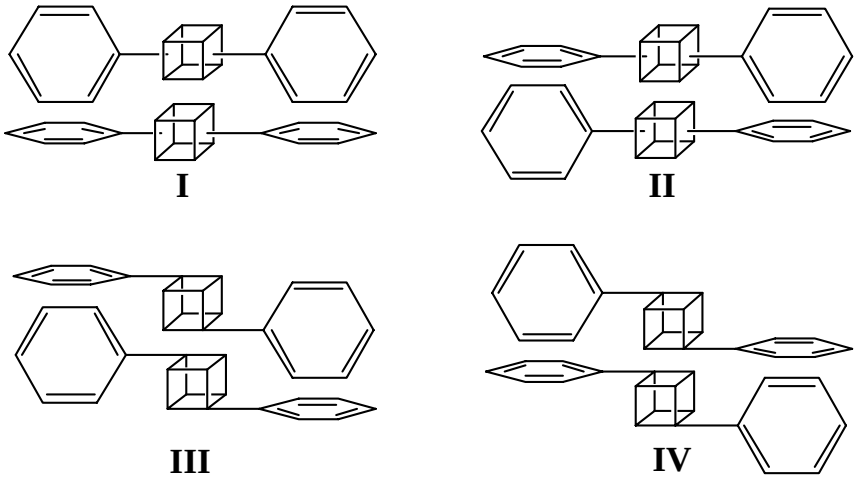
a. Complete cancellation b. Partial cancellation c. Parallel dipole alignment

Scheme 1-1. Dipole alignment in the solid phase.

The design of crystals with parallel dipole alignment (Scheme 1-1c) is our goal. In our strategy, two concepts have been developed to design polar crystals: lateral synthons and the minimization of dipole moments.[20] A synthon is a molecular fragment with capability in binding with certain other atoms or functional groups with high selectivity and high affinity, and a lateral synthon provides for an intra-layer interaction between molecules of the same layer.[21,22] The intra-layer interactions between lateral synthons are able to compensate the electrostatic repulsions in the dipole parallel-aligned crystals. Two types of lateral synthons have been used in our crystal lattices: arene-arene double T-contacts (DT) and azine-phenyl contacts. Arene-arene double T-contacts happen

when two phenyl rings interact with two other phenyl rings of an adjacent molecule in an edge-to-face manner.[23,24] The interaction between an azine bridge and a phenyl ring of neighboring molecules is named as azine-phenyl contact.

There are many geometries to form double T-contacts. Four possible conformations are shown in Scheme 1-2.[23-25] There are two molecules in each conformer and two phenyl rings in each molecule. For the molecules with collinear phenyl rings, **I** and **II** are the only possibilities to form equidistant double T-contacts. For the molecules with offset phenyl rings, there are many possible confirmations to form equidistant double T-contacts, and **III** and **IV** are just two examples. Within each molecule, the angular perturbations between the planes of the two phenyl rings could construct other possible conformers. The perpendicularity of two phenyl rings represented in **III** and **IV** is only one possibility.

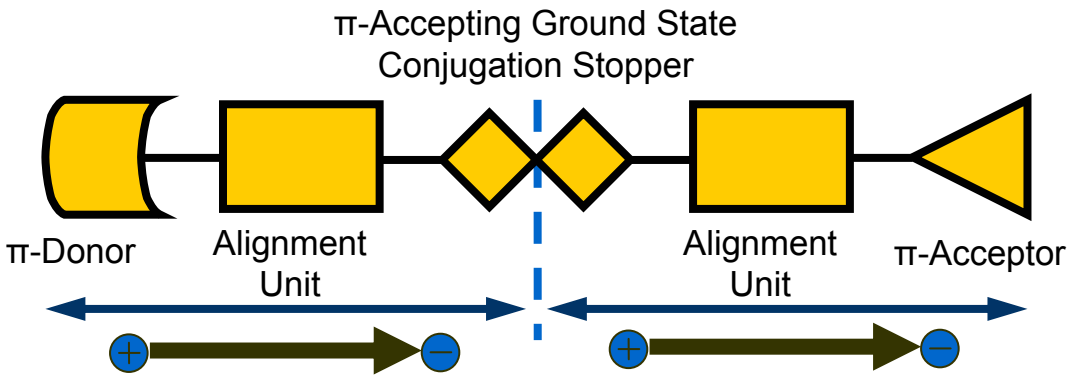


Scheme 1-2. Representation of Arene-Arene Double T-Contacts.[25]

The concept “dipole moment minimization” was introduced by Zyss, et al. in their work.[26] When polar molecules are combined to grow crystals, the electrostatic repulsion will be decreased due to the small dipole moments of the chromophores. Therefore, parallel dipole alignment will be achievable.

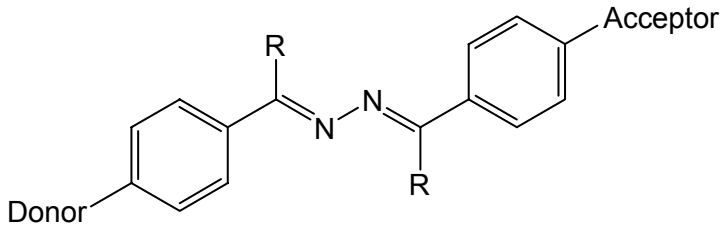
1.2 The Glaser approach

Our group addressed the challenge of making NLO crystals with parallel dipole alignment with azines, and, up to now, we have achieved the realization of several classes of perfectly aligned materials for azines.[19,20,27-35] The molecular design with azines is depicted in Scheme 1-3. For azines, the alignment unit equals a phenyl ring, and the conjugation stopper is the twisted azine bridge.



Scheme 1-3. Molecular design with azines.

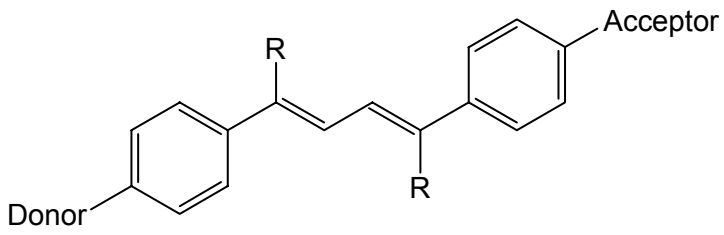
Our group has studied many acetophenone azines (Scheme 1-4), both the symmetric[30,32,34,35] and unsymmetric,[27-29,31,36] with the goal of achieving dipole parallel-aligned crystals. If both the donor and acceptor are identical, the azine is symmetric, otherwise, it is unsymmetric. In Scheme 1-4, we have used R=H and R=CH_3.



Scheme 1-4. General structure of azines.

1.3 Butadienes

To deeply analyze and support these assumptions, the next area of study is with the analog to the azine, which is 1,4-diphenylbutadienes and its derivatives (Scheme 1-5). We started with the crystal structure of the parent 1,4-diphenylbutadiene (R = Donor = Acceptor = H),[37] and are working with its another polymorph and 2,5-diphenyl-2,4-hexadienes (R = CH_3). We hypothesize that the 1,4-diphenylbutadienes and 2,5-diphenyl-2,4-hexadienes may exhibit arene-arene double T-contacts, and the butadiene bridges are analogous to azine bridges as conjugation stoppers. These materials may represent a new series of dipole parallel-aligned crystals.



Scheme 1-5. General structure of 1,4-diphenylbutadienes.

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CHAPTER 2. Ab Initio and Crystal Structures of (*E*,*E*)-1,4-Diphenylbutadiene

2.1 Introduction

Our group is interested in organic NLO crystals. We have crystallized several near-perfectly and perfectly dipole aligned crystals with azines. Unsymmetrical and symmetrical azine have been studied to analyze the assumptions mentioned in Chapter one.[1-7] We are investigating the crystal properties of a carbon analog in comparison to the azine to better understand the intra-molecular and inter-molecular forces (Figure 2-1).

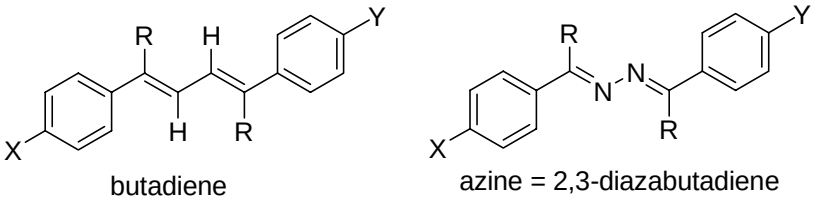


Figure 2-1. Butadienes and azines.[8]

The carbon analog is 1,4-diphenylbutadienes (Figure 2-1). There are three polymorphs of 1,4-diphenylbutadiene (**1**, R=X=Y=H), reported fifty years ago. Hengsttenberg and Kuhn reported one monoclinic polymorph (**I**) in 1930,[9] which was grown in glacial acetic acid. Drenth and Wiebenga published two more polymorphs in 1953.[10] One polymorph (**III**) was grown in chloroform with ethanol, and then the same polymorph was used to obtain polymorph (**II**) by sublimation (Table 2-1).

Our group obtained and reported **III** in 2003 with matching parameters (Table 2-1).[8] In that paper, the butadiene was analyzed by gas phase calculations, the crystal structure X-ray data of **III** was analyzed, crystal structure to the $P2_{1/c}$ structure of benzene was compared to **III**, and the possible reasons for this polymorph were proposed. The analysis of the computations suggest that there are two essentially isoenergetic symmetries, C_i and C_2. Both are s-trans with the planar central bond ($\tau = 180°$) and a phenyl twist ($\Phi = 20°$). The optimized C_i and C_2 structures are displayed in Figure 2-3.

Table 2-1. Lattice constants for 1,4-diphenylbutadiene.

Parameter	Hengstenberg & Kuhn[9] 1930	Drenth & Wiebenga 1953[10]		Glaser et al. 2003[8]	This work
	I	II	III	III	II
Crystal Prep.	Monoclinic glacial acetic acid	Orthorhombic III, 145° below mp.	Monoclinic EtOH or $CHCl_3$	Monoclinic EtOH diff into $CHCl_3$	Orthorhombic III, 120° below mp.
a (Å)	7.71	8.89	5.86	5.8106	8.0755
b (Å)	11.70	8.22	7.66	7.533	8.9868
c (Å)	13.41	16.68	53.1	53.367	16.5453
β (°)	97.	90.	91	91.067	90
Density (cal., mg/mm^3)	1.138	1.124	1.149	1.173	1.1410
Molec. Per unit cell	4	4	8	8	4
Space group		Pcab	$P2_1/n$	$P2_1/n$	Pbca
Number of Indep. Mol.	2	1	3	3	1

Table 2-2. Comparison of bond lengths of calculations[8], crystal **III**[8], and **II**

Bond	RHF /6-31G*	B3LYP /6-31G*	B3LYP /6-311G**	Average In **III**[8]	Crystal **II**
C1−C1'	1.459	1.442	1.441	1.437	1.436
C1=C2	1.330	1.354	1.351	1.332	1.335
C2−C3	1.475	1.462	1.461	1.463	1.461
C3--C8	1.393	1.409	1.407	1.398	1.392
C3--C4	1.396	1.410	1.408	1.394	1.391
C4--C5	1.385	1.394	1.391	1.374	1.376
C5--C6	1.383	1.395	1.393	1.382	1.371
C6--C7	1.388	1.398	1.396	1.380	1.374
C7--C8	1.382	1.392	1.388	1.369	1.385

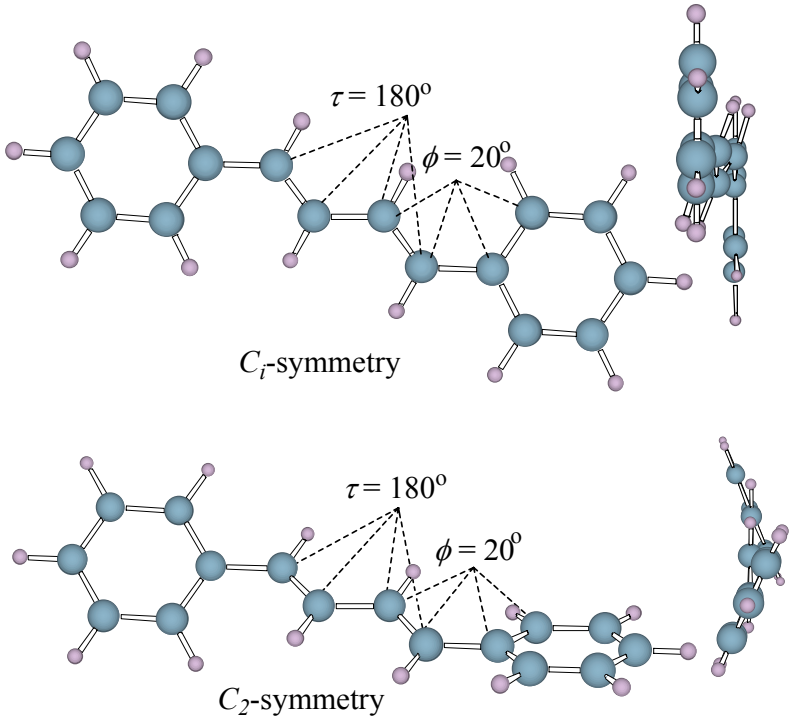


Figure 2-2. Molecular models of the MP2(full)/6-311G** optimized C_i and C_2 symmetric structures of *(E,E)*-1,4-Diphenylbutadiene[8]

Table 2-3. Crystal data and structure refinement.

Compound	C_6H_5-CH=CH-CH=CH-C_6H_5
Formula weight	206.27
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 8.0755(13) Å α = 90°
	b = 8.9868(14) Å β = 90°
	c = 16.545(3) Å γ = 90°
Volume	1200.7(3) $Å^3$
Z, Calculated density	4, 1.141 mg/m^3
Absorption coefficient	0.064 mm^{-1}
F(000)	440
Crystal size	0.45 x 0.40 x 0.05 mm
θ range for data collection	2.46 to 27.14°
Limiting indices	$-9 \leq h \leq 10$, $-11 \leq k \leq 11$, $-21 \leq l \leq 17$
Reflections collected / unique	6816 / 1332 [R_{int} = 0.0554]
Completeness to θ= 24.71	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.97
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1332 / 0 / 73
Goodness-of-fit on F^2	1.053
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0602, ωR^2 = 0.1082
R indices (all data)	R_1 = 0.1180, ωR^2 = 0.1237
Largest diff. peak and hole	0.168 and -0.126 $e.Å^{-3}$

The arene-arene interactions in the crystal structure of **III** are analogous to the crystal structure of benzene with the space group of $P2_{1/c}$. The crystal construction of **III** allows for more complex arene-arene interactions, which are caused by the spacers and lateral off-sets between the two phenyl rings of **1**, and the formation of diastereoisomeric contacts. The diastereoisomeric double T-contacts between two molecules can contribute the formation of two-dimensional layers. In this context, the present study is a continuation of our work on 1,4-diphenylbutadiene.

2.2 Experimental Section

The powder of (*E,E*)-1,4-diphenylbutadiene was purchased from Aldrich. Sublimation of **1** at 120° for overnight resulted in crystals of **1** (**II**, Table 2-1). The crystal structure of the polymorph **II** belongs to the P_{bca} space group with cell parameters a = 8.0755(13), b = 8.9868(14) and c = 16.545(3) Å. Crystallographic data for **II** is presented in Table 2–3 and selected geometric parameters are shown in Table 2–2. Table 2-2 contains the bond lengths in the crystal structure. The average bond lengths in the Table 2-2 are the average bond lengths for a particular bond in **III**.[8] The molecules in the crystal structure of **II** are shown in Figure 2-2.

2.3 Crystal Structure of *(E,E)*-1,4-Diphenylbutadiene

2.3.1 Single Molecule

The gas-phase structure of **1** was calculated,[8] and the geometry optimizations were carried out by using RHF/6-31G*, B3LYP/6-31G*, and B3LYP/6-311G** with using Gaussian 98.[11] The optimized structures, average bond lengths from the crystal structure of **III,** and the bond lengths of **II**, as given in Table 2-2.

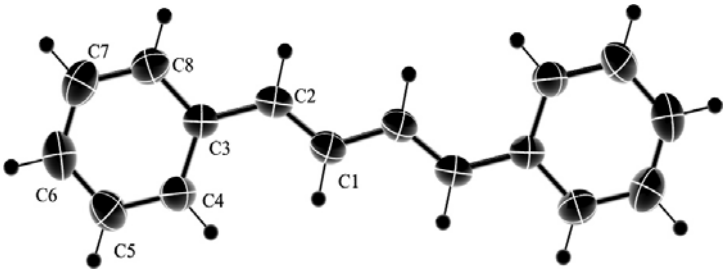


Figure 2-3. *ORTEP* II diagram for molecules in the crystal structure of **II**.

The polymorph **II** consists of one unique molecule (Figure 2-3). The bond length of C1-C1' (1.436 Å) is shorter than normal sp^2-sp^2 single bond (1.46 Å), and the bond length of C1=C2 (1.335 Å) is also slightly shorter than normal sp^2-sp^2 double bond (1.34 Å).[12] Compared to **III**, the length of single bonds in **II** are a little shorter with C1-C1' = 1.436 Å and C2-C3 = 1.461 Å. All bond lengths are shorter than the calculated values except bond C2-C3.

The space group of **II** is P_{bca}, and the structure of a single molecule is perfectly C_i-symmetric with a C=C—C=C dihedral angle τ of exactly 180º, as predicted by computations, but the rotation Φ of the phenyl groups is different from calculated angle (20º). The result is Φ = 6.3º, which is caused by intermolecular interactions. (Figure 2-4)

We define the phenyl twist angle as show in Figure 2-3, that is, as the dihedral angle C=C—C—C_{ortho}.

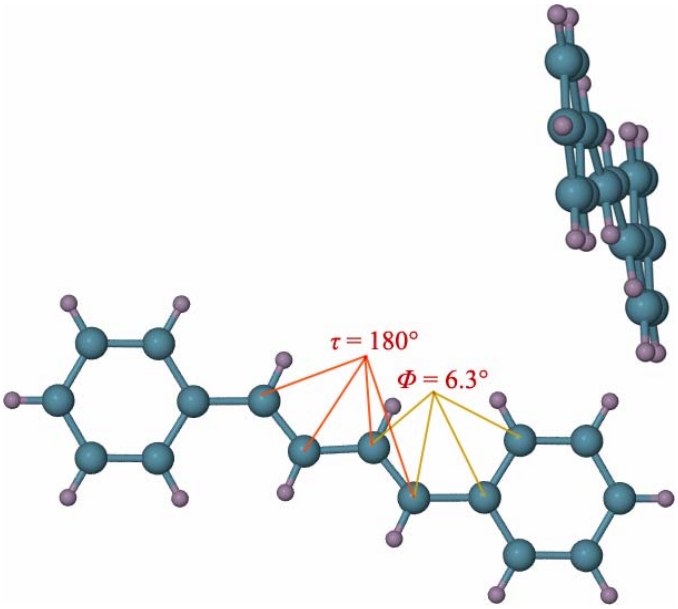
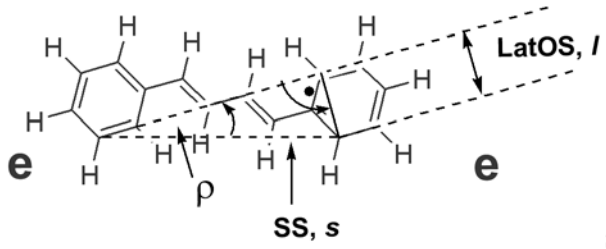


Figure 2-4. *XSeed* representation of single molecule of 1,4-diphenylbutadiene in **II**

A spacer which causes "lateral off-set" (LatOS, *l*) is prerequisite for the double T-contact between two planar molecules (shown as model I in scheme 1-2). Each benzene has a local rotational axis and a LatOS spacer is one that causes these two local rotational axes to be noncolinear. No lateral off-set requires $\rho = 0$ and the value for ρ depends on the lateral off-set *l* caused by the spacer and the length of the synthon spacing (SS, *s*). [8]



$$\sin(\rho) = l / s$$

Figure 2-5. Description of lateral off-set (LatOS, *l*) [8]

The LatOS values were measured and given in Figure 2-6. Compared the molecules in **III** (Figure 2-14), the most similar molecule in **III** is **B**.

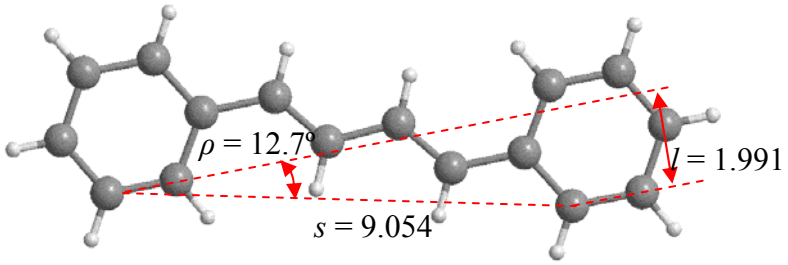


Figure 2-6. *Chem3D* representation of lateral off-set of single molecule of 1,4-diphenylbutadiene in **II**

2.3.2 Crystal Packing

We characterized double arene-arene contacts by specification of the type of coordination mode of the two arenes in each molecule, "f" for face or "e" for edge. Each molecule is characterized as (ee), (ff), (ef), or (fe), and a "double arene-arene contact" is characterized by two pairs that characterize the two molecules, and these are separated by a vertical bar.[8]

The crystal structure of **III** contains three independent molecules **A-C** with modest *Ci* symmetric (or *Ci*-like) deformations due to twisting about the C-Ph bonds.[8] The ab initio calculations show that the twisting in the crystal is much smaller than in the gas phase and only the **B** molecules show significant twisting.[8] In **II,** the molecules are perfectly s-trans, $\tau = 180°$, and the phenyl twists is $\Phi = 6.3°$, which is bigger than A ($\Phi_{A1} = 2.7$, $\Phi_{A2} = 3.9$) and C ($\Phi_C = 0.8$), and smaller than B ($\Phi_B = 12.7$).[8]

We had already compared **III** with the crystal structure of $P2_{1/c}$, benzene, and drawn the conclusion that the arene-arene interactions in **III** are analogous to the $P2_{1/c}$ structure of benzene.[8] Now, if we compare the structures of P_{bca} structure benzene[8,13-15] and **II**, (Figure 2-7, 2-8, and 2-9) we still may apply the conclusion to P_{bca} structure benzene and **II**. Clearly, these arene-arene intermolecular interactions are one of the main reasons for the planarization of **1**.

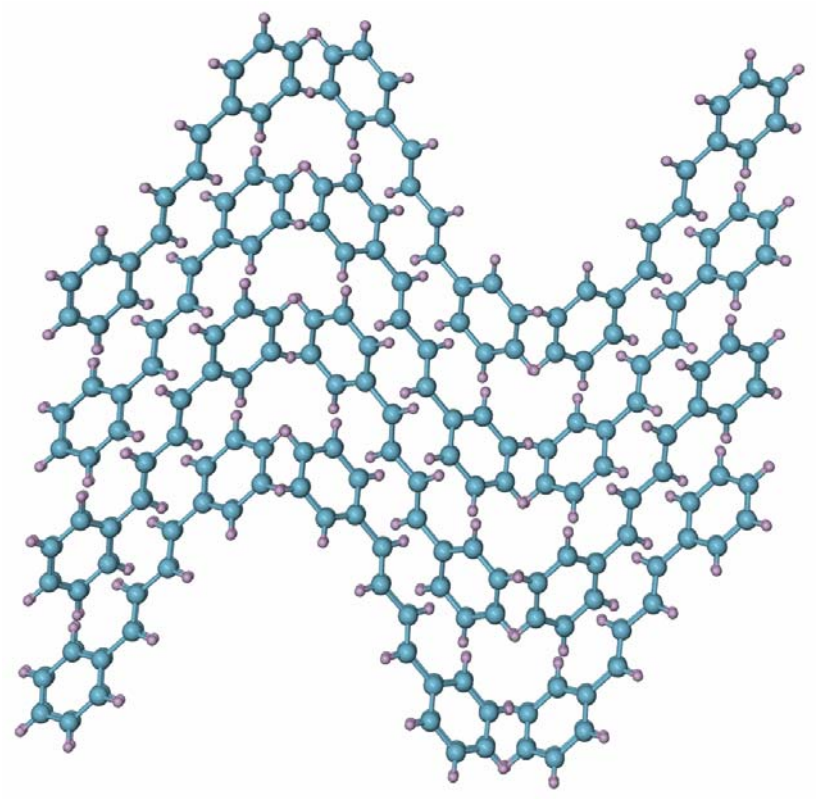


Figure 2-7. *XSeed* representation of the crystal packing of **II**, viewed down the diagonal of the **ab**-plane with the ***c***-axis aligned horizontally.

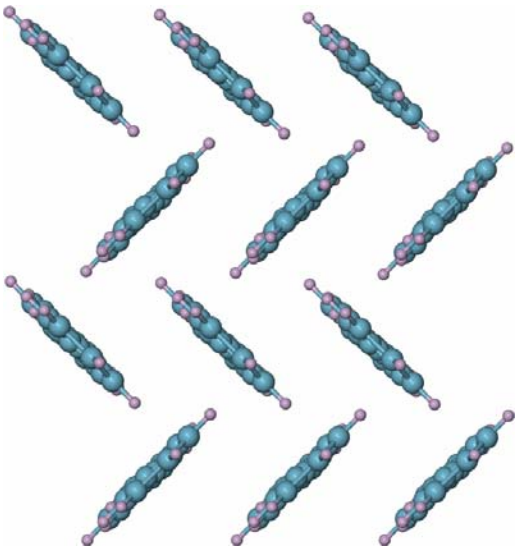


Figure 2-8. *XSeed* representation of the crystal packing of **II**, viewed from the side of one layer.

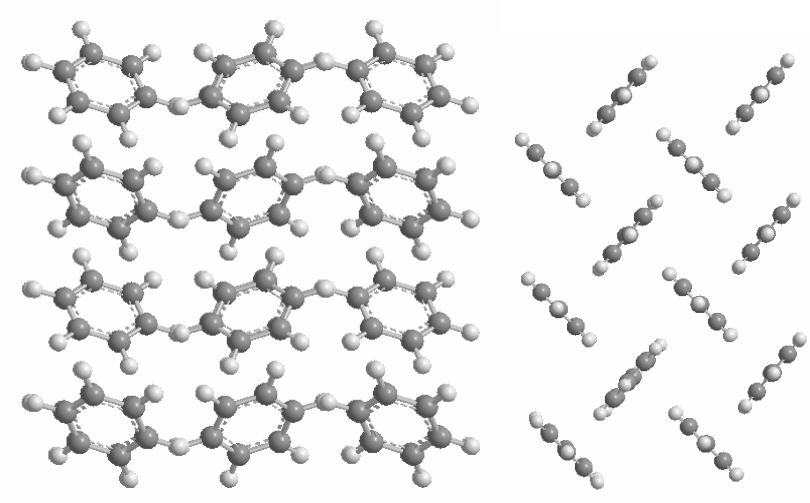


Figure 2-9. *Chem3D* representation of crystal structure of P_{bca} Benzene[8,13-15]

We see that the intermolecular interactions in crystal **II** are greatly different from that in **III**. The interactions between layers are edge to edge (ee) contacts (Figure 2-10). In Figure 2-11, we see that the interactions between layers in crystal **II** are much stronger, and these arene-arene T-contacts between molecules in different layers in detail.

Compared to edge-edge contacts in **III**, the angle between two layers also changed to form interlayer T-contacts, which is 98.28º.

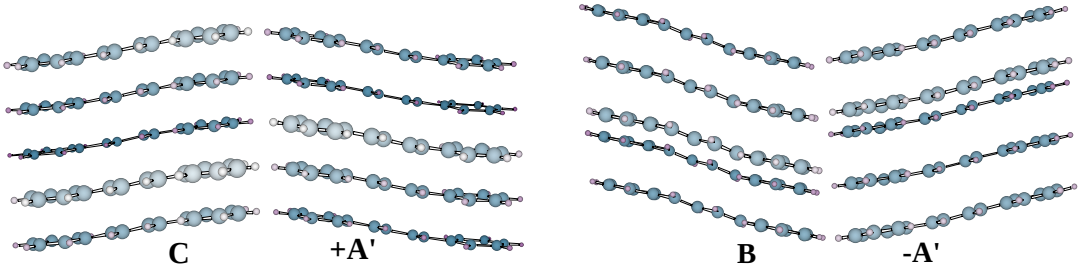


Figure 2-10. *Chem3D* representation of the crystal packing of **III**.[8]

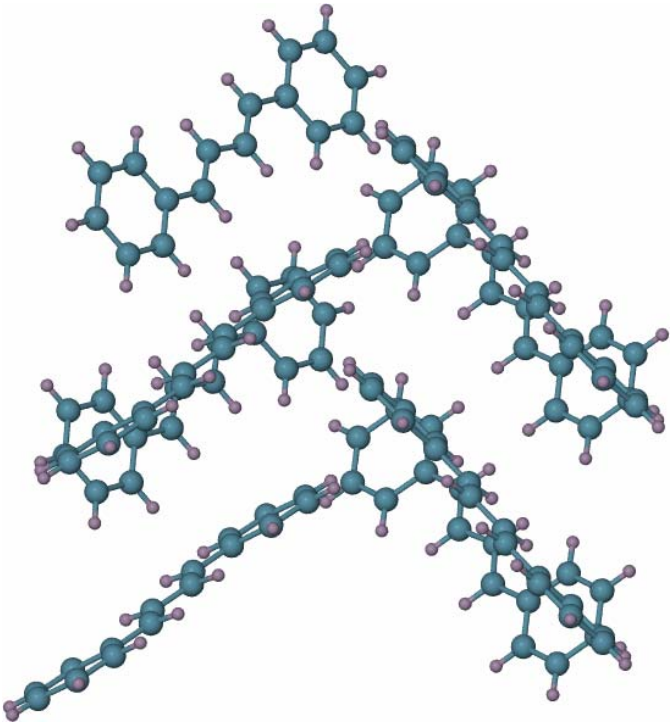


Figure 2-11. *XSeed* representation of the interlayer interactions in **II**.

In **III**, there are four arene-arene T-contacts for each phenyl group.[8] In **II**, there are strong T-contacts with big angles (98.28º) between layers, so the energy of **II** is lower than that of crystal **III**.

2.3.3 Intermolecular bonding

Characterization of the parallel off-set (ParOS, p) and the stacking distance (SD, d) between the faces of the molecules was accomplished by eqs 1 and 2 based on the distance m and the angle δ (Figure 2-12).[8]

$$\cos(\delta) = p / m \quad \text{(eq. 1)}$$

$$\sin(\delta) = d / m \quad \text{(eq. 2)}$$

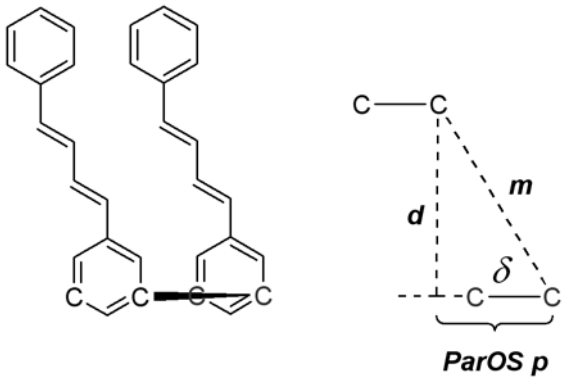


Figure 2-12. Description of parallel off-set (ParOS, p) and the stacking distance (SD, d) [8]

The ParOS values in **II** are shown in Figure 2-13. The distance (m = 8.987 Å) is much longer than that in **III** (m = 5.810 Å), but by the change of the angle δ (20.9º), the stacking distance (d_A = 3.232 Å) is very close to the distances in **III** (d_A = 3.232 Å, d_B = 4.398 Å, d_C = 3.071 Å) [8].

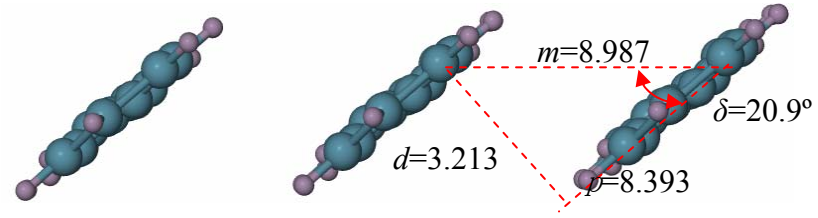


Figure 2-13. Description of one column in **II**. The molecules in one column interact with each other by way of double face-to-face arene-arene contacts (ff|ff).

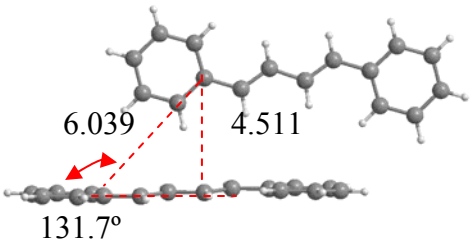


Figure 2-14. The one unique double T-contacts in **II**.

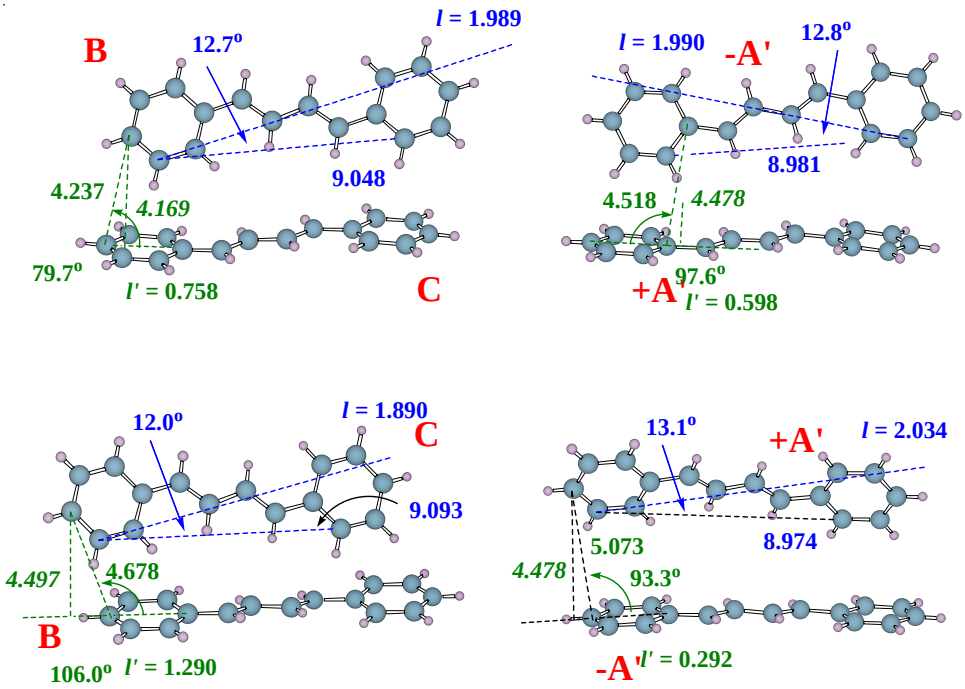


Figure 2-15. The four unique double T-contacts in **III** [8]

The parallel off-sets (ParOS, p) between a pair of neighbor molecules also different from ParOS values in **III**. By Figure 2-14 and 2-15, we can compare the shifts in two crystals. In **II**, the parallel off-sets are longer, and molecules are closer, so we may predict that the pairing energy of one pair of molecules in **II** is lower than that in **III.**

2.4 Computational Section

The computations was carried with Gaussian 98,[11] and methods MP2/6-31+G, MP2/6-31+G*, and MP2/6-311+G* were used. Three unique pairs of molecules were chosen (Figure 2-16). There are a double face-to-face contacts and a butadiene-butadiene contact in Pair A. The contacts in Pair B are double intra-layer butadiene-benzene contacts, and the contacts in Pair C are single inter-layer T-contacts. The results of calculations are summarized in Table 2-5, and calculated molecules are shown in Figure 2-16.

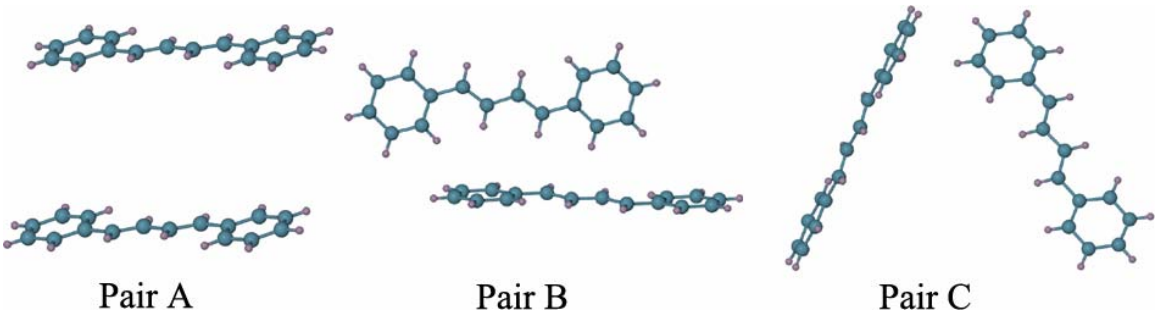


Figure 2-16. The three unique pairs of molecules in **III**

Table 2-4. Calculation of pairing energy in **II** (kcal/mol)

	MP2/6-31+G	MP2/6-31+G*	MP2/6-311+G*
Pair A	-2.11	-0.15	-0.80
Pair B	-5.04	-6.75	-7.75
Pair C	-5.10	-4.43	-4.70

Compared to Pair B and Pair C, the pairing energy of Pair A is the lowest because of the long distance between molecules, and the absence of T-contacts. At the MP2/6-31+G level, the pairing energy for Pair B and Pair C, but we used more accurate computation methods MP2/6-31+G* and MP2/6-311+G*, the pairing energy of Pair B is

much higher than that of Pair C. The pairing energy of Pair C is 4.70kcal/mol, which is still pretty high. If we think that there are two contacts in Pair B, and the average energy of each contact is -3.87kcal/mol, we may say that the T-contact in Pair C is the strongest contact in **II**.

2.5 Conclusion

The polymorph **II** of 1,4-diphenylbutadiene contains only one independent molecule with C_i symmetric deformations due to twisting about the C-Ph bonds, while the crystal **III** has three independent molecules with same symmetric deformations. The polymorph **II** was obtained by sublimation, and it is more stabilized thermally than the crystal **III**. By the analysis of crystal structure, we know there are butadiene-benzene contacts in polymorph **II** instead of double T-contacts in polymorph II. The contacts between layers are also different between polymorphs **II** and **III**. The interlayer contacts in **II** are T-contacts, and the edge-edge contacts are the contacts between layers in **II**. The double butadiene-benzene contacts in **II** are very strong while the T-contacts in layers are the strongest, which is observed by the calculated binding energies. The molecules in **II** are planar with exception to the slight rotation angle Φ = 6.3º. With comparing the crystal structures, we may draw the conclusion that the planarity of the molecule enhances the T-contacts between the molecular pairs.

2.6 References

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2.7 Appendix

Crystal Data and Atomic Coordinates for the Crystal Structure of **II**

Table 2-A1. Crystal data and structure refinement.

Compound	C_6H_5-CH=CH-CH=CH-C_6H_5
Formula weight	206.27
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 8.0755(13) Å α = 90°
	b = 8.9868(14) Å β = 90°
	c = 16.545(3) Å γ = 90°
Volume	1200.7(3) Å ^{3}
Z, Calculated density	4, 1.141 mg/m^3
Absorption coefficient	0.064 mm^{-1}
F(000)	440
Crystal size	0.45 x 0.40 x 0.05 mm
θ range for data collection	2.46 to 27.14^o
Limiting indices	$-9 \le h \le 10$, $-11 \le k \le 11$, $-21 \le l \le 17$
Reflections collected / unique	6816 / 1332 [R_{int} = 0.0554]
Completeness to θ= 24.71	99.9 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.99 and 0.97
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1332 / 0 / 73
Goodness-of-fit on F^2	1.053
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0602$, $\omega R^2 = 0.1082$
R indices (all data)	$R_1 = 0.1180$, $\omega R^2 = 0.1237$
Largest diff. peak and hole	0.168 and -0.126 e.Å^{-3}

Table 2-A2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **II**.

Atom	X	y	z	Ueq
C(1)	5207(2)	4459(2)	4697(1)	45(1)
C(2)	4627(2)	3068(2)	4673(1)	45(1)
C(3)	4997(2)	1921(2)	4074(1)	41(1)
C(4)	6178(2)	2121(2)	3471(1)	50(1)
C(5)	6485(3)	1039(3)	2903(1)	57(1)
C(6)	5626(3)	-276(3)	2920(1)	56(1)
C(7)	4470(3)	-524(2)	3515(1)	58(1)
C(8)	4157(2)	569(2)	4085(1)	51(1)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2-A3. Bond lengths [Å] and angles [°] for **II**.

C(1)-C(2)	1.335(3)
C(1)-C(1)#1	1.436(4)
C(2)-C(3)	1.461(3)
C(3)-C(4)	1.391(2)
C(3)-C(8)	1.392(3)
C(4)-C(5)	1.376(3)
C(5)-C(6)	1.371(3)
C(6)-C(7)	1.374(3)
C(7)-C(8)	1.385(3)
C(2)-C(1)-C(1)#1	125.1(2)

C(1)-C(2)-C(3)	127.58(18)
C(4)-C(3)-C(8)	117.21(19)
C(4)-C(3)-C(2)	122.32(17)
C(8)-C(3)-C(2)	120.47(18)
C(5)-C(4)-C(3)	121.45(19)
C(6)-C(5)-C(4)	120.3(2)
C(5)-C(6)-C(7)	119.9(2)
C(6)-C(7)-C(8)	119.8(2)
C(7)-C(8)-C(3)	121.4(2)

Symmetry transformations used to generate equivalent atoms:
1 -x+1,-y+1,-z+1

Table 2-A4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **II**.
The anisotropic displacement factor exponent takes the form:
$2 \pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
(1)	37(1)	53(1)	45(1)	4(1)	4(1)	3(1)
(2)	38(1)	54(1)	43(1)	8(1)	4(1)	0(1)
(3)	36(1)	45(1)	41(1)	8(1)	-4(1)	4(1)
(4)	46(1)	46(1)	57(1)	6(1)	5(1)	4(1)
(5)	52(1)	60(1)	59(2)	-3(1)	5(1)	13(1)
(6)	54(1)	58(2)	57(1)	-10(1)	-18(1)	19(1)
(7)	55(1)	50(1)	69(2)	-2(1)	-20(1)	-1(1)
(8)	43(1)	55(1)	54(1)	7(1)	-5(1)	-5(1)

Table 2-A5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **II**.

	x	y	z	U_{eq}
H(1)	5950	4754	4282	54
H(2)	3888	2793	5093	54

H(4)	6785	3026	3452	59
H(5)	7296	1203	2497	69
H(6)	5828	-1015	2522	67
H(7)	3888	-1442	3535	70
H(8)	3352	392	4493	61

Table 2-A6. Torsion angles [°] for **II**.

C(1)#1-C(1)-C(2)-C(3)	179.85(19)
C(1)-C(2)-C(3)-C(4)	6.3(3)
C(1)-C(2)-C(3)-C(8)	-173.30(19)
C(8)-C(3)-C(4)-C(5)	1.0(3)
C(2)-C(3)-C(4)-C(5)	-178.68(18)
C(3)-C(4)-C(5)-C(6)	-0.1(3)
C(4)-C(5)-C(6)-C(7)	-1.0(3)
C(5)-C(6)-C(7)-C(8)	1.2(3)
C(6)-C(7)-C(8)-C(3)	-0.4(3)
C(4)-C(3)-C(8)-C(7)	-0.7(3)
C(2)-C(3)-C(8)-C(7)	178.93(16)

Symmetry transformations used to generate equivalent atoms:
1 -x+1,-y+1,-z+1

CHAPTER 3. Unsymmetric synthesis of 2,5-Diphenyl-2,4-hexadiene

3.1 Introduction

Our group has investigated symmetric (X = Y) and unsymmetrically (X ≠ Y) substituted 1,4-diphenyl-2,3-diazabutadienes, and we believe that the azine spacer functions as a conjugation stopper and provides quadrupolarity.[1-9] The deep understanding of these assumptions needs us to investigate different spacers. 1,4-diphenylbutadienes are an ideal target because it is the carbon analog of azines (Figure 2-1). Before studying the butadiene series with donor-acceptor groups it is very important to study the parent compounds 1,4-diphenyl-1,3-butadiene (**1**) and 2,5-diphenyl-2,4-hexadiene (**2**) (Figure 3-1). The crystal structure of **1**, which was discussed in Chapter 2, shows arene-arene double T-contacts and the comparison of two known polymorphs of **1**. Now it remains a question whether molecule **2** also contains arene-arene contacts or arene-diene contacts.

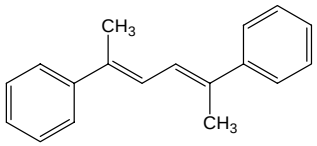
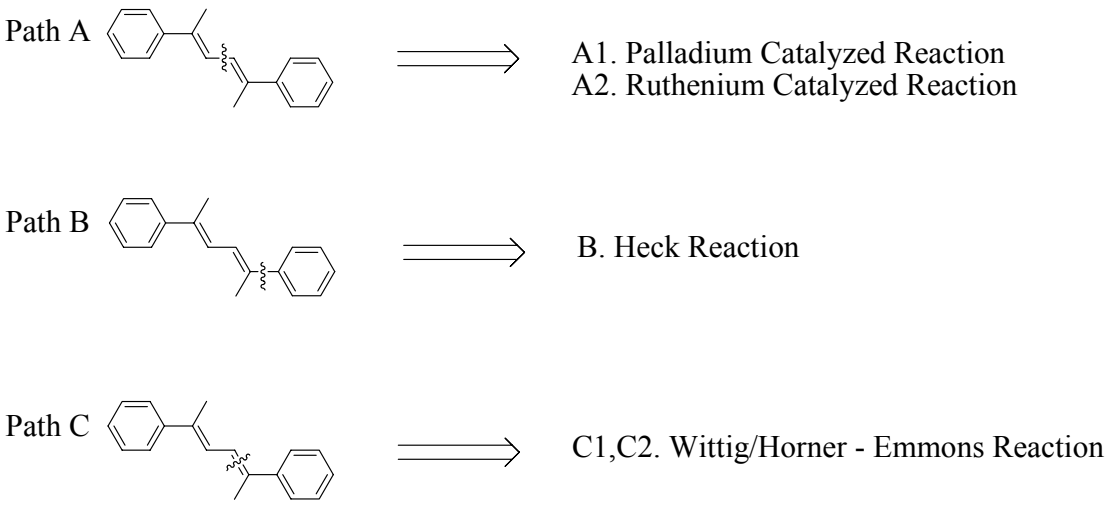


Figure 3-1. Structure of *(E,E)*-2,5-Diphenyl-2,4-hexadiene.

3.2 Synthetic Approaches

In retro-synthesis, molecule **2** may be dissected in three pathways. Path A involves dissecting molecule **2** into 2 2-phenyl-propene molecules. Path B involves dissecting molecule **2** into one 2-phenyl-hexa-2,4-diene molecule and one phenyl ring. Path C involves dissecting molecule **2** into one 2-phenyl-but-2-ene and one 1-ethylbenzene. Scheme 3-1 represents the asymmetrically synthetic approaches to molecule **2** and its derivatives.

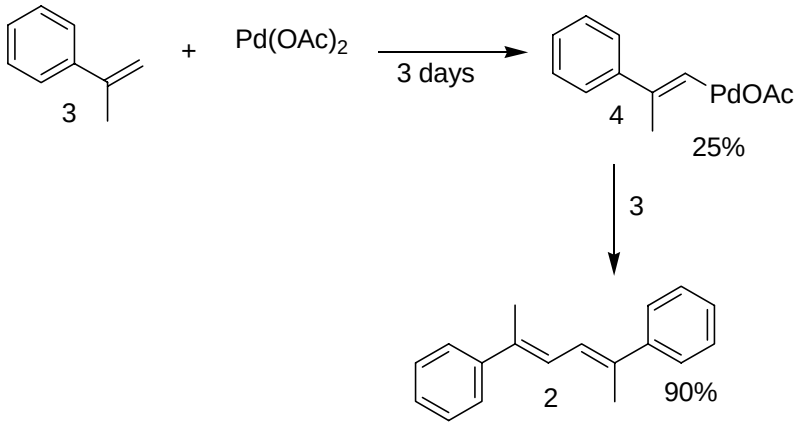


Scheme 3-1. Asymmetrically Synthetic Approaches to Molecule **2**

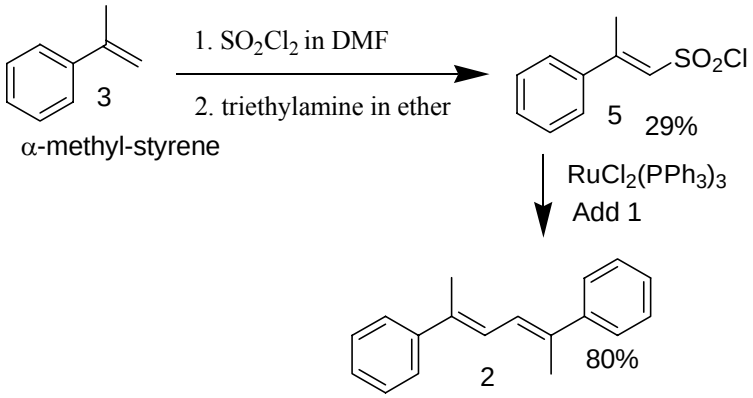
3.2.1 Path A and path B

Technically, we can use path A to synthesize molecule **2** with Palladium Catalyzed Reaction[10] (Scheme 3-2) or Ruthenium Catalyzed Reaction[11] (Scheme 3-3). Problems exist with the future use of these reactions in the asymmetric molecules (Scheme 1-5). We are going to use halides as acceptors to study the NLO activities of **2**, and halides will

be connected on the phenyl rings firstly, then the unsymmetric synthesis will be used to get NLO molecules. The aromatic halides may complex with metal catalysts, such as Palladium and Ruthenium. This is the reason that we did not choose path A. The same problem exists with the Heck Reaction (path B), which uses Palladium as a catalyst, therefore path B was also not investigated further.



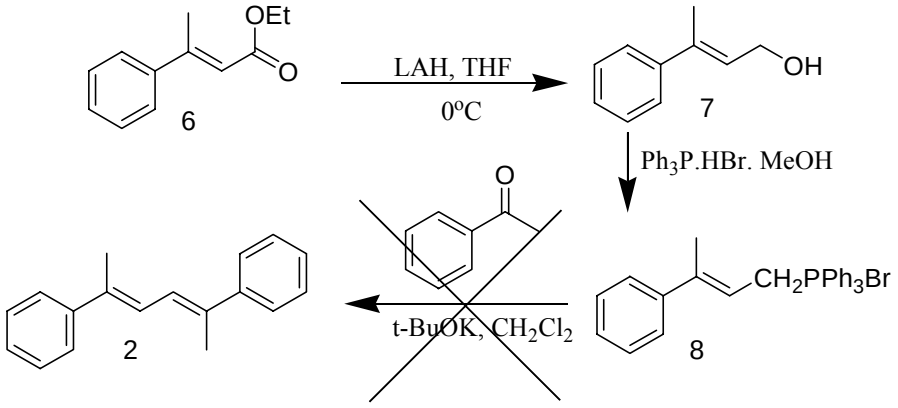
Scheme 3-2. Asymmetrically Synthetic Approach to Molecule **2** with Palladium Catalyzed Reaction (path A1)



Scheme 3-3. Asymmetrically Synthetic Approach to Molecule **2** with Ruthenium Catalyzed Reaction (path A2)

3.2.2 Path C

The Wittig reaction is a classic reaction to form conjugated alkenes. We used acetophenone in our reaction (Scheme 3-4), but no reaction occurred. The reason that the reactivity of Acetophenone is very low was recognized, and different conditions and derivatives for this reaction were used (Table 3.1), but the reaction still did not work.

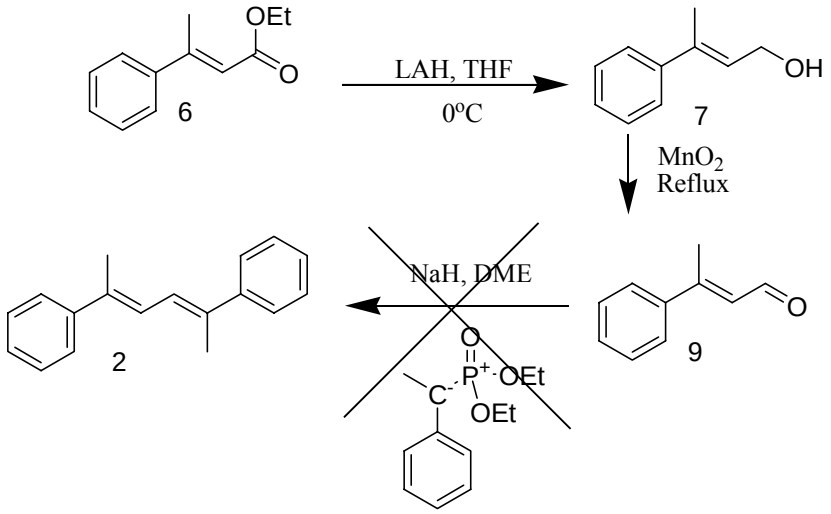


Scheme 3-4. Asymmetrically Synthetic Approach to Molecule **2** by a Wittig Reaction (Path C1)

Table 3-1 Conditions for Path C1

Phosphonium Salt : Ketone	Ketone	Base	Temp.	Time	Result
1 : 2	Acetophenone	t-BuOK	RT	8 hours	N.R.
1 : 1	Acetophenone	t-BuOK	Reflux	8 hours	N.R.
1 : 1	Acetophenone	n-BuLi	Reflux	2 Days	N.R.
1 : 1	Nitroacetophenone	t-BuOK	Reflux	1 Day	N.R.

To improve the reactivity, we switched the sides of ylide and carbonyl group, and use Hormer – Emmons Reaction to synthesize **2** (Schem 3- 5). This path did work, but the product is not **2**. The actual product is 1-Methyl-1,3,6-triphenyl-7-(2-phenyl-propenyl)-1,2-dihydro-naphthalene,(Figure 3-2) which is confirmed by 1H NMR, 13C NMR, Mass spectroscopy, and X-Ray crystallography. By the mechanism outlined in Scheme 3-6, we see the Michael Addition reaction and Aldol condensation reaction that happens before the Horner-Emmons reaction can take place. Therefore, if ylide is reactivated and the Michael Addtion and the Aldol reactions are stopped we may synthesize **2**.



Scheme 3-5. Asymmetrically Synthetic Approach to **2** with Horner-Emmons Reaction (Path C2)

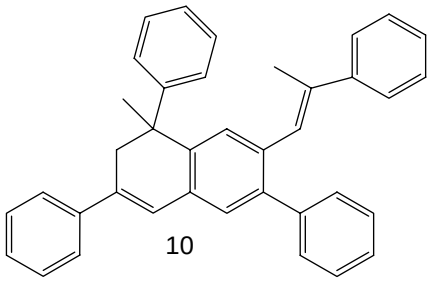
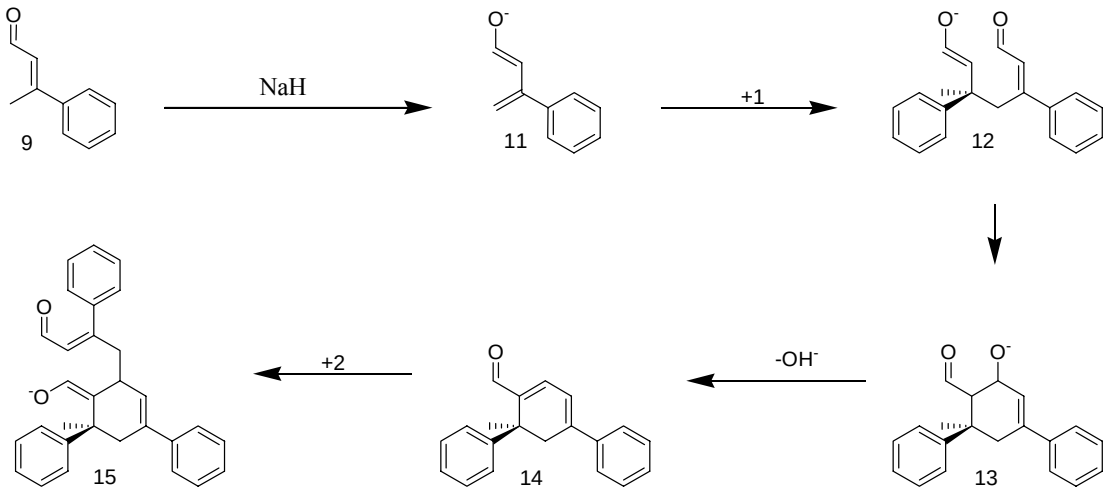
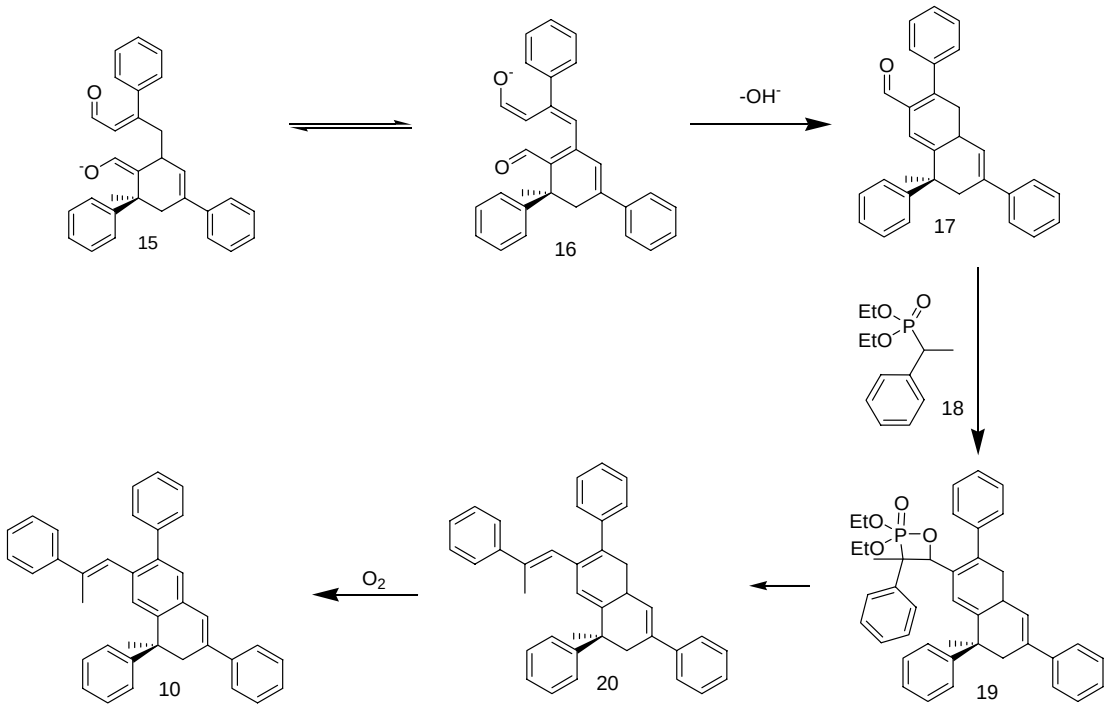


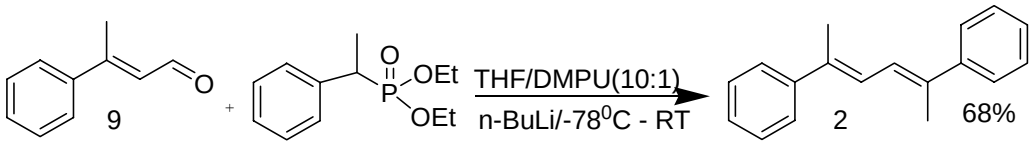
Figure 3-2. Structure of 1-Methyl-1,3,6-triphenyl-7-(2-phenyl-propenyl)-1,2-dihydro-naphthalene.





Scheme 3-6. The mechanism of synthesis of 1-Methyl-1,3,6-triphenyl-7-(2-phenylpropenyl)-1,2-dihydronaphthalene.

In some cases, the addition of DMPU creates more reactive ylide species.[12-22] The Aldol condensation reaction was controlled by doing the reaction at low temperature. Through the combination of the addition of DMPU and low temperatures, the synthesis of **2** was complished in 68 % yield. We did not find any literature that explains directly the mechanism that DMPU is needed in this reaction. In 1989, Reich and Green found that phenyl lithium exists as dimers and quadrumers, and HMPA is able to separate them into monomers and improve the reactivity of phenyl lithium.[15] Thinking that the ylide with lithium is similar to phenyl lithium, and DMPU is a safe substitute of HMPA, we believe that DMPU is a reagent to make ylide more reactive by separating the dimers of Lithium reagent into monomers.



Scheme 3-7. Asymmetrically Synthetic Approach to Molecule **2** with Horner-Emmons Reaction (Path C2) with low temperature and DMPU.

3.3 Experiments

All of following reactions are in path C1. All the chemicals were purchased from Aldrich. Unless specified most of the reactions were done in an inert atmosphere (nitrogen). Freshly distilled solvents were used. ^{1}H and ^{13}C NMR spectra were taken on Bruker 250 MHz and 300 MHz machines.

3.3.1 β-methylcinnamicalcohol (7)

Procedure adapted from previously reported work.[23] The β-methylcinnamicester (5.0ml 26.55mmol) as a solution in dry THF (60ml) was reduced with $LiAlH_4$ (1.012mg 26.61mmol) at 0 °C. The reaction was quenched by dropwise addition of ethyl acetate (40ml) followed by addition of 5% aq. HCl (50ml). The organic phase was separated, and the aqueous layer was extracted with ethyl acetate (3X40ml). The combined organic phases were washed with brine (2x40ml), dried (Na_2SO_4), and concentrated under reduced pressure to afford pure β-methylcinnamicalcohol (3.887g, 98.9%). (Found 1H NMR ($CDCl_3$) δ=1.33 (3H, t) 2.61 (1H, s), 4.26 (2H, q), 7.29 to 7.55 (5H, m)

3.3.2 β-methylcinnamicaldehyde (9)

Procedure adapted from previously reported work.[23] The β-methylcinnamicalcohol (450mg 3mmol) was dissolved in $CHCl_3$ (10ml) and treated at reflux with MnO_2 (2g, 11.5mmol) for 1h. The residue obtained upon filtration and evaporation of the $CHCl_3$ was purified by distillation to afford pure β-methylcinnamicaldehyde (0.215g 49.0%). (Found 1H NMR ($CDCl_3$) δ=2.58 (3H, s) 6.41 (1H, d), 7.39-7.57 (5H, m), 10.19 (1H, d)

3.3.3 1-Methyl-1,3,6-triphenyl-7-(2-phenyl-propenyl)-1,2-dihydro-naphthalene (10)

Procedure adapted from previously reported work.[24] 40mg (1.64mmol) of sodium hydride and 3ml DME are added to a dry, three-necked flask equipped with a stirrer and a condenser. The flask is immersed in an ice bath, and 0.4ml (1.64mmol) diethyl 1-phenylethylphosphonate is injected slowly. After the addition the solution is stirred at room temperature for 30 minutes, and then 200mg (1.37mmol) β-methylcinnamicaldehyde is added slowly. The solution is heated at reflux for 18 hours. The two-phase reaction mixture is cooled, and the flask is filled with water. The product is extracted from solution with three 20-ml portions of ether. The ethereal extracts are combined, dried over anhydrous sodium sulfate, and rotate evaporated. The mixtures were purified by gel-permeation chromatography using ethyl acetate and

hexanes as an eluent. The crystal is grown by slow diffusion of hexanes into a solution of this mixture in ethyl acetate, followed by washing with hexanes and drying to afford pure product (45mg 20%). (Found 1H NMR ($CDCl_3$) δ=1.79 (3H, s), 2.06 (3H, d, J=0.05 Hz), 2.88 (1H, d, J=0.06 Hz), 3.37 (1H, d, J=0.05 Hz), 6.66 (1H, s), 6.92 (1H, s), 7.26-7.55 (22H, m). 13C NMR ($CDCl_3$) δ17.3, 27.3, 42.7, 43.3, 76.4, 77.0, 77.5, 123.5, 125.0, 125.2, 125.7, 126.2, 126.9, 127.4, 127.5, 127.8, 128.0, 128.2, 128.4, 128.5, 128.6, 128.7, 129.5, 129.7, 133.1

Mass m/z (EI) 488 (M+), 489, 490, 486, 411)

3.3.4 2,5-Diphenyl-2,4-hexadiene (2)

Procedure adapted from previously reported work.[16] At -78 °C, 100 mg (0.685 mmol) of diethyl 1-phenylethylphosphonate was diluted in a 15.0/1.5 mL mixture of THF/DMPU, then 1.1 ml of *n*-BuLi (1.88 M in hexane) was added dropwise. After stirring for 30 min at this temperature, 100 mg (0.685 mmol) of the β-methylcinnamicaldehyde was diluted in 5 mL of dry THF was added dropwise. The mixture was then allowed to warm up slowly to room temperature and then quenched with water (40 mL) and extracted twice with EtOAc. The organic layer was dried over anhydrous sodium sulfate, filtered, and rotate evaporated. The crude oil was purified over silica gel column chromatography (eluant: 5% EtOAc/hexanes) to afford 109 mg (0.466 mmol, yield: 68%) of 2,5-diphenyl-2,4-hexadiene, the structure is confirmed by X-Ray crystallography. To do X-Ray crystallography, the crystal is grown by slow

diffusion of ethanol into a solution of this mixture in chloroform. (Found 1H NMR ($CDCl_3$), δ=2.25 (6H, s), 6.84 (2H, s), 6.84-7.54 (10H, m))

3.4 Conclusion

There are many possible synthetic pathways to synthesize **2** asymmetrical, but to achieve the molecules with halide substituents limits the use of metal catalysts. Classic Wittig type reactions or its derivatives, such as Hormer – Emmons reaction, are considered as ideal synthesis approaches. In one path way we used acetophenone and ylide, but it was limited by the reactivity of acetophenone; in another path way ylide and aldehyde were used, but **2** was not obtained after multiple attempts under various conditions. A major side product was separated, purified, and analyzed. We had to overcome two barriers in the synthesis pathway. The first barrier was that the α,β-unsaturated aldehyde with a methyl group in the β position is arranged to undergo an Aldol condensation. The second barrier is that the reactivity of ylide is low because it exists as dimmers in solution. Conducting the reaction at low temperatures prevented the Aldol condensation reaction, and the DMPU was added to break the possible dimers in solution making the ylide more reactive. The ground work is now in place for future synthesis of unsymmetrical 2,5-diphenyl-2,4-hexadienes.

3.5 References

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3.6 Appendix

Crystal Data and Atomic Coordinates for the Crystal Structure of **2** and **10**

Table 3-A1. Crystal data and structure refinement for **2**.

Identification code	YS-HEX-01
Empirical formula	$C_{18}H_{18}$
Formula weight	234.32
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 12.1639(7) Å α = 90 °.
	b = 7.3307(4) Å β = 100.2150(10) °.
	c = 15.2052(9) Å γ = 90 °.
Volume	1334.35(13) $Å^3$
Z, Calculated density	4, 1.166 Mg/m^3
Absorption coefficient	0.065 mm^{-1}
F(000)	504
Crystal size	0.45 x 0.40 x 0.10 mm
θ range for data collection	1.98 to 27.13 °.
Limiting indices	$-15 \le h \le 13$, $-6 \le k \le 9$, $-19 \le l \le 16$
Reflections collected / unique	6953 / 2920 [R(int) = 0.0173]
Completeness to θ = 27.13	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.97
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2920 / 0 / 165
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0472, ωR2 = 0.1321
R indices (all data)	R1 = 0.0587, ωR2 = 0.1412
Largest diff. peak and hole	0.370 and -0.163 $e.Å^{-3}$

Table 3-A2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **2**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)

C(1)	8862(1)	2668(2)	299(1)	29(1)
C(2)	8145(1)	2492(1)	876(1)	27(1)
C(3)	8545(1)	2551(1)	1856(1)	26(1)
C(4)	7941(1)	1701(2)	2445(1)	31(1)
C(5)	8309(1)	1758(2)	3362(1)	34(1)
C(6)	9281(1)	2686(2)	3718(1)	34(1)
C(7)	9895(1)	3534(2)	3146(1)	34(1)
C(8)	9535(1)	3461(2)	2231(1)	30(1)
C(9)	6911(1)	2159(2)	557(1)	39(1)
C(10)	8573(1)	2612(2)	-666(1)	29(1)
C(11)	9290(1)	2475(1)	-1245(1)	26(1)
C(12)	8863(1)	2405(1)	-2221(1)	25(1)
C(13)	9448(1)	1483(2)	-2801(1)	30(1)
C(14)	9031(1)	1383(2)	-3709(1)	34(1)
C(15)	8025(1)	2203(2)	-4065(1)	35(1)
C(16)	7437(1)	3139(2)	-3504(1)	34(1)
C(17)	7851(1)	3245(2)	-2596(1)	29(1)
C(18)	10536(1)	2316(2)	-934(1)	34(1)

Table 3-A3. Bond lengths [Å] and angles [°] for 2.

C(1)-C(2)	1.3486(16)
C(1)-C(10)	1.4472(17)
C(2)-C(3)	1.4826(16)
C(2)-C(9)	1.5130(16)
C(3)-C(4)	1.4017(16)
C(3)-C(8)	1.4059(16)
C(4)-C(5)	1.3877(17)
C(5)-C(6)	1.3879(18)
C(6)-C(7)	1.3892(18)
C(7)-C(8)	1.3838(16)
C(10)-C(11)	1.3492(16)
C(11)-C(12)	1.4843(15)
C(11)-C(18)	1.5099(16)
C(12)-C(13)	1.4006(15)
C(12)-C(17)	1.4035(15)
C(13)-C(14)	1.3864(16)
C(14)-C(15)	1.3841(17)
C(15)-C(16)	1.3884(18)
C(16)-C(17)	1.3844(16)
C(2)-C(1)-C(10)	126.03(11)

C(1)-C(2)-C(3)	121.06(10)
C(1)-C(2)-C(9)	121.71(11)
C(3)-C(2)-C(9)	117.19(10)
C(4)-C(3)-C(8)	117.36(11)
C(4)-C(3)-C(2)	120.87(10)
C(8)-C(3)-C(2)	121.76(10)
C(5)-C(4)-C(3)	121.08(11)
C(4)-C(5)-C(6)	120.55(11)
C(5)-C(6)-C(7)	119.32(11)
C(8)-C(7)-C(6)	120.20(11)
C(7)-C(8)-C(3)	121.48(11)
C(11)-C(10)-C(1)	126.50(11)
C(10)-C(11)-C(12)	120.19(10)
C(10)-C(11)-C(18)	122.08(11)
C(12)-C(11)-C(18)	117.69(10)
C(13)-C(12)-C(17)	117.58(10)
C(13)-C(12)-C(11)	121.25(10)
C(17)-C(12)-C(11)	121.16(10)
C(14)-C(13)-C(12)	121.02(10)
C(15)-C(14)-C(13)	120.53(11)
C(14)-C(15)-C(16)	119.39(11)
C(17)-C(16)-C(15)	120.27(11)
C(16)-C(17)-C(12)	121.20(10)

Symmetry transformations used to generate equivalent atoms:

Table 3-A4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **2**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	26(1)	30(1)	29(1)	1(1)	2(1)	-1(1)
C(2)	28(1)	24(1)	29(1)	0(1)	3(1)	0(1)
C(3)	27(1)	24(1)	28(1)	1(1)	5(1)	3(1)
C(4)	28(1)	31(1)	34(1)	1(1)	7(1)	0(1)
C(5)	33(1)	38(1)	32(1)	5(1)	12(1)	4(1)
C(6)	36(1)	41(1)	26(1)	1(1)	3(1)	7(1)
C(7)	33(1)	35(1)	33(1)	-1(1)	1(1)	-2(1)
C(8)	30(1)	30(1)	30(1)	3(1)	5(1)	-1(1)
C(9)	29(1)	54(1)	33(1)	-1(1)	4(1)	-7(1)

C(10)	26(1)	30(1)	30(1)	0(1)	2(1)	-1(1)
C(11)	26(1)	24(1)	29(1)	1(1)	3(1)	-1(1)
C(12)	24(1)	23(1)	29(1)	2(1)	4(1)	-2(1)
C(13)	25(1)	31(1)	33(1)	1(1)	6(1)	2(1)
C(14)	33(1)	38(1)	32(1)	-4(1)	10(1)	2(1)
C(15)	36(1)	43(1)	25(1)	-1(1)	2(1)	-2(1)
C(16)	29(1)	38(1)	33(1)	2(1)	1(1)	5(1)
C(17)	28(1)	30(1)	30(1)	0(1)	6(1)	3(1)
C(18)	26(1)	43(1)	33(1)	4(1)	2(1)	3(1)

Table 3-A5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **2**.

	x	y	z	U(eq)
H(1)	9627	2844	549	35
H(4)	7268	1074	2213	37
H(5)	7893	1158	3749	40
H(6)	9525	2740	4347	41
H(7)	10563	4167	3384	41
H(8)	9966	4038	1848	36
H(9A)	6686	2678	-42	58
H(9B)	6484	2740	970	58
H(9C)	6765	844	537	58
H(10)	7801	2679	-916	35
H(13)	10141	918	-2568	36
H(14)	9438	746	-4091	41
H(15)	7740	2126	-4687	42
H(16)	6747	3710	-3743	41
H(17)	7443	3898	-2220	35
H(18A)	10752	2984	-372	52
H(18B)	10926	2833	-1388	52
H(18C)	10740	1028	-841	52

Table 3-A6. Torsion angles [°] for **2**.

C(10)-C(1)-C(2)-C(3)	179.28(10)
C(10)-C(1)-C(2)-C(9)	1.50(18)
C(1)-C(2)-C(3)-C(4)	-155.04(11)

C(9)-C(2)-C(3)-C(4)	22.82(15)
C(1)-C(2)-C(3)-C(8)	25.26(16)
C(9)-C(2)-C(3)-C(8)	-156.87(11)
C(8)-C(3)-C(4)-C(5)	-0.04(16)
C(2)-C(3)-C(4)-C(5)	-179.74(10)
C(3)-C(4)-C(5)-C(6)	0.89(18)
C(4)-C(5)-C(6)-C(7)	-1.03(18)
C(5)-C(6)-C(7)-C(8)	0.31(18)
C(6)-C(7)-C(8)-C(3)	0.55(18)
C(4)-C(3)-C(8)-C(7)	-0.68(16)
C(2)-C(3)-C(8)-C(7)	179.02(10)
C(2)-C(1)-C(10)-C(11)	-167.89(12)
C(1)-C(10)-C(11)-C(12)	179.01(10)
C(1)-C(10)-C(11)-C(18)	1.40(18)
C(10)-C(11)-C(12)-C(13)	-150.86(11)
C(18)-C(11)-C(12)-C(13)	26.86(15)
C(10)-C(11)-C(12)-C(17)	28.51(15)
C(18)-C(11)-C(12)-C(17)	-153.77(10)
C(17)-C(12)-C(13)-C(14)	-1.01(16)
C(11)-C(12)-C(13)-C(14)	178.38(10)
C(12)-C(13)-C(14)-C(15)	0.32(18)
C(13)-C(14)-C(15)-C(16)	0.32(19)
C(14)-C(15)-C(16)-C(17)	-0.24(19)
C(15)-C(16)-C(17)-C(12)	-0.49(18)
C(13)-C(12)-C(17)-C(16)	1.09(16)
C(11)-C(12)-C(17)-C(16)	-178.29(10)

Symmetry transformations used to generate equivalent atoms:

Table 3-A7. Crystal data and structure refinement for **10**.

Identification code	John
Empirical formula	C_{38} H_{32}
Formula weight	488.64
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 16.714(3) Å α = 90 °.
	b = 7.8991(14) Å β = 104.081(3) °.
	c = 21.215(4) Å γ = 90 °.
Volume	2716.8(8) $Å^3$
Z, Calculated density	4, 1.195 Mg/m^3
Absorption coefficient	0.067 mm^{-1}
F(000)	1040
Crystal size	0.40 x 0.35 x 0.10 mm
θ range for data collection	1.78 to 24.71 °.
Limiting indices	$-19 \leq h \leq 18$, $-9 \leq k \leq 9$, $-24 \leq l \leq 24$
Reflections collected / unique	13155 / 4626 [R(int) = 0.0636]
Completeness to θ = 24.71	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.99 and 0.97
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4626 / 0 / 345
Goodness-of-fit on F^2	1.106
Final R indices [I>2σ(I)]	R1 = 0.0825, ωR2 = 0.1531
R indices (all data)	R1 = 0.1251, ωR2 = 0.1664
Largest diff. peak and hole	0.271 and -0.241 $e.Å^{-3}$

Table 3-A8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **10**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)

C(1)	2254(2)	10272(4)	1473(1)	18(1)
C(2)	1696(2)	8759(4)	1502(1)	17(1)
C(3)	1851(2)	7240(4)	1196(1)	19(1)
C(4)	2575(2)	7140(4)	928(2)	23(1)
C(5)	3205(2)	8228(4)	1098(2)	22(1)
C(6)	3136(2)	9571(4)	1599(1)	21(1)
C(7)	1050(2)	8776(4)	1804(1)	19(1)
C(8)	543(2)	7386(4)	1822(1)	19(1)
C(9)	658(2)	5914(4)	1477(1)	19(1)
C(10)	1309(2)	5883(4)	1167(1)	20(1)
C(11)	2004(2)	11129(4)	797(1)	19(1)
C(12)	2578(2)	11971(5)	538(2)	34(1)
C(13)	2345(3)	12804(5)	-50(2)	39(1)
C(14)	1536(2)	12796(5)	-398(2)	35(1)
C(15)	955(2)	11978(5)	-150(2)	35(1)
C(16)	1193(2)	11148(4)	443(2)	25(1)
C(17)	2217(2)	11613(4)	1992(2)	24(1)
C(18)	3949(2)	8175(4)	837(2)	23(1)
C(19)	4680(2)	8994(5)	1138(2)	30(1)
C(20)	5376(2)	8931(5)	895(2)	34(1)
C(21)	5360(2)	8053(5)	336(2)	38(1)
C(22)	4647(3)	7220(5)	20(2)	43(1)
C(23)	3951(2)	7279(5)	263(2)	36(1)
C(24)	-132(2)	7509(4)	2157(2)	21(1)
C(25)	-126(2)	8282(4)	2723(2)	21(1)
C(26)	-897(2)	8399(4)	2956(2)	23(1)
C(27)	-1024(2)	9775(5)	3334(2)	28(1)
C(28)	-1747(2)	9931(5)	3536(2)	37(1)
C(29)	-2352(2)	8728(5)	3378(2)	42(1)
C(30)	-2238(3)	7343(6)	3014(2)	47(1)
C(31)	-1520(2)	7174(5)	2806(2)	38(1)
C(32)	625(2)	9096(5)	3151(2)	29(1)
C(33)	107(2)	4413(4)	1420(2)	19(1)
C(34)	-42(2)	3608(4)	1963(2)	26(1)
C(35)	-547(2)	2196(4)	1904(2)	31(1)
C(36)	-910(2)	1557(4)	1299(2)	30(1)
C(37)	-780(2)	2331(5)	757(2)	34(1)
C(38)	-272(2)	3740(4)	814(2)	30(1)

Table 3-A9. Bond lengths [Å] and angles [°] for **10**.

C(1)-C(2)	1.527(4)
C(1)-C(6)	1.537(4)
C(1)-C(17)	1.541(4)
C(1)-C(11)	1.549(4)
C(2)-C(7)	1.382(4)
C(2)-C(3)	1.417(4)
C(3)-C(10)	1.394(4)
C(3)-C(4)	1.461(5)
C(4)-C(5)	1.339(5)
C(5)-C(18)	1.480(5)
C(5)-C(6)	1.526(4)
C(7)-C(8)	1.394(4)
C(8)-C(9)	1.411(4)
C(8)-C(24)	1.475(4)
C(9)-C(10)	1.402(4)
C(9)-C(33)	1.488(5)
C(11)-C(16)	1.380(4)
C(11)-C(12)	1.385(5)
C(12)-C(13)	1.381(5)
C(13)-C(14)	1.374(5)
C(14)-C(15)	1.373(5)
C(15)-C(16)	1.387(5)
C(18)-C(19)	1.393(5)
C(18)-C(23)	1.409(5)
C(19)-C(20)	1.385(5)
C(20)-C(21)	1.368(5)
C(21)-C(22)	1.383(5)
C(22)-C(23)	1.383(5)
C(24)-C(25)	1.346(4)
C(25)-C(26)	1.491(5)
C(25)-C(32)	1.504(4)
C(26)-C(27)	1.397(5)
C(26)-C(31)	1.401(5)
C(27)-C(28)	1.383(5)
C(28)-C(29)	1.369(5)
C(29)-C(30)	1.378(5)
C(30)-C(31)	1.382(5)
C(33)-C(34)	1.391(4)
C(33)-C(38)	1.392(4)

C(34)-C(35)	1.386(5)
C(35)-C(36)	1.374(5)
C(36)-C(37)	1.366(5)
C(37)-C(38)	1.386(5)
C(2)-C(1)-C(6)	106.3(2)
C(2)-C(1)-C(17)	112.2(3)
C(6)-C(1)-C(17)	109.1(2)
C(2)-C(1)-C(11)	110.5(2)
C(6)-C(1)-C(11)	110.5(3)
C(17)-C(1)-C(11)	108.3(2)
C(7)-C(2)-C(3)	118.0(3)
C(7)-C(2)-C(1)	124.3(3)
C(3)-C(2)-C(1)	117.6(3)
C(10)-C(3)-C(2)	118.8(3)
C(10)-C(3)-C(4)	122.1(3)
C(2)-C(3)-C(4)	119.0(3)
C(5)-C(4)-C(3)	122.1(3)
C(4)-C(5)-C(18)	123.9(3)
C(4)-C(5)-C(6)	116.6(3)
C(18)-C(5)-C(6)	119.5(3)
C(5)-C(6)-C(1)	111.1(3)
C(2)-C(7)-C(8)	123.6(3)
C(7)-C(8)-C(9)	118.3(3)
C(7)-C(8)-C(24)	120.2(3)
C(9)-C(8)-C(24)	121.4(3)
C(10)-C(9)-C(8)	118.5(3)
C(10)-C(9)-C(33)	118.9(3)
C(8)-C(9)-C(33)	122.6(3)
C(3)-C(10)-C(9)	122.4(3)
C(16)-C(11)-C(12)	117.6(3)
C(16)-C(11)-C(1)	121.1(3)
C(12)-C(11)-C(1)	121.3(3)
C(13)-C(12)-C(11)	121.1(3)
C(14)-C(13)-C(12)	120.4(4)
C(15)-C(14)-C(13)	119.5(3)
C(14)-C(15)-C(16)	119.8(3)
C(11)-C(16)-C(15)	121.6(3)
C(19)-C(18)-C(23)	116.3(3)
C(19)-C(18)-C(5)	122.6(3)
C(23)-C(18)-C(5)	121.1(3)
C(20)-C(19)-C(18)	122.4(4)

C(21)-C(20)-C(19)	119.9(4)
C(20)-C(21)-C(22)	119.7(4)
C(21)-C(22)-C(23)	120.5(4)
C(22)-C(23)-C(18)	121.2(4)
C(25)-C(24)-C(8)	128.3(3)
C(24)-C(25)-C(26)	120.3(3)
C(24)-C(25)-C(32)	123.9(3)
C(26)-C(25)-C(32)	115.8(3)
C(27)-C(26)-C(31)	117.3(3)
C(27)-C(26)-C(25)	120.2(3)
C(31)-C(26)-C(25)	122.5(3)
C(28)-C(27)-C(26)	120.9(3)
C(29)-C(28)-C(27)	120.7(4)
C(28)-C(29)-C(30)	119.6(4)
C(29)-C(30)-C(31)	120.3(4)
C(30)-C(31)-C(26)	121.1(4)
C(34)-C(33)-C(38)	117.2(3)
C(34)-C(33)-C(9)	121.9(3)
C(38)-C(33)-C(9)	120.9(3)
C(35)-C(34)-C(33)	121.3(3)
C(36)-C(35)-C(34)	120.1(3)
C(37)-C(36)-C(35)	119.8(3)
C(36)-C(37)-C(38)	120.3(3)
C(37)-C(38)-C(33)	121.3(3)

Symmetry transformations used to generate equivalent atoms:

Table 3-A10. Anisotropic displacement parameters ($Å^2$ x 10^3) for **10**.
The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

	U1	U22	U33	U23	U13	U12
C(1)	21(2)	12(2)	19(2)	-2(1)	2(1)	1(1)
C(2)	22(2)	13(2)	15(2)	1(1)	3(1)	3(1)
C(3)	23(2)	18(2)	15(2)	1(1)	4(1)	4(2)
C(4)	32(2)	15(2)	23(2)	3(2)	8(2)	4(2)
C(5)	26(2)	19(2)	21(2)	7(1)	6(2)	7(2)
C(6)	25(2)	22(2)	17(2)	3(1)	3(2)	0(2)
C(7)	22(2)	15(2)	18(2)	-2(1)	2(1)	3(2)

C(8)	21(2)	19(2)	15(2)	0(1)	2(1)	2(2)
C(9)	24(2)	16(2)	15(2)	2(1)	2(1)	2(2)
C(10)	28(2)	13(2)	18(2)	-1(1)	6(2)	2(2)
C(11)	28(2)	10(2)	17(2)	-6(1)	4(2)	4(2)
C(12)	29(2)	41(2)	30(2)	10(2)	6(2)	1(2)
C(13)	44(3)	45(3)	33(2)	18(2)	19(2)	7(2)
C(14)	53(3)	32(2)	19(2)	5(2)	4(2)	15(2)
C(15)	39(2)	24(2)	34(2)	0(2)	-9(2)	5(2)
C(16)	30(2)	16(2)	26(2)	2(2)	-2(2)	-2(2)
C(17)	33(2)	17(2)	22(2)	-4(1)	8(2)	-4(2)
C(18)	27(2)	20(2)	24(2)	10(2)	8(2)	7(2)
C(19)	31(2)	37(2)	24(2)	8(2)	9(2)	4(2)
C(20)	24(2)	43(2)	37(2)	11(2)	10(2)	2(2)
C(21)	36(2)	39(2)	48(2)	15(2)	27(2)	11(2)
C(22)	54(3)	38(2)	43(2)	-1(2)	27(2)	5(2)
C(23)	38(2)	33(2)	42(2)	-6(2)	19(2)	-3(2)
C(24)	22(2)	16(2)	25(2)	0(2)	4(2)	-1(2)
C(25)	24(2)	16(2)	23(2)	1(2)	6(2)	0(2)
C(26)	25(2)	23(2)	22(2)	1(2)	7(2)	-1(2)
C(27)	34(2)	28(2)	24(2)	-3(2)	12(2)	-5(2)
C(28)	40(2)	42(2)	35(2)	-8(2)	19(2)	0(2)
C(29)	34(2)	52(3)	45(2)	-6(2)	21(2)	0(2)
C(30)	42(3)	48(3)	59(3)	-17(2)	28(2)	-15(2)
C(31)	44(3)	29(2)	46(2)	-12(2)	20(2)	-6(2)
C(32)	30(2)	33(2)	25(2)	-8(2)	7(2)	0(2)
C(33)	20(2)	16(2)	22(2)	1(1)	6(1)	6(2)
C(34)	26(2)	26(2)	24(2)	3(2)	5(2)	1(2)
C(35)	36(2)	24(2)	35(2)	10(2)	16(2)	2(2)
C(36)	31(2)	14(2)	48(2)	-4(2)	13(2)	-2(2)
C(37)	42(2)	24(2)	34(2)	-7(2)	6(2)	-5(2)
C(38)	43(2)	20(2)	27(2)	-2(2)	11(2)	0(2)

Table 3-A11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **10**.

	x	y	z	U(eq)
H(4)	2600	6274	622	28
H(6A)	3523	10508	1581	26
H(6B)	3294	9069	2040	26

H(7)	946	9793	2010	23
H(10)	1384	4902	929	24
H(12)	3141	11976	770	40
H(13)	2748	13386	-216	47
H(14)	1379	13352	-806	42
H(15)	392	11981	-383	42
H(16)	787	10578	609	30
H(17A)	2393	11105	2425	36
H(17B)	1650	12030	1925	36
H(17C)	2583	12558	1956	36
H(19)	4701	9619	1524	37
H(20)	5866	9497	1116	41
H(21)	5835	8015	166	46
H(22)	4636	6602	-366	51
H(23)	3465	6706	38	43
H(24)	-635	6973	1946	25
H(27)	-608	10616	3453	34
H(28)	-1825	10884	3788	45
H(29)	-2848	8846	3518	50
H(30)	-2655	6501	2906	57
H(31)	-1448	6212	2557	46
H(32A)	1122	8638	3046	44
H(32B)	641	8859	3608	44
H(32C)	602	10323	3080	44
H(34)	207	4034	2384	31
H(35)	-644	1670	2281	37
H(36)	-1250	580	1258	36
H(37)	-1038	1902	338	40
H(38)	-182	4256	433	35

Table 3-A12. Torsion angles [°] for **10**.

C(6)-C(1)-C(2)-C(7)	138.0(3)
C(17)-C(1)-C(2)-C(7)	18.9(4)
C(11)-C(1)-C(2)-C(7)	-102.1(3)
C(6)-C(1)-C(2)-C(3)	-42.3(3)
C(17)-C(1)-C(2)-C(3)	-161.4(3)
C(11)-C(1)-C(2)-C(3)	77.6(3)
C(7)-C(2)-C(3)-C(10)	5.1(4)

C(1)-C(2)-C(3)-C(10)	-174.6(3)
C(7)-C(2)-C(3)-C(4)	-174.4(3)
C(1)-C(2)-C(3)-C(4)	5.9(4)
C(10)-C(3)-C(4)-C(5)	-162.0(3)
C(2)-C(3)-C(4)-C(5)	17.5(5)
C(3)-C(4)-C(5)-C(18)	-179.9(3)
C(3)-C(4)-C(5)-C(6)	1.0(5)
C(4)-C(5)-C(6)-C(1)	-40.5(4)
C(18)-C(5)-C(6)-C(1)	140.4(3)
C(2)-C(1)-C(6)-C(5)	58.6(3)
C(17)-C(1)-C(6)-C(5)	179.8(3)
C(11)-C(1)-C(6)-C(5)	-61.3(3)
C(3)-C(2)-C(7)-C(8)	-0.2(5)
C(1)-C(2)-C(7)-C(8)	179.5(3)
C(2)-C(7)-C(8)-C(9)	-4.4(5)
C(2)-C(7)-C(8)-C(24)	179.7(3)
C(7)-C(8)-C(9)-C(10)	3.9(4)
C(24)-C(8)-C(9)-C(10)	179.7(3)
C(7)-C(8)-C(9)-C(33)	-174.8(3)
C(24)-C(8)-C(9)-C(33)	1.0(4)
C(2)-C(3)-C(10)-C(9)	-5.6(5)
C(4)-C(3)-C(10)-C(9)	173.8(3)
C(8)-C(9)-C(10)-C(3)	1.0(5)
C(33)-C(9)-C(10)-C(3)	179.8(3)
C(2)-C(1)-C(11)-C(16)	32.2(4)
C(6)-C(1)-C(11)-C(16)	149.6(3)
C(17)-C(1)-C(11)-C(16)	-91.0(3)
C(2)-C(1)-C(11)-C(12)	-150.8(3)
C(6)-C(1)-C(11)-C(12)	-33.5(4)
C(17)-C(1)-C(11)-C(12)	85.9(4)
C(16)-C(11)-C(12)-C(13)	0.2(5)
C(1)-C(11)-C(12)-C(13)	-176.8(3)
C(11)-C(12)-C(13)-C(14)	-0.8(6)
C(12)-C(13)-C(14)-C(15)	1.2(6)
C(13)-C(14)-C(15)-C(16)	-1.0(6)
C(12)-C(11)-C(16)-C(15)	-0.1(5)
C(1)-C(11)-C(16)-C(15)	177.0(3)
C(14)-C(15)-C(16)-C(11)	0.5(5)
C(4)-C(5)-C(18)-C(19)	-162.2(3)
C(6)-C(5)-C(18)-C(19)	16.8(5)
C(4)-C(5)-C(18)-C(23)	17.8(5)

C(6)-C(5)-C(18)-C(23)	-163.2(3)
C(23)-C(18)-C(19)-C(20)	-0.5(5)
C(5)-C(18)-C(19)-C(20)	179.5(3)
C(18)-C(19)-C(20)-C(21)	0.6(6)
C(19)-C(20)-C(21)-C(22)	-0.6(6)
C(20)-C(21)-C(22)-C(23)	0.5(6)
C(21)-C(22)-C(23)-C(18)	-0.4(6)
C(19)-C(18)-C(23)-C(22)	0.4(5)
C(5)-C(18)-C(23)-C(22)	-179.6(3)
C(7)-C(8)-C(24)-C(25)	-40.3(5)
C(9)-C(8)-C(24)-C(25)	143.9(3)
C(8)-C(24)-C(25)-C(26)	174.6(3)
C(8)-C(24)-C(25)-C(32)	-4.3(5)
C(24)-C(25)-C(26)-C(27)	-149.4(3)
C(32)-C(25)-C(26)-C(27)	29.7(4)
C(24)-C(25)-C(26)-C(31)	29.8(5)
C(32)-C(25)-C(26)-C(31)	-151.1(3)
C(31)-C(26)-C(27)-C(28)	-1.4(5)
C(25)-C(26)-C(27)-C(28)	177.9(3)
C(26)-C(27)-C(28)-C(29)	0.7(6)
C(27)-C(28)-C(29)-C(30)	0.2(6)
C(28)-C(29)-C(30)-C(31)	-0.4(6)
C(29)-C(30)-C(31)-C(26)	-0.3(6)
C(27)-C(26)-C(31)-C(30)	1.2(6)
C(25)-C(26)-C(31)-C(30)	-178.1(4)
C(10)-C(9)-C(33)-C(34)	126.4(3)
C(8)-C(9)-C(33)-C(34)	-54.8(4)
C(10)-C(9)-C(33)-C(38)	-52.5(4)
C(8)-C(9)-C(33)-C(38)	126.2(3)
C(38)-C(33)-C(34)-C(35)	-0.1(5)
C(9)-C(33)-C(34)-C(35)	-179.0(3)
C(33)-C(34)-C(35)-C(36)	0.4(5)
C(34)-C(35)-C(36)-C(37)	-0.9(5)
C(35)-C(36)-C(37)-C(38)	1.1(6)
C(36)-C(37)-C(38)-C(33)	-0.8(6)
C(34)-C(33)-C(38)-C(37)	0.3(5)
C(9)-C(33)-C(38)-C(37)	179.3(3)

Symmetry transformations used to generate equivalent atoms:

CHAPTER 4. Chemistry Is in the News Webtool: To Achieve Lifelong Education with Three Tier Information System

4.1 Introduction

The technical knowledge explosion of recent years has caused increases in cost and time required to train professionals and prepare students for life outside of the university. Higher education has to confront this challenge by teaching students not only content but also how to become lifelong learners. Life-long learning involves continually accessing new information, thus the general consensus is that information technology (IT) should be involved in education. However, how to integrate IT into education is the topic of considerable debate. In Larry Cuban's book, *Oversold and Underused --- Computers in the classroom*,[1] he argues, "history-and-contexts explanations can partially account for the underuse of computers in the classroom, it does not give adequate weight to the discretion of individual teachers as gatekeepers to their classrooms". However, there are obvious advantages to integrating computers into the class, which include timely access of information and ease of electronic communication.

The success of achieving effective education depends not only on technology, but also the approaches of implementing technology. In the science, mathematics and engineering fields, improving teaching and learning with information technology has been attempted in undergraduate education.[2-7] However, the use of IT in science

education has been focused on re-presenting fundamental content from textbooks or re-creating lab experiences virtually. These methods of integration are distant from the current state of the sciences in the technological context of today. *The Chemistry Is in the News (CIITN)* project is designed to help student link the science they are studying, IT, and the real-world context in a dynamic manner. It does this through the *CIITN* webportal which is located at http://ciitn.missouri.edu.

4.2 *Chemistry Is in the News (CIITN)* and its Webtool

CIITN is based on the fact that there is always a break between the knowledge in the classroom and the leading edge of the science, and, unfortunately, this gap has been widening. Science education is becoming more challenging because what students are learning from textbooks is far removed from the issues of which they are aware. According to the National Research Council, chemistry is invisible in the media,[8] such as newspapers, magazines, television, and radio. Even though "hard" chemistry is not largely evident in popular media, knowledge of chemistry is necessary to understand many hot topics in the media including energy, pharmaceuticals, and nutrition. Rationally utilizing the media not only improves students' interests in chemistry, but also trains them as lifelong learners. The *CIITN* project was encouraged by this fact, and started in 1997. It facilitates learning activities based on authentic news media. We also introduced peer-review as a measurement, in which small collaborative groups are used in the context of large lecture setting.

The *CIITN* activities include studying news articles, creating and updating portfolios, and completing intergroup peer-reviews and intragroup peer-reviews. The portfolios are used for facilitating news media. Generally, each portfolio consists of an electronically published news article, interpretive comments, web links, references to professional journals, and questions.[9] *CIITN* helps instructors and students with teaching and learning science in the real world.

If *CIITN* were to be carried out in traditional, paper-based format, the major barrier of implementation of *CIITN* would be the workload. Instructors and TAs would need to independently manage students and groups, collect and distribute multiple copies of student-created documents, and manually prepare grade reports for students. Beside the time-consuming aspect of this method, this manner of managing projects would lack the lifelikeness, colors, and animations. It also would limit the scale of classes and render interstate or international cooperation unfeasible. Thus, the *CIITN* webtool was designed with these points in mind, particularly to reduce the workload for instructors, TA's, and students and facilitate its implementation in large classes.

The *CIITN* webtool was based on Internet and database technologies (Figure 4-1). The first version of the webtool provided students the convenience of accessing the website to manage their projects with any networked computer. With the HTML interface, students used the webtool with simple training. Database technology allowed students to store and fetch their information easily. In addition, with the webtool,

instructors and TA's do not need to manually maintain or distribute student-created documents.

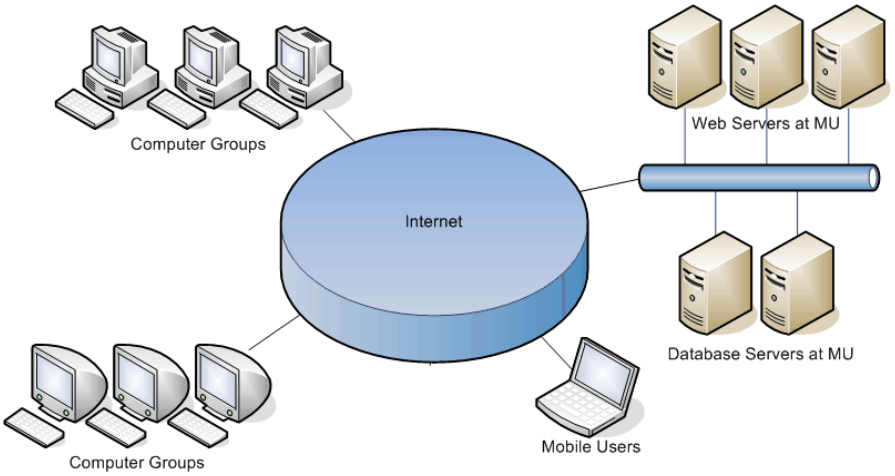

Figure 4-1. Network of *CIITN*

4.3 Analysis of the First Version of *CIITN* Webtool

Though the first version of the *CIITN* webtool was a success,[10] some improvements were called for. Increases in the number of students and courses in the webtool caused flaws to emerge in the user interface, data flow and storage, and programming.

User interface (UI): The first disadvantage is that the UI is based on Hypertext Markup Language (HTML). Compared to traditional software, the characters of web design, such as graphic interface, WYSIWYG (What You See Is What You Get), and online help, empower training users easily.[11,12] When more web pages are added into the webtool, the absence of web page style management causes inconsistencies to occur: these effect colors, fonts, menus, layouts, and user hints. Some of them affect the readability of context, and some of them confuse users.

Programming: The second disadvantage is that the Perl programming language, the language chosen for *CIITN*, has three shortcomings all Perl programmers have to compensate for. The first shortcoming is that Perl is a cumbersome choice for a growing website like *CIITN* even though it is wise for CGI (Common Gateway Interface). Perl is a powerful, modern script language and is a wide ranging tool that is compatible with new web-based technologies.[13,14] However, it is unavoidable to include HTML codes in Perl files to dynamically output web pages. As the web pages become more complicated, more HTML codes need to be added into Perl source codes, and the Perl codes become very difficult to read. The second shortcoming is that Perl is just a structured script language, not Object-Oriented (OO), which means that the change in one module could cause some problems in another related module, even though the related module is already tuned and tested. The third shortcoming is that debugging a Perl program is not as easy as a local compiled language. There are always some potential errors in the executable files, and someday they will show up.

Data flow and storage: The third disadvantage is the response of the webtool. For now, the response time of the webtool is acceptable, but the current data flow and storage will not satisfy the requirement of more classes or larger classes. For example, in the winter semester of 2004, it took more than ten seconds to show the score report of a course with 73 groups, which included two classes and two instructions. In the future, we may have more than two classes in one *CIITN* course, and the international

cooperation may require the use of much slower Internet connections than the MU campus network currently being used.

Data mining: The fourth disadvantage in the webtool is the absence of a data mining system. Data mining, also known as knowledge-discovery in databases (KDD), is the practice of automatically searching large stores of data or patterns.[15] The more *CIITN* courses are taught, the more useful the information will become for teaching. In particular, the statistics and analysis of courses through the years could help the improvement of the *CIITN* project and the information from data mining also can guide the development of *CIITN* for different kinds of courses, including all chemistry sub-disciplines and other fields like biochemistry and biology.

New functions: The fifth disadvantage in the webtool is the lack of certain functions; as the *CIITN* project has grown and the webtool has been built up, more functions are demanded. For example, with the first version, when each group was working with their project, they made pictures and sent them to their TA, then the TA send the pictures to the administrator of the webtool, who uploaded the pictures to the students' folder one the *CIITN* server, and then the students could use links to show the pictures in their project. This posed a problem especially when students need to update pictures and when groups have several pictures. This is a heavy burden for the TA's and administrators, and it is not convenient for students. Another example is peer review assignment. It is very difficult to assign peer review manually without either assigning two groups to review each other or violating the anonymity of the reviewing groups, both

of which open the review process up to abuse. All these issues should be solved with new version of *CIITN* webtool.

4.4 Design of the second version of *CIITN* webtool

The redesign of the *CIITN* webtool is based on the characteristics of news flow and education. News flow means that information is fresh and unstable, and there are various formats. Education decides the weakness of computer knowledge in users, and computing conditions may not be ideal.

4.4.1 Framework

The second version of *CIITN* webtool is a three tier information management system based on multimedia, internet, and database technologies. The three tier architecture includes web interface, middle software, and database tiers. Compared to programming software, the development of internet technology makes the *CIITN* Webtool easy to use and convenient on any computer with network systems. Compared to file systems, the integration with database technology makes information storage and management fast and organized; compared to client/server architecture. The three tier architecture with CGI technology provides increased performance, flexibility, maintainability, reusability, and scalability, while hiding the complexity of distributed processing from the user. The first version of *CIITN* Webtool adopted some aspects of three tier structure, however,

the new version completely follows the rules of the three tier information system, and thus is more versatile.[16-18]

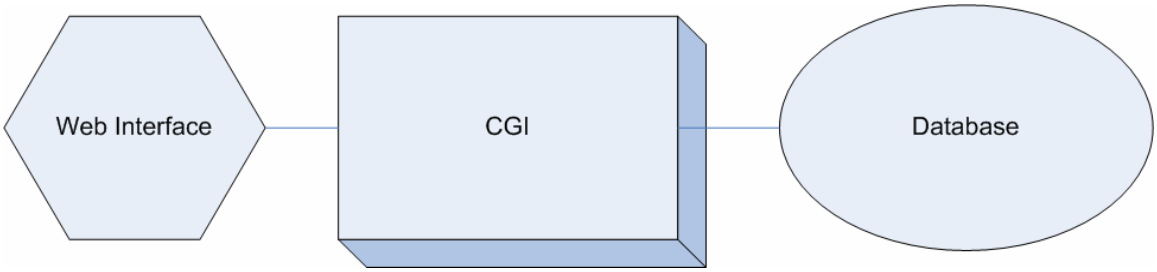

Figure 4-2 Three tier architecture of *CIITN*

4.4.2 Work flow and data flow within the *CIITN* Webtool

For each information system, data flows should be designed in conformity with work flows. There are four stages to accomplish a *CIITN* course. (Figure 4-3)

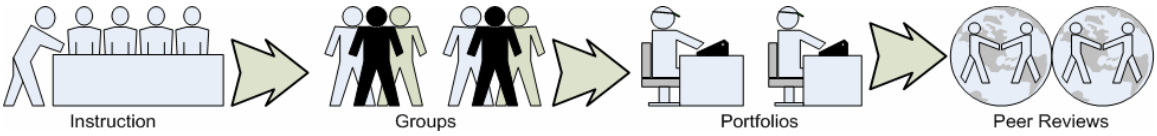

Figure 4-3 Work flow of *CIITN* Course

First, along with lectures, discussions, and exams, instructors create portfolios to integrate into the day-to-day teaching of the course. Students learn the chemistry and its link to the real-world by reading these portfolios and answering the questions they pose, while they also learn the format and structure of the portfolios.

Next, students are put into groups to group members work together to create their own portfolio. In this step, the students explore a wealth of news media resources and select an article and other sources. Then, they write interpretive comments that are

composed of hypertext, pictures, animations, and links to outside resource to provide background information, and finally write and answer their own questions.

Finally, students are engaged in two rounds of peer review, constructive and final. In this stage, they read and assess portfolios created by other groups, assign scores to the portfolio, and provide a justification for the score. To cap off the process, students engage in an examination of how well the group worked to create their project. They assess their group members through intra-group peer review at the end of the semester. This process is meant to prevent freeloading and help students reflect on the process of collaboration and improve their collaborative skills.

The data flow of *CIITN* webtool is not just a copy of its work flow. It's abstracted from its work flow. The following diagram shows the basic data flow of *CIITN* Webtool in the second version. Two strategies are adopted to optimize the data flow. One is that data structure is balanced between data redundancy and response time; another is that the data views are used for improving response time without redundancy.

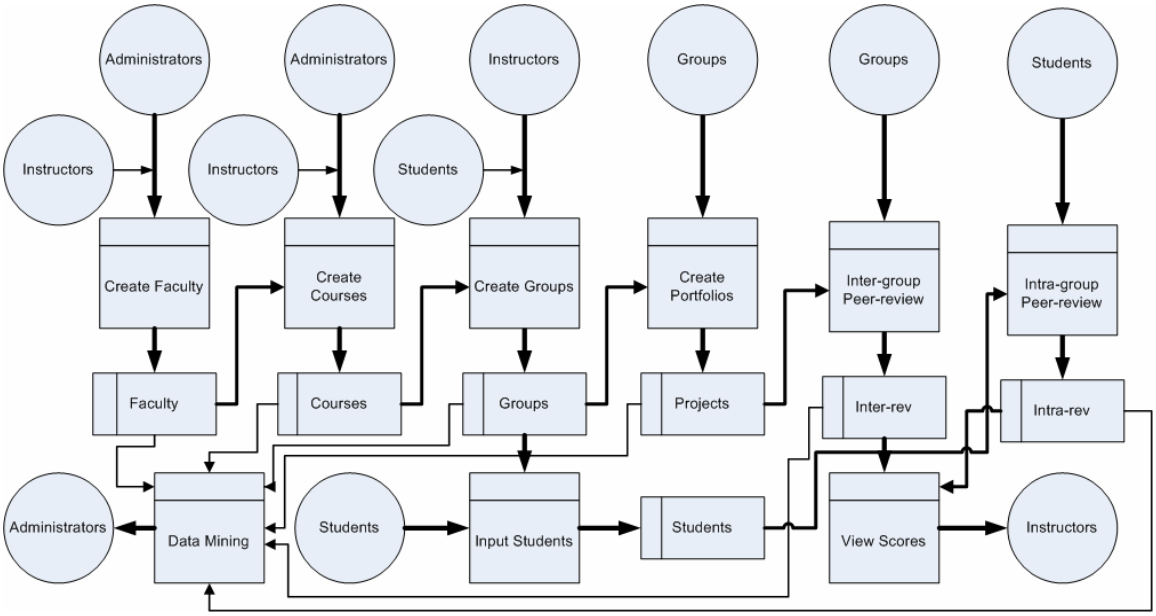

Figure 4-4. Data Flow Diagram (DFD) of *CIITN* Webtool

4.5 Developing the New Version of *CIITN* Webtool

Three goals are focused when we developed the second version: usability, security, and availability. The new strategies in the second version are expounded by different tiers.

4.5.1 Web interface

The interface between computers and users decides if users like to accept the information system. Web technologies, including HTML, CSS, VRML, etc., make the interface friendly. All of the knowledge that users need to learn is how to use web browsers, such as Internet Explorer, Netscape Navigator, Mozilla and Firefox. This minimizes the amount of technology training that instructors and students must engage in.

In addition, this makes the webtool accessible and usable from any computer with Internet access and an Internet browser.

In the design of interface, we have redesigned or improved the layout, the style, the format, and the color of the whole web site. Framesets is still used, but with concisely adjustment, the whole page looks uniform now. Because of the absence of managing styles, the fashions in the old version are different page by page. In the new version, the Cascading Style Sheet (CSS) technology is introduced, and colors, fonts and sizes could be tuned easily without revising every file. With adjustments of format, the design of pages could fit into all of common display resolution, keeping a clean look. The colors of the website are redesigned based blue series colors, so the whole screen is equilibrated, and the content in pages could be read clearly and comfortably.

Figure 4-5. The new web interface of *CIITN* Webtool

4.5.2 Common Gateway Interface (CGI)

The middle tier is the executable part in the whole system, and the Common Gateway Interface (CGI) technologies, such as Perl, PHP, VBScrip and Javascript, are adapted. In the webtool, we are using Perl as the CGI language. The codes of Perl in the system are improved by centralized management, which is an ideal way to lower errors and ease program maintain. In the new version of *CIITN* webtool, we have used CSS technology to reduce lines of HTML codes for style and format management, and reusable modules to encapsulate public HTML codes. With these methods, we have already removed 50% of HTML codes from CGI files, and kept Perl codes.

4.5.3 Database

We have been using Oracle database as the backend of *CIITN* Webtool because of the high stability of database system and database servers hosted by the University of Missouri-Columbia's Information Access and Technology Services (IATS). The following is the Data Flow Diagram (DFD) of the *CIITN* database.

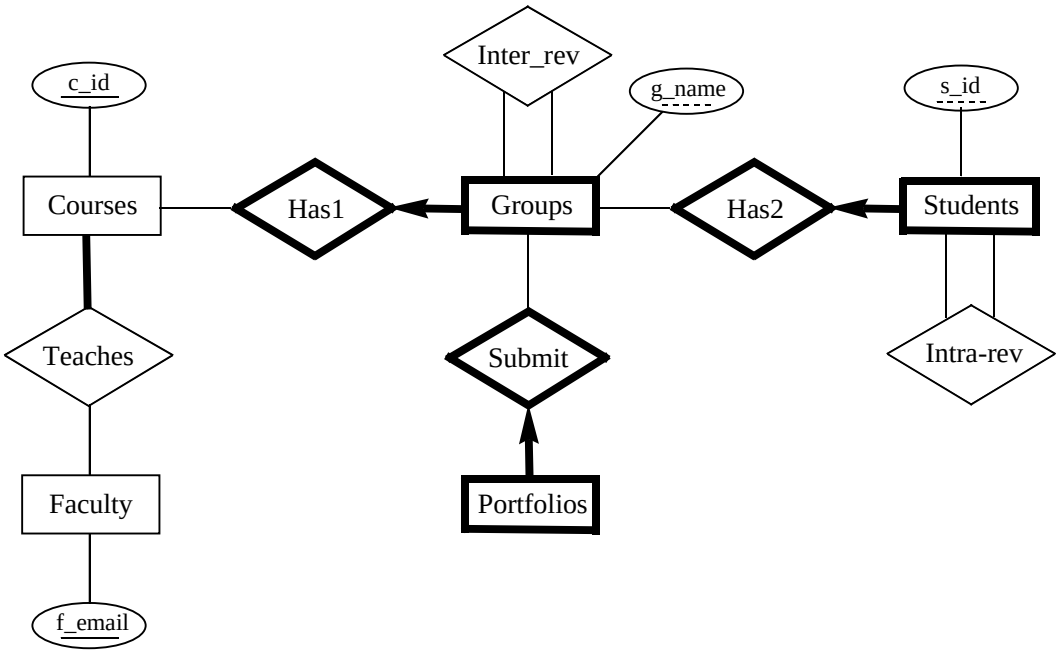

Figure 4-6: The diagram of entity relationship in *CIITN* database[10]

In the second version, the data structure is extended to fit in some new functions, such as deadline management, cooperation course management, etc. The main improvement for database management system (DBMS) is to solve the limit of fields. The solution adopted is to use multimedia files as a reinforce. One of the benefits of this solution is that students can use some new technologies to publish their portfolio, such as Macromedia Flash, Virtual Reality Modeling Languages (VRML).

4.5.4 New functions

In retuning the *CIITN* Webtool, new functions were added to meet the increased demands on webtool and to resolve the disadvantages of the first version. The following are the most important functions.

Multimedia files support: In the second version, a wider variety of multimedia content is allowed, such as: web page or archive files (.html and .mht), document files (.pdf, .doc, and .txt), graphic files (.gif, .png, .jpg, .jpeg, and .bmp), 3D files (.pdb and .wrl) and animation files (.avi and .swf). This is a major improvement over the first version, which supported only a handful of file types (.html, .gif, and .jpg). To solve the problem of unstable URL, students may make a copy of any article. Interactive media, such as Macromedia Flash, Chime PDB viewer and Parallelgraphic VRML (Virtual Reality Modeling Language) are also supported, so students may build much vivid demonstrations.

Individual peer-review support: It is now possible to tailor the inter-group peer review to fit in different kind of classes. In the first version, there was one form that was not course-adaptable. Now a general chemistry class will use different peer-review forms than an organic chemistry class while still using the same peer review system.

Media source guide: To assistant students easily, conventional media sources are organized and integrated into the website. The main newspaper links are made as flash show to guide students.

Online help: When students are working with their portfolios, they need some instant help with the limits of database, available resources, and supported functions, especially HTML tags. In the second version, this information is arranged at hand. While that helps students with convenience, the pressure of training and support is also released.

Deadline management: Deadline Management, including portfolio deadline, two rounds of intra-group peer review deadlines and two rounds of inter-group peer review deadlines, has to confront the challenge of the internationality of *CIITN*, because that several time zones are involved, and, particularly, in a *CIITN* course cooperated with several institutions. The second version accepts the server time as standard time, and converts to local time automatically as opposed to the first version, which accepted the local computer's time causing confusion about submission dates and allowing students to circumvent the deadline by changing the local computer's time.

File transfer tool: For each *CIITN* course, every group needs to upload some files, including documents, pictures and movies. Previously, students had to send these files to administrators, and waited for administrators to upload them. This is a time-consuming work for both of students and administrators. Using the file transfer tool, students are able to upload files by themselves and test their projects immediately. If some errors exist in files, such as illegal names or incorrect formats, this tool gives helpful hints.

AutoSet peer-review function: After groups are created, instructors need to set peer review groups. With AutoSet Peer-review function, instructors could appoint groups with only one click. This is a significant time saver as groups no longer need to be manually assigned provided that there are enough groups in the class to meet the AutoSet function limitations.

4.6 Conclusions

We have four *CIITN* courses running in this semester (Fall semester of 2004), Presently, with using the second version of *CIITN* webtool, *CIITN* is working smoothly with the support of *CIITN* Webtool. Less technology training and support is needed and system reliability is much better. With new web interface, webtool is much friendlier to users than before. Training, which is still available for students, is limited in basic knowledge of HTML and the usage of regular chemistry software, such as ChemDraw and Chem3D. Faculty and public users can also access *CIITN* without any training. In addition, the improvements of CGI programming make codes management easier, remaining Perl scripts are of self-explanatory and of convenience in cooperation between programmers. Because of this, the bugs that have been found were fixed immediately and relatively easily.

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