

Experiment 3: Part A. Preparation of Trans-9-(2-phenylethenyl)anthracene with the Horner-Wadsworth-Emmons Reaction.

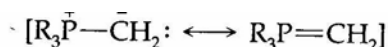
References:

CGWW, pp 814-818

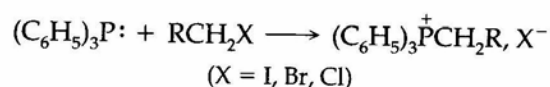
Background:

The Wittig reaction constitutes a valuable method for the preparation of alkenes. The major advantages of this approach are that (1) there is no ambiguity in the location of the C=C generated by the reaction, as there can be in many elimination reactions and (2), there is no potential for rearrangements, as there can be in E1 elimination reactions.

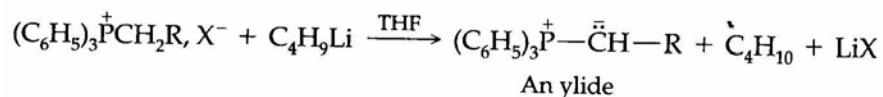
An *ylide* is a neutral species whose Lewis structure contains opposite charges on adjacent atoms. The atoms involved are carbon and an element from either group 15 (VA) or 16 (VIA) of the period table, such as N, P, or S. The Wittig reaction uses phosphorus ylides, which are obtained by deprotonation of a phosphonium salt with a strong base. Phosphorus ylides are relatively stable, but reactive species, for which the following resonance structures may be written; it has been suggested that the phosphorus atom can exceed an octet by accommodating electron donation into its 3d orbital.



The phosphonium salts are available through a nucleophilic displacement reaction of triphenylphosphine with various alkyl halides. Triphenylphosphine is a good nucleophile, and thus most phosphonium salts are easily prepared.



The hydrogen atoms on the carbon attached to the resulting phosphorus cation are somewhat acidic because they are adjacent to a positive charge, a significant electron-withdrawing group. Thus, treatment of the phosphonium salt with a strong base, such as butyllithium in THF or sodium hydride in DMSO, removes one of these protons and produces the ylide.



The ylides are generally not isolated, but rather generated in situ and reacted directly with the carbonyl compound.

So-called “instant ylides” that are solid-phase mixtures of a phosphonium salt with sodium amide (NaNH_2 , a strong base and the conjugate base of ammonia) and are commercially available. In the solid phase, no reaction between the strong base and the phosphonium salt occurs. To generate the desired ylide, the “instant ylide” mixture need only be placed in a suitable solvent. This process is a marked advantage over the usual methods used to obtain these species. Ylides, because of the significant negative charge density on carbon, are nucleophilic enough to attack electrophiles as reactive as the carbon of a carbonyl group. When the ylide is reacted with an aldehyde or a ketone, an intermediate *oxaphosphetane* (a four-membered ring containing an oxygen and a phosphorus atom) is formed, which decomposes to give the alkene product.

The Wittig reaction is very general. The significant limitation is that the carbonyl compound cannot contain acidic hydrogen atoms, such as in an alcohol or carboxyl group, or electrophiles more reactive than the aldehyde or ketone itself. The Wittig reaction can be quite stereoselective for the formation of either Z or E alkenes, but the factors involved in such stereoselectivity are sometimes difficult to predict and may be difficult to explain. A reasonably general rule states that the Z alkene predominates if a non-resonance stabilized ylide is used in the reaction. The E alkene is preferred when a stabilized ylide is used as is the case with the Horner-Wadsworth-Emmons reaction described below.

An important modification (often called the Horner-Wadsworth-Emmons reaction) of the Wittig reaction makes use of phosphonate esters, $\text{RPO}(\text{OR})_2$. It is highly stereoselective for the formation of E-alkenes. The reaction and mechanism are depicted below for the preparation of (E)-stilbene. Instead of using a phosphorus cation to stabilize the negative charge, as in the phosphonium ylide above, a phosphonate ester group is used to stabilize an adjacent carbanion. Most important

Concentrate the solution, which contains the desired product, almost to dryness on a sand bath under a slow stream of nitrogen gas. Now add approximately 1-2 mL portions of 2-propanol (isopropanol) to the flask and allow the resulting solution to stand at room temperature for 10-15 min, and then place it in an ice bath to complete the crystallization of the product.

Purification and Characterization. Collect the yellow crystals by vacuum filtration, using a Hirsch funnel, and wash the filter cake with two 1-mL portions of *cold* methanol. Main the vacuum for an additional 10 min to partially dry the crystalline product. Then place the material on a clay plate, or on filter paper, and allow it to dry thoroughly.

The purity of the product may be checked using *thin-layer chromatography*. Dissolve a small amount of the starting aldehyde and the product in ethanol and apply a sample to the TLC plate. Use toluene as the elution solvent, silica gel (containing a fluorescent indicator) as the stationary phase, and UV light for visualization. Typical R_f values are 0.92 for *trans*-9-(2-phenylethenyl)anthracene and 0.50 for 9-anthraldehyde, 0.50.

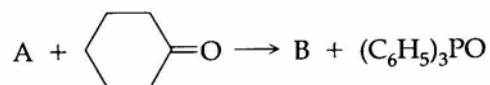
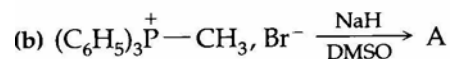
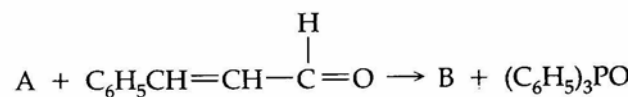
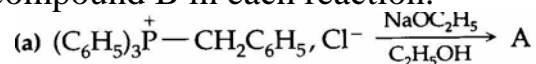
Weigh the product and calculate the percent yield. A portion of the material may be further purified by recrystallization from 2-propanol using the Craig tube.

Determine the melting point and compare it with the literature value. Obtain the IR spectrum of the alkene product. The material should have a strong absorption band at 962 cm^{-1} , which confirms the presence of a *trans* double bond.

This material has a characteristic UV spectrum in methanol. Obtain a UV spectrum at a concentration in the region of $3 \times 10^{-6}\text{ M}$. Be sure to record the final concentration of your solution and calculate the molar absorptivity ϵ_{max} for λ_{max} at 255 and 383 nm of the UV spectrum. Include the values in your report.

Questions:

1. Complete each of the following reactions by giving a suitable structure for the species represented by the letters. Is the ylide generated in (a) stabilized by resonance? If your answer is YES, write the resonance canonical forms. Give a suitable name for compound B in each reaction.



2. Show how you would synthesize the products B of (a) and (b) with the Horner-Wadsworth-Emmons reaction.

Experiment 3: PART B. Molecular Modeling and UV Spectrum Simulation of *Trans*-9-(2-phenylethenyl)anthracene with HYPERCHEM

The purpose of this portion of the lab is to simulate ultraviolet (UV) spectra of the *trans*-9-(2-phenylethenyl)anthracene. To record an ultraviolet (UV) spectrum experimentally, a sample in solution is irradiated with electromagnetic radiation (UV light in this case) and the wavelengths that are absorbed or transmitted are recorded as a spectrum. UV spectra are obtained when UV photons are absorbed and excite a molecule from its ground state to an excited state; an electron is excited from one occupied orbital to an unoccupied “virtual” orbital as in the case of a $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ excitation. Since ultraviolet spectroscopy is an “electronic” phenomenon, it is necessary to use quantum mechanical (QM) calculations to model the electronic structures of the molecules. Due to the computational restraints imposed by the relatively large systems studied in this case, a semi-empirical QM method rather than a more rigorous *ab initio* QM calculation is used to calculate/simulate the UV spectra.

While the equilibrium optimized geometry of *trans*-9-(2-phenylethenyl)anthracene can be obtained with molecular mechanics (MM) calculations, the computers in ABB and BSB are sufficiently powerful so the optimized geometry can be obtained with a semi-empirical QM method like PM3. The electronic structure of the excited states will be obtained by starting with a Restricted Hartree-Fock (RHF) wavefunction and applying the Singly excited Configuration Interaction Method (RCIS). This means that in the ground state the occupied molecular orbitals (MOs) are filled with paired electrons (RHF) and the excited states are factored in by allowing single-electron excitations (CIS). The ZINDO/S method that is parameterized to give UV spectra will be used with a so-called minimal basis set (1s, 2s, 2p_x, 2p_y and 2p_z) of orbitals to calculate the MOs of the two states that are required to simulate the UV spectrum. So the terminology that describes this method appears as, RCIS/ZINDO/S//PM3; the single point method appears first followed by a separator (//) and the method used to obtain the optimized geometry.

HyperChem has a user-friendly graphical-user interface (GUI). A number of the toolbar buttons allow you to “draw” the structure and use the Model Builder to obtain a suitable input geometry for the PM3 optimization. Remember computational methods should not replace your chemical intuition, only

complement it. *Does the structure look good? Does it make sense that your structure has a planar or non-planar geometry?* When you are satisfied that you have a good optimized geometry (**use a RMS gradient setting of 0.05 for your optimizations in this case**) carry out the single-point ZINDO/S calculation for each isomeric butadiene to simulate the UV spectra. Remember to save your work (optimized geometries) on a diskette as you go on!! You'll save time should your computer crash and a reboot is required or if you don't complete the modeling in one "sitting". **We'll start this tutorial by using HYPERCHEM to model the two conformations of cyclohexane and then move on to *trans*-9-(2-phenylethenyl)anthracene.**

INTRODUCTION TO MOLECULAR MODELLING

Computational chemistry is a new discipline whose advent and popularity have paralleled improvements in computing power (now calculations on fairly large molecules can be carried out on PCs) and software over the last decade. As with other disciplines in chemistry, computational chemistry involves the use of techniques and tools to gain understanding of chemical reactions, to enhance chemical knowledge, and to make predictions about the equilibrium geometrical structures of molecules and their reactions. The challenges of computational chemistry are to characterise and predict the structure and stability of chemical systems, to estimate the energy difference between different states, and to explain reaction pathways and mechanisms at the atomic level. Ideally it is desirable for users to understand how the techniques and tools are implemented and the nature of the databases used to parameterise the methods.

Most modelling/computational packages provide for:

- (a) building and displaying molecules and reading structural parameters such as bond lengths, bond angles and torsional angles - the so called internal coordinates of molecules
- (b) obtaining optimised equilibrium geometrical structures
- (c) generating and viewing molecular orbitals and electronic properties such as the electrostatic potential and the total spin density of a radical - a species which has an unpaired electron
- (d) calculating the geometrical structures and energies of transition structures (states) of chemical reactions
- (c) calculating and displaying spectral properties (UV and IR) and displaying the vibrations of molecules

In general, most high-level computational chemistry packages allow users to model molecules and chemical reactions at the three levels of theory.

Molecular Mechanics (Force Field) Methods

Molecular mechanical (MM) force fields use the equations of classical mechanics to describe the potential energy surfaces and physical properties of molecules. A molecule is described as a collection of atoms whose interactions can be described by simple empirical analytical functions which require specific parameters which depend on the types of functional groups present in a molecule. Consequently, reliable molecular mechanics calculations can only be carried out if the parameters for a specific connections of atoms (functional groups) are available in the parameter database. The collection of 5 or 6 analytical functions describes a **force field**. One component of a force field is the energy arising from compression and stretching of a bond. This component is often approximated as a harmonic oscillator (the bond between atoms is analogous to a spring connecting two particles) and is calculated with Hooke's Law where K_r is the force constant for the spring and r and r_0 are the displaced and equilibrium

$$V_{\text{spring}} = 1/2 K_r (r - r_0)^2$$

distances between the particles (atoms). PCMODEL uses harmonic functions to calculate

$$V_{\text{stretch}} = \sum_{\text{bond}} K_r (r - r_0)^2; \quad V_{\text{bend}} = \sum_{\text{angle}} K_\theta (\theta - \theta_0)^2$$

potentials for bonds and bond angles. K_r and K_θ are the parameters for different types of groups included in the PCMODEL molecular mechanics parameter files. Because a molecular mechanics calculation is fully parameterized (the calculation can only be carried out when the parameters are available), it is known as an empirical computational method. Because of the simple nature of the analytical functions and the parameterization, MM calculations are fast even for large molecules. This is the reason why they are used in calculations on large biomolecules such as proteins and polysaccharides. AMBER and CHARMM are the force fields currently used in calculations of this type.

***Ab initio* and Semi-empirical Quantum Mechanics Methods**

Electrons, which are more than three orders of magnitude lighter than nuclei, are too small for classical mechanics calculations. Electronic energy must be computed by solving the quantum mechanical Schrodinger equation. The lowest energy solution to this equation is called the ground-state wave function. Molecular orbital (MO) methods provide approximate solutions of the Schrodinger equation, the groundstate wave function, and certain low energy excited states. Quantum mechanics methods have several attractive features: (a) **unlike** MM calculations, they require no information about the location or geometry of bonds in a molecular system and (b) parameters for elements known as basis functions in *ab initio* (*ab initio* means 'from scratch') methods are independent of the chemical environment. In contrast, parameters used in molecular mechanics methods often depend on the chemical environment, that is the nature of the functional group(s). Computational packages like HyperChem and GAUSSIAN 98 can perform quantum mechanics MO calculations on molecules containing 100 or more atoms. While there is no real restriction on the number of atoms, larger structures studied at high levels of theory require excessive computing times and computer main memory. Even though calculations of this type are usually run on parallel supercomputers such as the Cray, workstations based on the current Pentium and RISC processors now have the computing power to carry out full *ab initio* calculations on relatively large molecules, even *trans*-9-(2-phenylethenyl)anthracene.

MOLECULAR MODELLING WITH HYPERCHEM

Chemists use molecular models (plastic or metal) in an attempt to get a 3-dimensional image of molecules. A 3-D image is extremely important as it aids in understanding the reactivity and reaction mechanisms of molecules. It also allows one to predict, by changing (twisting) dihedral angles, which conformers are likely to be the most stable. A number of difficulties are encountered in using molecular models: i) models may give incorrect predictions of stable conformations and interatomic distances because they use 'generic' bond lengths and angles; ii) no quantitative information about the relative stabilities of different structures or conformations can be obtained and transition states cannot be located; (iii) **no information is gained about electronic structure and bonding**. Another less obvious difficulty is deciding what to do about big molecules like proteins, for gravity tends to break the partial structure apart before the molecule can be constructed.

In this tutorial you will use the modelling package HYPERCHEM to calculate the relative energies of a) the chair and twist-boat conformations of cyclohexane and b) calculate the UV spectrum of *trans*-9-(2-phenylethenyl)anthracene.

PROCEDURE

The program is available through the network. The procedure below works on the computers of the cluster in ABB 417. You may run HYPERCHEM at any time when the room is free and use it in other courses. It is **HIGHLY RECOMMENDED** that you bring a diskette so you can save your optimised geometrical structures along the way to avoid having to go back and start from scratch if you can't finish your work in one sitting or the computer crashes.

Getting Started

- 1) Re-boot the computer or turn it on and wait for the login window to appear, then type in your McMaster ID and your password (the same as you e-mail passwd). Leave the last entry unchanged and wait for the login to be completed.*
- 2) Double-click (from this point on I will use the acronym DC for Double-Click) on the Course Folders icon. This will take you to a new window where you DC on the Chemistry icon. When you next DC on the 2BA3/2BB3 icon you will move to the window from which you will run HYPERCHEM by DCing on the icon.*

PART 1: Two Conformers of Cyclohexane

In HYPERCHEM an “activity” can be selected by clicking on one of the drag-down menus (DDM) at the top of the input window. This hand-out shows the File, Edit, Build, Select, Display, Setup, and Compute DDMs. Your TA will explain the meaning of some of the important highlighted and non-highlighted selections. There are also a number of tools that you must use to draw and manipulate your structure on the screen. They are identified/labelled on the hand out sheet and your TA will demonstrate how they are to be used. The draw tool \oplus is used to generate a crude structure. To say that is a crude structure is an understatement. You will see that that all the carbon atoms of the cyclohexane (hexagon) ring that you

generate initially lie in the plane of the screen (the XY plane). This is the case for all structures you draw. The first order of business is to left-click (L-CLK) on the Build DDM, position the cursor on Default Element and release the button to ascertain whether carbon is the default element. When you L-CLK on Properties a list of useful properties of the element are displayed. Exit the element table and draw the planar carbon framework of cyclohexane by dragging the cursor around and releasing the left mouse button at each point where you want an atom –try to draw a symmetrical hexagon. To label the atoms, L-CLK on Display, select Labels and tick Symbol. To generate a double bond, move the draw cursor between two atoms and L-CLK; for a triple bond L-CLK twice. To delete a bond, position the draw cursor between two atoms and right-click (R-CLK). To change the default element, go to Build/Default Element and CLK on the oxygen symbol, go back to the input screen, and L-CLK on one of the carbon atoms. You have effectively converted cyclohexane to oxacyclohexane. Note the change in colour as the change is made. Now go back to the cyclohexane. By selecting the x,y,z rotation tool, positioning its cursor anywhere on the input screen, and moving the mouse you can rotate the THINGY you thought you generated in 3-D and confirm that it is *planar*. To dramatically improve this structure, use the MODEL BUILDER. Go to the Build DDM and select Add H & Model Build and voila you have generated the chair conformation of cyclohexane. CONGRATULATIONS!!!! However, it is not an equilibrium optimised geometry because “standard” geometrical parameters of a database were used to generate an improved molecular geometry on the basis of the “valency” of the atoms of your initial structure. To optimize the geometry, go to the Setup DDM, L-CLK on Semi-empirical, and release the button. This takes you to the DDM that allows you to select the quantum mechanical method that is used for the optimization. In this case use PM3 because it has been shown that this method statistically yields the best heats of formation for organic molecules. Now L-CLK on Options to access the DDM that allows you to set the charge and multiplicity of your molecule. For cyclohexane the charge is 0 and the multiplicity is 1 (this means the molecule is in its singlet state with all the electrons paired). L-CLK on OK to move back to the input screen. Now L-CLK on Compute and select Geometry Optimization. This DDM allows you to select an optimizer – the algorithm which “walks” the structure over the molecular potential energy (PE) surface – to locate a minimum. Select Polak-Ribiere that is the default optimizer. Also select the appropriate RMS gradient (in this case use 0.1) which is the threshold that is used to determine at what point a geometry is considered to be optimized and to halt the calculation. For high quality data (for publications) one would use a RMSG of 0.001. You may wish to play around with

the value of the RMSG. When you L-CLK on OK the calculation will start and a running dialogue is displayed at the bottom of the input screen. When the RMSG drops below your selection on a consistent basis, the calculation stops. The terms N cycles and N2 points mean that N steps were taken on the PE surface with the energies of N2 points (geometries) being calculated in order to locate the minimum. The calculation was fast because the model builder provided you with a reasonably good starting geometry. Whether the calculation “converges” and how fast it converges depends on how crude the starting geometry is and what computational method is used in the calculation. It is clear that a good knowledge of structure and stereochemistry of organic (and inorganic) molecules is crucial in recognising whether a starting geometry is acceptable and when the results of a calculation are meaningful. Now save the geometry of your chair cyclohexane to your diskette by L-CLKing on File and selecting Save As. Type in the correct path to the diskette drive along with a suitably descriptive file name and save the geometry in the MOPAC Z-MATRIX format. You can read the optimized geometry from the diskette if the need arises. Now reset the path back to the C:\ drive. To obtain the heat of formation for the chair and write the information to your diskette, L-CLK on File and select Start Log. Type in a filename, set the Quantum Print Level to 1, and L-CLK on OK. Now L-CLK on Compute and select Single Point. The calculation starts and data are written to your diskette. **Be sure to use Stop Log otherwise the results of all your following HYPERCHEM calculations will be written to your diskette.** Note that HYPERCHEM assigns the 3D3 point group to the chair cyclohexane. Is this correct?

Now you will use the selection tool © to select a plane through which you will reflect a methylene group to generate a the boat conformation. L-CLK on this tool then L-CLK on the four carbon atoms of the seat of the chair. Pull down the Select menu, go to Name Selection and tick PLANE. Now go back to the input screen. Now go back to the input screen and L-CLK on the carbon and the hydrogens of the methylene group you wish to flip (reflect through the plane). Voila you have generated the boat form. Deselect the atoms (see above) and carry out a geometry optimisation with PM3. Note that it remains in the boat form. Occasionally a molecule gets “stuck” in a symmetrical form when one starts from a symmetrical input geometry even though the symmetrical species is not a minimum. Your TA will explain why this is so. To “nudge” the boat into the twist-

boat, delete one of the C-C bonds, change the torsional angle (you can't alter a torsional angle in HYPERCHEM when it is in a ring), connect the atoms (although you don't really have to do so; WHY?) and re-optimize the geometry. You should end up with the twist-boat if you tweaked the torsional angle sufficiently. Now open a log file and run a single point calculation to obtain the heat of formation. Compare the values for the chair, the boat, and the twist-boat. To obtain ball and cylinder "models", go to the Display DDM, select Rendering and tick on Balls and cylinders. You may also wish to view the overlapping sphere models as well. These space-filling pictures are based on the van der Waals radii of the atoms.

To change the input window colour to white, go to the File DDM and select Preferences. Change the Window colour from Black to White. This reduces the amount of ink/toner that is used when you obtain plots.

PART 2: The UV Spectrum of *trans*-9-(2-phenylethenyl)anthracene.

Now use HYPERCHEM to generate and optimize *trans*-9-(2-phenylethenyl)anthracene and calculate its UV spectrum. Some helpful hints on generating the *trans*-9-(2-phenylethenyl)anthracene follow. Generate and optimize anthracene. Construct/attach the *trans*-2-phenylethenyl group at C9 of your anthracene. It is advantageous to use the draw tool (draw the benzene ring as accurately as possible) with carbon and add the hydrogens "manually" or use 'add hydrogens' of the builder. DON'T USE 'add hydrogens and model build' after you draw/attach the *trans*-2-phenylethenyl group at C9 because the model builder overlaps the phenyl groups and makes the optimization difficult and time consuming...who knows why!!!! It may be advantageous to twist the 2-phenylethenyl group out of planarity with the anthracene ring before you attempt the final geometry optimization. The optimization will take less CPU time.

When you have obtained an optimized geometry go to **Setup**, select **Semi-empirical**, choose the **ZINDO/S** method and select **options**. Your alkene *trans*-9-(2-phenylethenyl)anthracene that is neutral and has a singlet ground state. Set the **total charge** to **0** and the **spin multiplicity** to **1**. Under **spin pairing** select **RHF** since the ground state will have all the spins paired in the first approximation. Under **state** select **lowest** since excitations from the ground state will be examined. Click on **Configuration Interaction** and select **singly excited**. Now choose **Orbital Criterion**. This option selects how many MOs will be involved in the CI (Configuration Interaction) expansion. Select **3 occupied** and **3**

unoccupied orbitals. This means the calculation will consider all the possible single-electron excitations from the 3 highest occupied molecular orbitals to the 3 lowest unoccupied orbitals. This is an important part of the calculation and is reflected in the name RCIS(6,6)/ZINDO/S//PM3. The (6,6) stands for the number of electrons and orbitals included in the expansion, respectively. Now click on **OK** for all three boxes you have opened. Start/open a Log file and under **Compute** select **single point**; the electronic configuration will be optimized (the MOs calculated) fairly quickly. **BE SURE TO “STOP” THE LOG FILE. ALSO REMEMBER TO TOGGLE OFF THE CI CALCULATION IF YOU GO ON TO ANOTHER OPTIMIZATION.**

Now let's examine the simulated UV spectra. Under **Compute** select **Electronic Spectrum**. The simulated spectrum will appear. The lines along the bottom of the spectrum correspond to the wavelength in nm. Click on the two most intense band between 200 and 400 nm and record the values. Why do they appear as single lines instead of the broad bands observed experimentally? Click on the **copy** button to copy – make sure the background colour is white – the spectrum to the clipboard. The simulated spectrum can now be pasted into **WORD** (it has to be opened first) for inclusion into your report. **Include a copy(figure) of your optimized geometry in your report.**

Be sure to compare the λ_{max} values calculated by ZINDO/S with the experimental values for *trans*-9-(2-phenylethenyl)anthracene in your report.

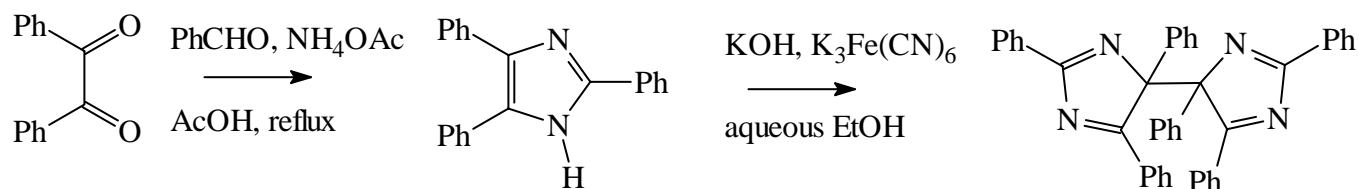
Obtain plots of the HOMO and the LUMO of *trans*-9-(2-phenylethenyl)anthracene To accomplish this, go to the Compute DDM and select Orbitals. On the screen you will see the colour-coded energy levels of the occupied and unoccupied MOs. Use the cursor to select a MO (or use the dialogue box) for viewing. Go to Options to set the Grid Mesh Size to Fine, the Orbital contour value to 0.03 and Rendering to Gouraud shaded surface. Over what ring system(s) is the HOMO delocalised? Over what ring system(s) is the LUMO delocalised?

To get a picture of the total electron density of *trans*-9-(2-phenylethenyl)anthracene go to the Compute DDM and select Plot Molecular Properties and select Total Charge Density. Make sure to the set the Grid Mesh Size to Fine and the Total Charge Density contour value to 0.01 in Isosurface Rendering. This contour value includes 99% of the electrons of the molecule.

HAVE FUN !!!! ☺

Experiment 4. Preparation of 2,4,5-triphenylimidazole (lophine) and Conversion into its Piezochromic and Photochromic Dimers

The preparation of 2,4,5-triphenylimidazole is simply carried out by refluxing a solution of benzil, benzaldehyde and ammonium acetate in ethanoic acid to give the condensation product. The oxidative dimerization has been described using either sodium hypochlorite or potassium ferricyanide and use of the latter oxidant is described here.



Materials

1. Preparation of 2,4,5-triphenylimidazole

benzaldehyde (FW 106.1)	2.65g, 2.5mL (25mmol)	toxic
benzil (FW 210.2)	5.25g (25mmol)	irritant
ammonium ethanoate (FW 77.1)	ca.10g (130mmol)	
glacial ethanoic acid (100%)		CARE !!, corrosive
ethanol (95%)		flammable, toxic
ammonium hydroxide (ca. 30% NH ₃)		corrosive, irritant

2. Preparation of piezochromic and photochromic dimers

2,4,5-triphenylimidazole (from part 1) (FW 296.4)	1.5g (5mmol)	
potassium ferricyanide	4.5g	
potassium hydroxide pellets	12.0g	corrosive,
hygroscopic		
ethanol (95%)		flammable, toxic
light petroleum (bp 40–60°C)		flammable
toluene		flammable

Procedure:**CARRY OUT THE REACTIONS AT ONE-HALF SCALE.****1. Preparation of 2,4,5-triphenylimidazole**

Dissolve the benzyl, benzaldehyde and ammonium ethanoate in 100 mL glacial ethanoic acid in a 250 mL round-bottomed flask containing a magnetic stirrer bar, and heat the mixture to reflux for 1h with stirring (the solution **must** be stirred). After this time, cool the mixture to room temperature and filter to remove any precipitate which may be present. Add 300 mL of water to the reaction filtrate and

If the precipitate is gooey, don't do the filtration and simply decant the solution, add the water to the decanted solution, and proceed with the neutralization.

collect the precipitate by filtration with suction. Neutralize the filtrate with ammonium hydroxide and collect the second crop of solid. Combine the two crops of precipitate and recrystallize from aqueous ethanol. Record the yield and mp of your purified material.

2. Preparation of piezochromic and photochromic dimers

Dissolve the potassium hydroxide in 100 mL of 95% ethanol with heating and to this add 1.5 g of 2,4,5-triphenylimidazole. When fully dissolved add the mixture to a 1 L beaker containing a large magnetic stirrer bar and cool to 5°C in an ice-water bath with stirring. Prepare a solution of the potassium ferricyanide in 450 mL of water and place this in an addition funnel clamped securely over the beaker. Add the potassium ferricyanide solution to the vigorously stirred ethanolic mixture at such a rate that the temperature of the reaction does not exceed 10°C. (This should require about 1 h.) Near the end of addition, the rate can be increased. In the initial stages of the addition, a violet colouration develops to be replaced by a lightly-coloured precipitate. After addition is complete, filter off the precipitate with suction, washing thoroughly with water (5 x 50 mL). Dry the precipitate on the filter by rapid washing with *cold* 50% ethanol (10 mL) followed by light petroleum (2 x 25 mL). Record the yield, appearance and mp of your material and store it in the dark. Place a small quantity of your product in a mortar, grind it and observe the colour change. Dissolve 20 mg of the material in 30 mL of toluene, stopper and store the mixture in the dark. After the solution has become colourless or nearly so, stand the solution in strong sunlight or irradiate it with a bright tungsten light and note the effect. Return the solution to the dark and observe it after a day or so. Interpret the results.

Questions:

1. Propose a mechanism for the formation of 2,4,5-triphenylimidazole.
2. Discuss any chemical or physical method that might be used to demonstrate that the violet colouration is caused by radical species.
3. Propose a mechanism by which the oxidative coupling of two molecules of 2,4,5-triphenylimidazole occurs.
4. What features of the radical favour its formation? Give other examples of relatively long-lived radical species.

Further reading

For spurious piezochromism of dianthraquinone, see: A. Schönberg and E. Singer, *Tetrahedron Lett.*, 1975, 1925.

For the procedures on which this experiment is based, see: D.M. White and J. Sonnenberg, *J. Am. Chem. Soc.*, **88**, 3825 (1966).