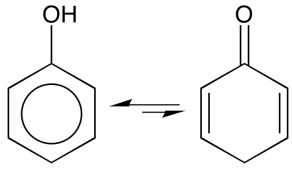
Chapter 15
Using the Cambridge Structural Database

The Cambridge Structural Database (CSD) is a well-organized and easily-accessible depository of over 1 million experimental structures, almost entirely from X-ray crystallography. It is available on a yearly subscription basis, and when installed and licensed may be seamlessly accessed from ***Spartan****. Searches may be carried out based on substructure (as in SMD and SSPD databases) as well as using molecule names. The tutorials in this chapter are intended to illustrate the interface and more importantly the types of questions to which the database may be used in conjunction with quantum chemical calculations. This requires access to the CSD.*

Stable Tautomers of Phenol



1. Build or sketch 2,5-cyclohexadienone. You need to put an explicit hydrogen on one of the free valences at C_4. Select **Structure Query** ( ) from the **Search** menu and *click* on all open free valences. Select **Databases** ( ) from the **Search** menu and *click* on the **CSD** tab. *Click* on ( ) to the right of the **Search** button, select **Organics** under **Filters** and **Structure** under **Search By** and in the **Search Options** dialog that results and *click* on **OK**. *Click* on the **Search** button. Molecules that incorporate the 2,5-cyclohexadienone substructure will appear at the right of the dialog. As you select (*click* on) each of the entries its structure will appear at the left. The simplest molecule among the "hits" is 3,5-di-*tert*-butyl-2,4-dichloro-

2,5-cyclohexadienone, identified as ***DOBHEH***. *Click* on (▾) to the right of the **Retrieve** button, select **New Document** under **Retrieve To** and all entries under **Retrieval Filters** in the **Retrieve Options** dialog that results and *click* on **OK**. *Click* on the entry (***DOBHEH***) and *click* on the **Retrieve** button. The molecule will appear on screen in a separate document.

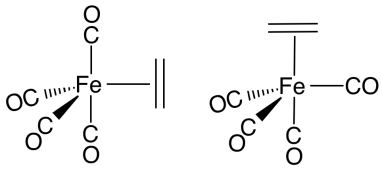
2. Bonds to hydrogen in X-ray crystal structures are almost always too short, typically by ≈0.1Å, and should be adjusted before using as a start for quantum chemical calculations. To do so without affecting heavy-atom positions, select **Minimize** from the **Build** menu ( ).

3. Build the enol tautomer (3,5-di-*tert*-butyl-2,4-dichlorophenol), placing it in the same document as the cyclohexadienone derivative. Select **Build New Molecule** ( ) or **Sketch New Molecule** ( ) instead of **New Build** or **New Sketch**. You now have structures for both tautomers in a single document.

4. Select **Calculations** from the **Setup** menu ( ). Specify **Equilibrium Geometry** using the ωB97X-D/6-31G* density functional model. Submit the job. Which tautomer is favored? Are their energies close enough to allow both to be seen in an equilibrium mixture?

Binding to Iron Tetracarbonyl

An olefin bonded to iron tetracarbonyl may occupy either an *equatorial* or *axial* position. Search CSD to see if one of the two if seen more frequently than the other.



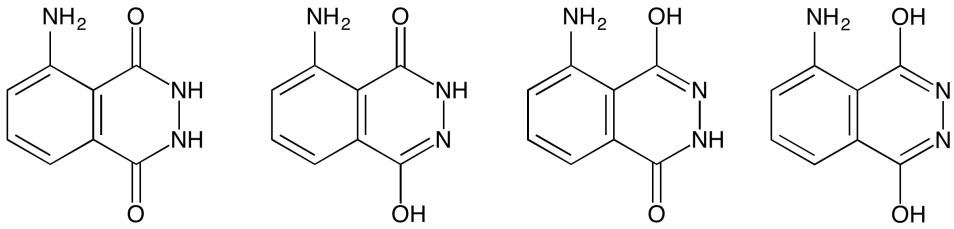
1. Build ethylene iron tetracarbonyl. For the purpose of the CSD search it does not make a difference whether the ethylene ligand is *equatorial* or *axial*. Select **Structure Query** ( ) from the **Search** menu and *click* on all the four free valence on ethylene.

Select **Databases** ( ) from the **Search** menu and *click* on the CSD tab. *Click* on ( ) to the right of the **Search** button, select **Inorganics*** under **Filters** and **Structure** under **Search By** and in the **Search Options** dialog that results and *click* on **OK**. *Click* on the **Search** button. Molecules with four carbonyl and one olefin ligand in CSD will be listed at the right of the dialog. Does there appear to be a clear preference for *equatorial* over *axial* olefin binding or vice versa?

2. Build the other conformer and put in the same document as the one that you used to query the CSD. Select **Calculations** from the **Setup** menu ( ) and specify calculation of equilibrium geometry with the ωB97X-D/6-31G* density functional model. Make sure that **Global Calculations** is checked. Submit the job. Execution will take several minutes. Which conformer is favored and by how much? Is your result consistent with what you found (or didn't find) in the CSD search?

Luminol

Several reasonable tautomers may be drawn for the luminol, four of which are shown below.



Which is the most stable tautomer? Which if any are represented by crystal structures in CSD?

1. In turn, draw or build each of the four tautomers. Provide explicit hydrogens (replacing free valences) for atoms that are involved in the tautomerization. Select **Structure Query** ( ) from the **Search** menu and *click* on all free valences. Select **Databases** ( ) from the **Search** menu and *click* on the CSD

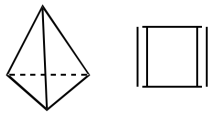
* This limits the search to about half of CSD with a corresponding reduction in search time.

tab. *Click* on (▾) to the right of the **Search** button, select **Organics** under **Filters** and **Structure** under **Search By** and in the **Search Options** dialog that results and *click* on **OK**. *Click* on the **Search** button. For which tautomer(s) do you find crystal structures? Is luminol itself among them?

2. Obtain equilibrium geometries for each of the four tautomers using the ωB97X-D/6-31G* model and follow these with energy calculations with the ωB97X-V/6-311+G(2df,2p) model. You can do this in a single step. Select **Calculations** from the **Setup** menu. Select **Energy**, **Density Functional**, **ωB97X-V** and **6-311+G(2df,2p)** from the menus to the right of **Calculate** and **Density Functional**, **ωB97X-D** and **6-31G*** from the menus to the right of **Start From**. Submit the job (geometry calculations followed by "better" energy calculations on four molecules). It will take several minutes to complete. What is the lowest energy tautomer? Is it the same as found in the crystal? Are any other tautomers low enough in energy to contribute significantly to the properties of luminol?

Tetrahedrane and Cyclobutadiene

The C_4H_4 isomers, tetrahedrane and cyclobutadiene, are among the most unlikely of hydrocarbons. It is hard to imagine a molecule that is more strained than the former while the latter is the prototypical antiaromatic molecule. Use the CSD to see if derivatives have actually been characterized.



1. Build cyclobutadiene. Select **Structure Query** ( ) from the **Search** menu and *click* on all open free valences. Select **Databases** ( ) from the **Search** menu and click on the CSD tab. *Click* on (▾) to the right of the **Search** button, select **Organics** under **Filters** and **Structure** under **Search By** and in the **Search Options** dialog that results and *click* on **OK**. *Click* on the **Search** button.

2. Repeat the process for tetrahedron.

3. Identify the simplest system that is common to both cyclobutadiene and tetrahedrane, that is, one where the substituents are the same. Build the two molecules (or extract the two from the "hits" on CSD. Calculate equilibrium geometries for the two using the ωB97X-D/6-31G* model. Select **Calculations** from the **Setup** menu and inside the dialog select **Density Functional**, **ωB97X-D** and **6-31G*** from the menus to the right of **Calculate**. Submit the job (two molecule). It will require several minutes to complete. Which molecule is more stable?