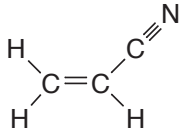
Chapter 7

Spectra, Properties and Graphical Models for Organic Molecules from Quantum Chemical Calculations

The tutorials in this chapter provide the earliest and simplest examples of specifying and performing quantum chemical calculations. As in the previous two chapters, they refer back to molecules examined in ***Chapters 3*** *and* ***4****. Calculations are done utilizing the* ωB97X-D/6-31G* *model, and time estimates are based on this model using a quad-core desktop machine (3.2 GHz Intel I5 processor, 8 GB RAM, 600 GB hard drive) running in serial on Windows 10. Alternate computational models can be used in place of* ωB97X-D/6-31G**. Completion times will vary accordingly.*

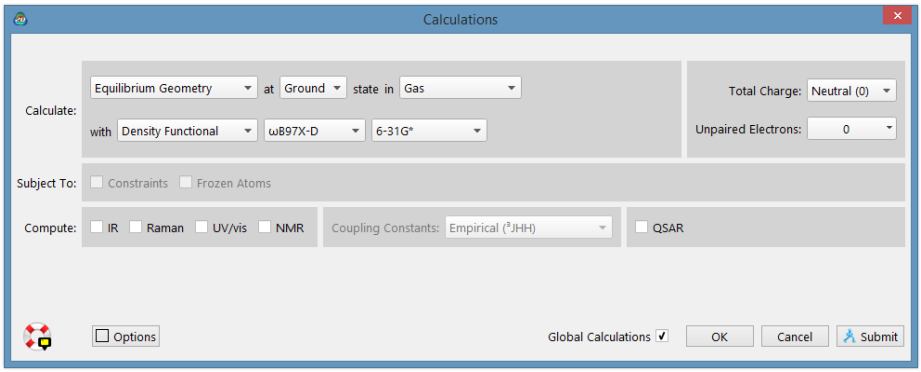
5 min

Acrylonitrile



We return to acrylonitrile for the first tutorial that actually involves quantum chemical calculations.

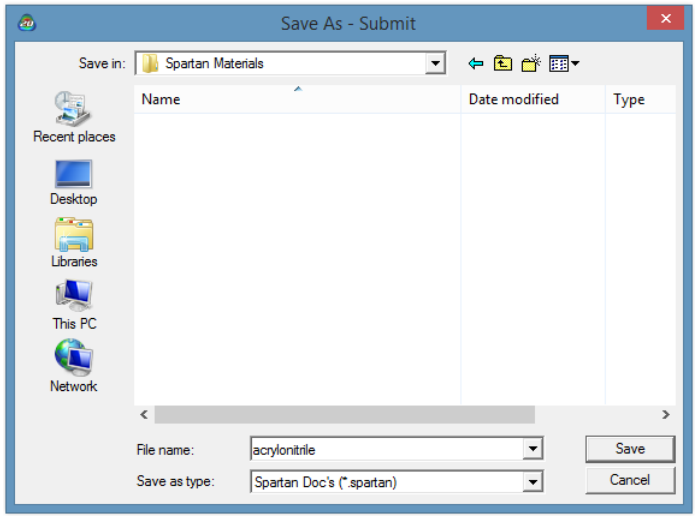
1. Build or sketch acrylonitrile.
2. Select **Calculations...** from the **Setup** menu or *click* on () if it appears at the top of the screen, and perform the following operations in the **Calculations** dialog that appears.



a. Select **Equilibrium Geometry** from the top menu to the right of **Calculate**. This specifies optimization of equilibrium geometry. At **Ground** state in **Gas** should appear in the menus to the right of **Equilibrium Geometry**.

b. Select **Density Functional**, **ωB97X-D** and **6-31G*** from the three bottom menus to the right of **Calculate**. This requests that the ωB97X-D/6-31G* density functional model is to be used for this calculation.

c. *Click* on **Submit** at the bottom of the dialog. A file browser appears.



Because the molecule is in SSPD (even though we will not use the data), the name ***acrylonitrile*** will be presented to you in the box to the right of **File name:**. Either use it or type in whatever

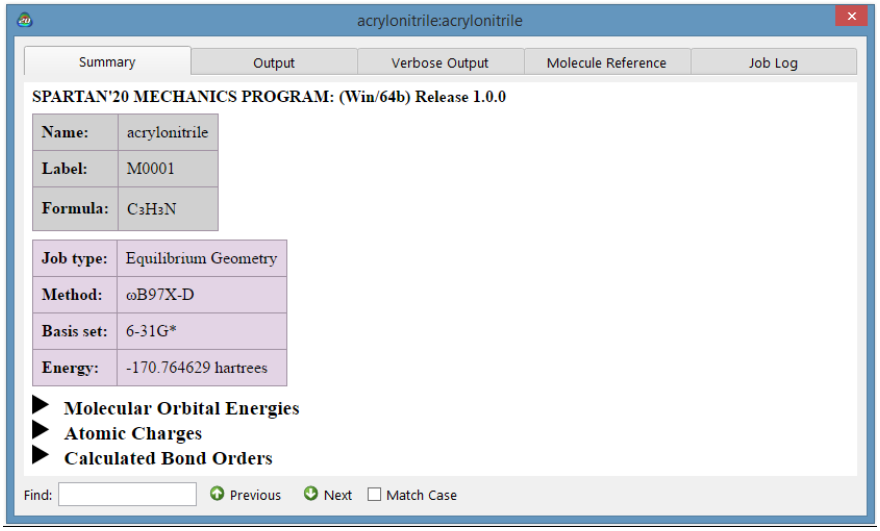
name you like and then *click* on **Save**. You will be notified that the calculation has been submitted.

Click on **OK** to remove the message from the screen.

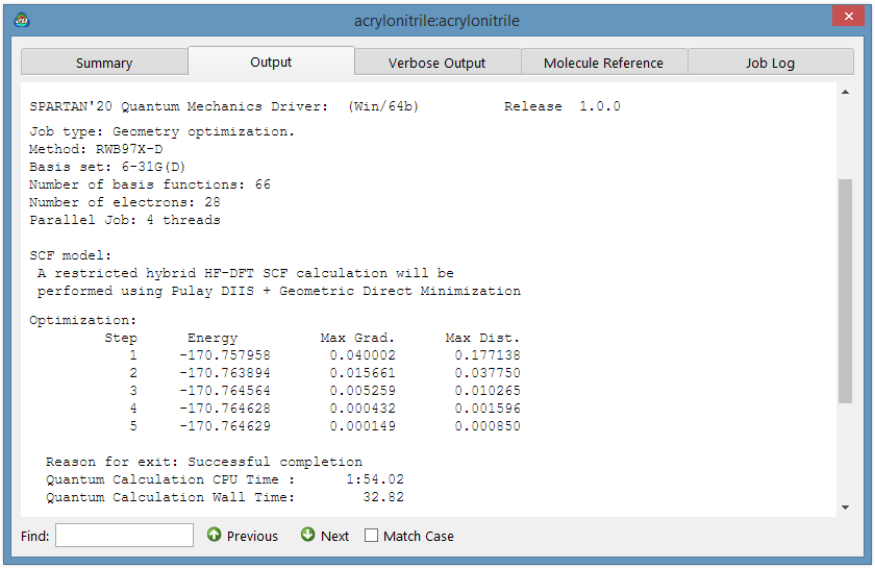
> After a molecule has been submitted, and until the calculation has completed, you will not be permitted to modify any dialogs or other information associated with it.

3. You will be notified when the calculation has completed.

Click on **OK** to remove the message from the screen. Select **Output** from the **Display** menu or *click* on ( ) if it appears at the top of the screen. Displayed initially is a brief summary, describing the task and providing the molecule name and molecular formula together with the total charge (if it is not 0) and number of unpaired electrons (if it is not 0), the calculation model and the total energy.



The summary may be all that you really want (or need) but more detailed information can be obtained by selecting **Output** from the menu at the top of the dialog.

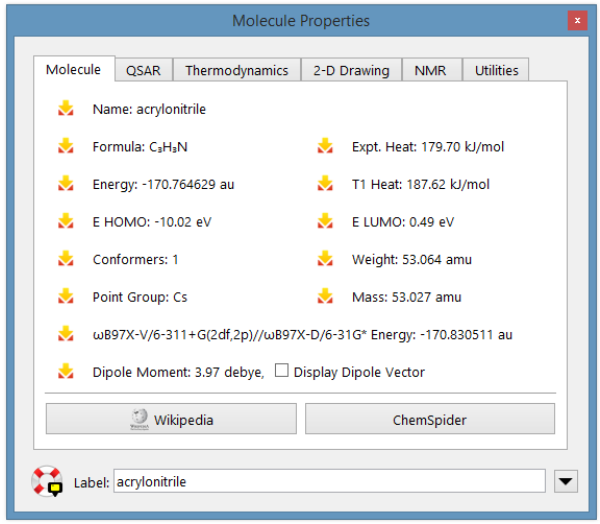


You can scan the output from the calculation by using the scroll bar at the right of the window or by *clicking* (left button) inside the output window and using the scroll wheel on your mouse. Information at the top of the dialog is similar to that reported in the summary, although additional details are provided. Eventually, a series of lines appear, under the heading ***Optimization***. These tell the history of the optimization process. Each line (or ***Step***)

provides results for a particular geometry. Ideally, the energy will monotonically approach a minimum value for an optimized geometry. If the geometry was not optimized satisfactorily an error message, such as: ***Optimization has exceeded N steps – Stop***, will be displayed following the last optimization cycle. Optimization failure is not common, so if it occurs, check to see if you have correctly built the structure.

Near the end of the output is the final total energy* (-170.764629 atomic units for acrylonitrile if you used the ωB97X-D/6-31G* model)**, and the computation time. *Click* on at the top of the output dialog to close it.

You may examine the total energy and dipole moment among other calculated properties without having to go through the output. Select **Properties** from the **Display** menu to bring up the **Molecule Properties** dialog (make certain that the **Molecule** tab and not the **QSAR**, **Thermodynamics**, **2D Drawing**, **NMR** or **Utilities** tab is selected).

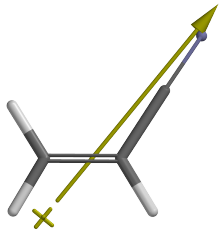


To see the dipole moment vector (indicating the sign and direction of the dipole moment), *check* the box to the left of

* See **Calculations...** (**Setup** menu; **Chapter 21**) for a discussion of how total energy relates to heat of formation and strain energy.

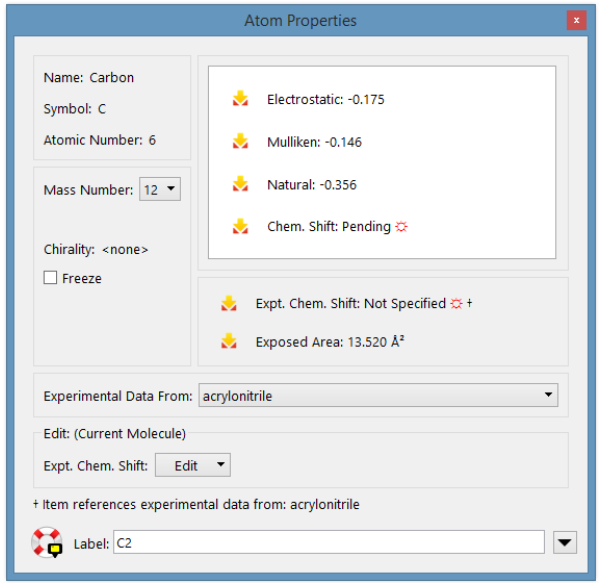
** The number you actually get will likely differ in the last decimal place due to machine precision.

Display Dipole Vector. Wire, ball-and-wire or tube models are best for this display.



Uncheck the box to remove the dipole moment vector.

Click on an atom. The (**Molecule Properties**) dialog will be replaced by the **Atom Properties** dialog.



Among other things, this provides three different sets of atomic charges: **Electrostatic**, **Mulliken** and **Natural**.* To obtain the charge on another atom, simply *click* on it. Inspect all the atomic charges on acrylonitrile (by *clicking* on the appropriate atoms). When you are finished, *click* on  at the top of the **Atom Properties** dialog to close it.

4. Select **Surfaces** from the **Display** menu (). *Click* on **Add** at the bottom of the **Surfaces** dialog that results, and select

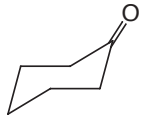
* Atomic charge is not (and cannot be) a measurable property and numerous ways have been formulated to calculate it. It is not surprising that they can and do lead to markedly different results.

electrostatic potential map from the menu. This requests an electrostatic potential map (an electron density surface onto which the value of the electrostatic potential is mapped). The graphics calculation will run without needing to resubmit the job. When it completes in a few seconds, *check* the box to the left of ***electrostatic potential map*** in the **Surfaces** dialog. The surface itself corresponds to the electron density and provides a measure of the overall size and shape of acrylonitrile. The colors indicate values of the electrostatic potential on this surface; by convention, colors toward red correspond to negative potential (stabilizing interaction between the molecule and a positive charge), while colors toward blue correspond to positive potential. The nitrogen (the most electronegative atom) is red and the hydrogens (the most electropositive atoms) are blue.

5. Close ***acrylonitrile*** and any open dialogs.

5 min

Cyclohexanone



This tutorial offers another example of a quantum chemical calculation on a very simple molecule. It also provides an opportunity to further illustrate graphical models for elucidating the stereochemistry of organic reactions.

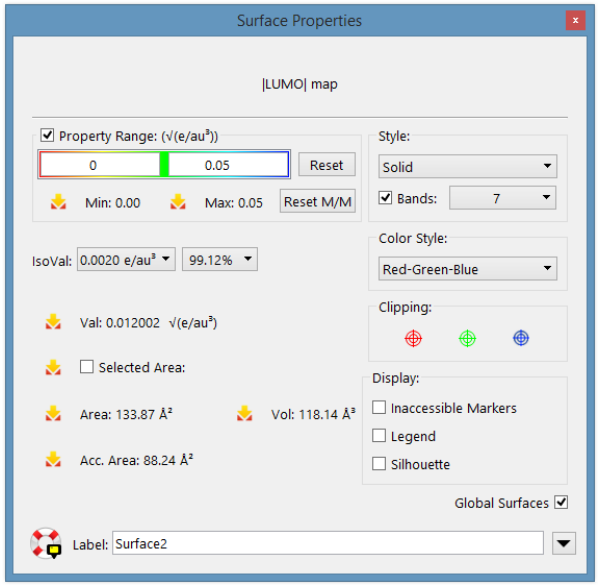
1. Build or sketch cyclohexanone.
2. Select **Calculations...** from the **Setup** menu ( ). Specify **Equilibrium Geometry**, **Ground** and **Gas** from the top menus to the right of **Calculate**, and **Density Functional**, ω**B97X-D** and **6-31G*** from the menus specifying computational model. *Click* on **Submit** and accept the name ***cyclohexanone***. Wait until the calculation completes before proceeding to the next step.
3. Cyclohexanone undergoes nucleophilic attack at the carbonyl carbon, and it is reasonable to expect that the molecule's lowest-

unoccupied molecular orbital (the LUMO) will be localized here. To visualize the LUMO, bring up the **Surfaces** dialog (**Surfaces** from the **Display** menu or *click* on ). *Click* on **Add** and select **LUMO** from the menu. Also request an electron density surface onto which the (absolute) value of the LUMO has been mapped in color (a so-called LUMO map). *Click* on **Add** and select **|LUMO| map** from the menu. The two graphics calculations will run automatically and will require only a few seconds.

4. *Check* the box to the left of **LUMO** in the **Surfaces** dialog. You will see that the resulting graphic is a π* orbital primarily localized on the carbonyl group, consistent with the fact that nucleophiles (electron pairs) add to the carbonyl carbon. See if you can tell which face of the carbonyl carbon the LUMO is more concentrated on.

5. *Uncheck* the box to the left of **LUMO** in the **Surfaces** dialog (to turn off the display of the LUMO). Then *check* the box to the left of ***|LUMO| map*** to display the electron density surface onto which the (absolute) value of the LUMO has been mapped. By convention, colors toward red indicate small (absolute) values of the LUMO (near zero), while colors toward blue indicate large (absolute) values of the LUMO. We are looking for a "blue spot". Note that it is directly over the carbonyl carbon. This corresponds to the maximum value of the LUMO and is where nucleophilic attack will occur.

6. You will see that the blue spot over the *axial* face of the carbonyl carbon is bigger (and more blue) than that over the *equatorial* face. This indicates preferential attack by nucleophiles onto the *axial* face. Quantify the difference by measuring the (absolute) value of the LUMO on these two faces. Select **Properties** from the **Display** menu () and *click* anywhere on the LUMO map surface to bring up the **Surface Properties** dialog.

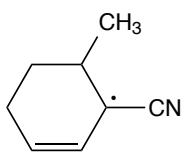


Check the box to the left of **Display Legend** to display the property range on screen. The legend is useful when making qualitative comparisons of property values. Turn the map such that you can clearly see the *axial* face of the carbonyl carbon, and *click* on the area of maximum blue. The (absolute) value of the LUMO at the surface point you have selected is provided in the dialog to the right of **Val**. Note the value, and then turn the map over such that you can see the *equatorial* face of the carbonyl carbon, and *click* on the region of maximum blue on this face. You will find that they support your qualitative conclusions from viewing the image.

7. Close ***cyclohexanone*** and any open dialogs.

5 min

3-Cyano-4-methylcyclohexenyl Radical



3-cyano-4-methylcyclohexene radical will be used to introduce graphical models associated with radicals (molecules with one

unpaired electron).

1. Build or sketch 3-cyano-4-methylcyclohexenyl radical.

2. Select **Calculations...** from the **Setup** menu (). Specify **Equilibrium Geometry** at **Ground** state in **Gas** from the top menu to the right of **Calculate**, **Density Functional** and ω**B97X-D** and **6-31G*** and from the menus specifying computational model.

   This molecule has one unpaired electron. Change **Unpaired Electrons** from **0** to **1**. *Click* on **Submit** at the bottom of the **Calculations** dialog.* Name it ***3-cyano-4-methylcyclohexenyl radical***. (A name will not be provided as the radical is not in the SSPD.**) Wait (a few minutes) for the calculation to complete before proceeding.

3. Select **Surfaces** from the **Display** menu (). *Click* on **Add** and select **spin density** from the menu. *Click* on **Add** and select **spin density map** from the menu. You have requested two different representations of spin distribution. The first presents spin density as a surface of constant value, while the second uses color to map the value of the spin density onto an electron density surface. Finally, request the singly-occupied molecular orbital. *Click* on **Add** one more time and select **aHOMO** (the highest-occupied molecular orbital of α spin that is, the orbital that contains the unpaired electron) from the menu.

4. The three graphics you requested will run without having to resubmit the job and will require only a few seconds to complete. When they are done, *check* the box to the left of ***spin density*** in the **Surfaces** dialog to display the spin density surface. Note that the spin density is delocalized over two of the ring carbons and onto the cyano group.

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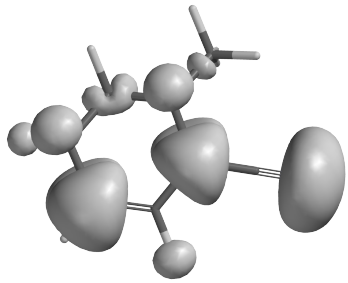
* ***Spartan*** checks that the structure and the number of electrons specified from **Charge** and **Unpaired Electrons** settings are compatible and if they are not will return an error message.

** With very few exceptions, SSPD contains only neutral closed-shell (all electrons paired) molecules.



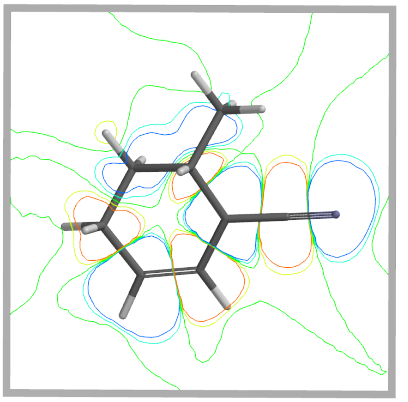
5. Remove the spin density surface (*uncheck* the box to the left of ***spin density*** in the **Surfaces** dialog) and then *check* the box to the left of ***spin density map*** to display a surface on which the spin density is mapped onto the electron density. Note that the areas of maximum spin (colored blue) closely match those where the surface is large in the previous image.

6. Remove the spin density map (*uncheck* the box to the left of ***spin density map***), and then *check* the box to the left of ***aHOMO*** (the molecular orbital which holds the unpaired electron). Aside from the colors (different signs of the orbital), note that this graphic is nearly identical to the previously-displayed image of the spin.

7. *Uncheck* the box to the left of ***aHOMO***. *Click* on **More Surfaces...** at the bottom of the (**Surfaces**) dialog, and select **Slice** from the **Surfaces** menu and ***spin density*** from the **Properties** menu. *Click* on **OK**. A new line ***Slice***, ***spin density*** appears in the window at the top of the dialog.* Select it by *checking* the box at the left. A plane (a slice of spin density) surrounded by a frame appears in the middle of the model on screen. *Click* inside the frame to select. The frame will turn gold. Position the cursor outside the frame, then use the scroll wheel to zoom the plane. You can also translate and rotate the plane independently of the molecule using the usual mouse operations. Alternatively, you can move the molecule and plane together by first *clicking* on the molecule (the frame will now turn white) and then using the mouse. For all operations, be certain to keep the cursor positioned outside of the frame. Size

* You can change the display style from **Contours** to **Solid** or **Transparent** using the **Style** menu at the bottom right of the screen. This will appear only when the slice is selected.

and orient the slice as you wish.

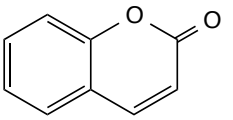


Tap on the graphic to select the graphic and on the frame to select the frame. Use one finger to rotate and two fingers to translate the graphic or frame. Pinch two fingers to zoom the graphic or frame.

8. Close ***3-cyano-4-methylcyclohexenyl radical*** and any open dialogs.

5 min

Coumarin

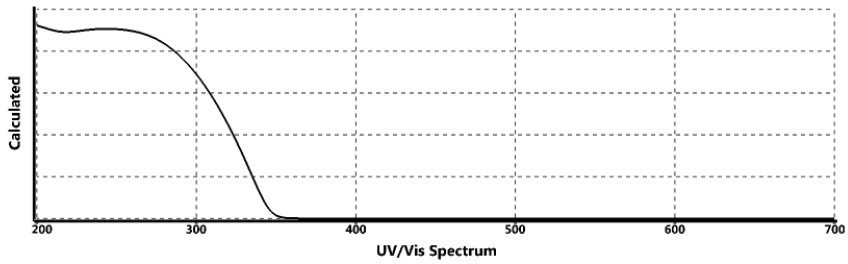


Coumarin illustrates the calculation of a UV/visible spectrum.

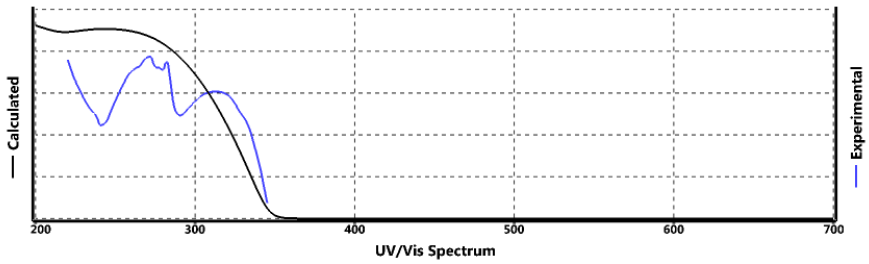
1. Build or sketch coumarin.
2. The name ***coumarin*** appears at the bottom of the screen. *Click* on it, make sure that ωB97X-D/6-31G* is selected from the dialog that appears and *click* on **Replace**.
3. Select **Calculations...** from the **Setup** menu ( ). Select **Energy** from the top menu to the right of **Calculate**. (**Density Functional**, ωB97X-D and **6-31G*** should already be selected

from three menus immediately below.) You already have the equilibrium structure from SSPD and only need to obtain the energy and wave function as the basis of a UV/visible spectrum calculation. *Check* the box to the left of **UV/vis** (to the right of **Compute**). *Click* on **Submit**. Accept the name ***coumarin***.

4. The calculation will take several minutes. While coumarin is relatively small, calculations on several low-lying excited states in addition to the ground state are required to produce a UV/visible spectrum. When completed, select **Spectra** from the **Display** menu ( ). *Click* on ( ) inside the spectra pane, and select ( ). The calculated UV/visible spectrum will appear in the spectra pane.



5. *Click* again on and this time select ( ). The experimental UV/visible spectrum from the freely available NIST database will be superimposed onto the calculated spectrum.



6. Close ***coumarin***.