Instructions for the PPP-MO method for Colour Prediction.

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1.0 General Points

The PPP-MO method considers “relevant atoms” as those those atoms which are an integral part of the conjugated π-electron system, and excludes such atoms as hydrogen, alkyl substituents, etc., that are part of the sigma framework. Halogen atoms may or may not be included as π-centers, and both approaches can produce good results.

1.1 Required Input Data for a Calculation:

(a) A numbering sequence for all relevant atoms.

(b) All relevant bond lengths and bond angles

(c) The number of filled molecular orbitals (this value is equal to the number of π-electrons divided by 2)

(d) The charge on each relevant atomic nucleus, when all π-electrons have been removed (i.e. the Core Charge)

(e) The Valence State Ionization Potential (VSIP) of each relevant atom.

(f) The Electron Affinity (EA) of each relevant atom.

(g) The Bond Resonance Energy (β) for each pair of bonded atoms.

1.2 Planarity of Molecules

The computer needs to be instructed if the molecule is planar or non-planar. In the majority of cases better results can be obtained by assuming planarity and adjusting certain input parameters to compensate for known deviations from planarity. (For example, using $\beta\cos\theta$ as the Bond Resonance Energy, where θ is the angle of deviation from planarity).

1.3 Configuration Interaction.

To improve wavelength and intensity predictions, the program modifies the first set of calculations by a process known as Configuration Interaction (CI), and the computer requires instruction as to the extent of CI required. Experience has shown that good results can be obtained by extending CI over those excited states involving all molecular orbitals between Highest Occupied Molecular Orbital [HOMO] minus two (i.e. HOMO - 2) and the HOMO plus three (i.e. HOMO + 3). Thus the CI is extended over the nine lowest excited states.

1.4 Energy Parameters

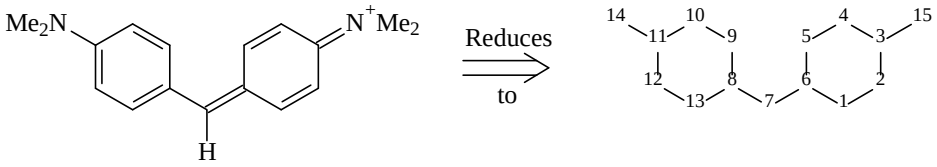
The various energy parameters required (VSIP, EA, β) are measured in electron volts (eV) and are recorded in the attached parameter tables. It should be noted that these values are the result of many calculations with model dye structures, and are to a certain extent empirical. As such, they strictly refer to spectra measured in non-polar solvents (e.g. cyclohexane), therefore solvent effects must be taken into account when comparing predicted and actual λ_{max} values.

2.0 The Data Input File

To generate the data input file the following steps should be adhered to*:

(a) Draw out the molecule and devise a convenient numbering scheme. (Note. It is always a good idea to number the ring systems first and the pendant conjugated groups last).

For example, for the Michlers Hydrol Blue structure:



(b) Write out the following sequence of numbers:

A B C D E
F G
H

Where:

Variable	Description
A	Number of atoms in the π-system
B	Program control variable (1)
C	Program control variable (1)
D	Planarity variable (0 = planar, 1 = non-planar)
E	CI control variable (0 = no CI, 1 = total CI and 2 = limited CI treatment)
F	Number of upper orbitals for limited CI (i.e. when E = 2)
G	Number of lower orbitals for limited CI (i.e. when E = 2)
H	Number of filled orbitals (i.e. the number of π electrons divided by 2, or the HOMO)

Thus for Michlers Hydrol Blue A=15, B=1, C=1, D=0, E=2, F=11 (HOMO + 3), G=6 (HOMO - 2) and H=8 (HOMO = 16/2), thus the sequence should be:

```
15 1 1 0 2
11 6
8
```

* It has been found that writing out the input file on paper prior to entering the data into a computer makes inputting the data file easier.

(c) Write out, in the same order as your chosen numbering scheme, the VSIP values for each atom:

For Michlers Hydrol Blue,

11.16 11.16 11.16 11.16 11.16 11.16 11.16 11.16 11.16 11.16 11.16 11.16 11.16 12.70 12.70

(d) Write out, in the same order as your chosen numbering scheme, the Electron Affinity (EA) values for each atom:

For Michlers Hydrol Blue,

0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.03 6.60 6.60

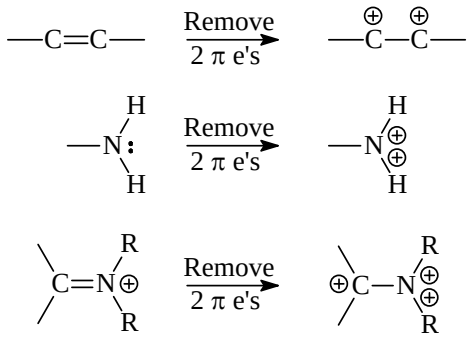
(e) Write out, in the same order as your chosen numbering scheme, the Core Charge (Z) values for each atom:

For Michlers Hydrol Blue,

1 1 1 1 1 1 1 1 1 1 1 1 2 2

The Core Charge values can be obtained by deducting the π-electrons on a particular atom and noting the resultant residual charge. The appropriate Core Charge values are noted in the parameter tables.

For Example:



(e) Write out all of the bond β values, specifying the relevant bonds in the following order:

-1 β A1 A2 -1

Where A1 and A2 are the previously assigned sequence numbers, and β is the corresponding bond resonance energy value for the bond between A1 and A2. The -1 at the start and end of the line indicates the start and end of blocks of data for the program. This allows bonds with the same energy to be grouped together for convenience.

By way of example, Michlers Hydrol Blue could be written as:

```
-1 -2.4 1 2 -1
-1 -2.4 2 3 -1
-1 -2.4 3 4 -1
-1 -2.4 4 5 -1
-1 -2.4 5 6 -1
-1 -2.4 6 7 -1
-1 -2.4 6 1 -1
-1 -2.4 7 8 -1
-1 -2.4 8 9 -1
-1 -2.4 9 10 -1
-1 -2.4 10 11 -1
-1 -2.4 11 12 -1
-1 -2.4 12 13 -1
-1 -2.4 13 8 -1
-1 -2.75 14 11 -1
-1 -2.75 15 3 -1 0
```

NOTE: This list must be terminated with a zero to signify the end of the bond resonance energy information.

This could be simplified to read;

```
-1 -2.4 1 2 2 3 3 4 4 5 5 6 6 7 6 1 7 8 8 9 9 10 10 11 11 12 12 13 13 8 14 11 15 3 -1
-1 -2.75 14 11 -1
-1 -2.75 15 3 -1 0
```

(f) The final set of input data concerns the molecular geometry. For most inter-atomic bonds the bond angles are idealized (i.e. $\mathbf{120^0}$ for **sp2** hybridized atoms, $\mathbf{180^0}$ for **sp** hybridized atoms, $\mathbf{108^0}$ for **five membered rings**, etc.) The bond lengths cited in the parameter tables are adequate for calculations. The molecular geometry is written as follows:

A1 A2 X Y

Where A1 and A2 are the previously assigned sequence numbers and X is the bond length between atoms A1 and A2. Y is the bond angle, where the **1,2** bond is taken as the reference axis and the next bond (**2,3**) is specified by extending the **1,2** bond forward and measuring the angle <u>CLOCKWISE</u> to the **2,3** bond. The **3,4** bond is specified in the same way, relative to the **2,3** bond

For Michlers Hydrol Blue:

```
 1   2   1.40    0.0
 2   3   1.40  300.0
 3   4   1.40  300.0
 4   5   1.40  300.0
 5   6   1.40  300.0
 6   7   1.40   60.0
 6   1   1.40  300.0
 7   8   1.40   60.0
 8   9   1.40   60.0
 9  10   1.40   60.0
10  11   1.40  300.0
11  12   1.40  300.0
12  13   1.40  300.0
13   8   1.40  300.0
11  14   1.38   60.0
 3  15   1.35   60.0 0
```

NOTE, The list must be terminated by a zero. Additionally it is unnecessary for every pair of atoms to have a specified bond length. The "bond lengths" are for connectivity and are used to place the nuclei, thus the rings can be left "open" but these openings require β values.

3.0 Typing and Editing the Data File.

The data can be entered into a computer and saved as a text file using any available text editor; such as notepad in Microsoft Windows. The file should be saved with the file extension '.dta'

4.0 Running a PPP_MO Calculation.

If using Microsoft Windows, start a 'command' or 'cmd' shell and change drives and directories to the directory where the PPP executable files are stored. It may be convenient to place the input data file in the same directory. At the DOS-prompt type the name of the program, **PPP**. The program will invite you to enter the input file name. This should be provided without the file extension. For example, type 'myfile' rather than 'myfile.dta' or the program will report an error.

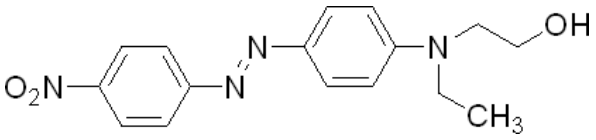
5.0 Results from a calculation.

After running a calculation, the results will be saved in the same directory with a file extension of '.res' and, in addition, a graphical display of the geometry will be presented on screen. The results are saved as text, which can be printed after pruning any unwanted data.

The results file contains an amount of information about the molecular orbitals (such as *Eigenvectors* and *Eigenvalues* etc.) and towards the end of the file there is a section entitled "Transitions After CI". In the table is listed the first nine transitions, with the first transition usually corresponding to the λ_{max}. The Final two columns give the oscilator strength (which is an indication of absorption intensity) and the wavelength of absorption (in nm).

6.0 An Example calculation.

6.1 The input file for CI Disperse Red 1:




```
18 1 1 0 2 13 8 10
11.16 11.16 11.16 11.16 11.16 11.16 14.7 14.7 11.16 11.16 11.16 11.16 11.16 11.16 17.5
24.8 21 21
0.03 0.03 0.03 0.03 0.03 0.03 2.3 2.3 0.03 0.03 0.03 0.03 0.03 0.03 7.5 12.5 2.5 2.5
1 1 1 1 1 1 1 1 1 1 1 1 1 2  2 1 1
-1 -2.4 1 2 2 3 3 4 4 5 5 6 6 1 -1
-1 -2.48 3 7 8 9 -1
-1 -2.9 7 8 -1
-1 -2.4 9 10 10 11 11 12 12 13 13 14 14 9 -1
-1 -2.75 12 15 -1
-1 -2.0 6 16 -1
-1 -3.05 16 17 16 18 -1 0
 1  2 1.40   0
 2  3 1.40  60
 3  4 1.40  60
 4  5 1.40  60
 5  6 1.40  60
 3  7 1.40 300
 7  8 1.23 300
 8  9 1.40  60
 9 10 1.40 300
10 11 1.40  60
11 12 1.40  60
12 13 1.40  60
13 14 1.40  60
12 15 1.38 300
 6 16 1.49 300
16 17 1.21 300
16 18 1.21  60 0
```

6.2 The results file generated for CI Disperse Red 1:

```
PPP PROGRAM
PASCAL VERSION BY DR.G.CASTELLANI


NUMBER OF CENTRES  =  18
NUMBER OF DOUBLY OCCUPIED SHELLS  =  10
UPPER LIMIT OF CI  13
LOWER LIMIT OF CI  8
MAX NUMBER OF SCF ITERATIONS  15


CONVERGENCE CRITERION =   0.0001000

RESONANCE INTEGRAL MATRIX
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  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
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  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000 -2.400000
  0.000000 -2.400000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
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  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  0.000000 -2.400000  0.000000 -2.400000  0.000000  0.000000  0.000000  0.000000
  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000 -2.400000  0.000000
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  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  0.000000 -2.750000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  0.000000  0.000000  0.000000  0.000000  0.000000 -2.000000  0.000000  0.000000  0.000000  0.000000
```

```
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  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
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  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  0.000000  0.000000  0.000000  0.000000  0.000000 -3.050000  0.000000  0.000000



INTER-ATOMIC DISTANCE MATRIX
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  7.689129  8.316291  7.735421  6.361979  9.696106  2.503227  3.594604  2.799848
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  7.127885  7.280434  6.305613  4.931407  8.602004  3.789210  4.198229  4.765199
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  8.376678  8.621293  7.689130  6.305613  9.958938  2.503219  2.799842  3.594594
  1.400010  2.424878  2.800003  2.424872  1.400000  0.000000  4.200003  4.931419  6.305623  7.280441
  8.621299  9.077707  8.316296  6.916560 10.449427  1.490000  2.342457  2.342457
  3.704053  2.424872  1.400000  2.424869  3.704051  4.200003  0.000000  1.230000  2.279228  3.543848
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  8.316291  6.916555  6.305613  7.280434  8.621293  9.077707  4.931408  4.199993  2.799993  2.424872
  1.400000  0.000000  1.400000  2.424872  1.380000 10.558861 11.309161 11.110009
  7.735421  6.361978  5.516954  6.305613  7.689130  8.316296  4.117622  3.704048  2.424866  2.800003
  2.424872  1.400000  0.000000  1.400000  2.407570  9.806098 10.448882 10.478373
  6.361979  5.003280  4.117622  4.931407  6.305613  6.916560  2.718978  2.424869  1.400000  2.424878
  2.800003  2.424872  1.400000  0.000000  3.685159  8.406282  9.054897  9.088912
  9.696106  8.296294  7.669323  8.602004  9.958938 10.449427  6.285901  5.579993  4.179993  3.685161
  2.407572  1.380000  2.407570  3.685159  0.000000 11.932632 12.667482 12.490007
  2.503227  3.789215  4.290003  3.789210  2.503219  1.490000  5.690003  6.394349  7.778283  8.708135
 10.066061 10.558861  9.806098  8.406282 11.932632  0.000000  1.210000  1.210000
  3.594604  4.765204  5.005911  4.198229  2.799842  2.342457  6.381626  7.225877  8.574455  9.604125
 10.928274 11.309161 10.448882  9.054897 12.667482  1.210000  0.000000  2.095780
  2.799848  4.198234  5.005911  4.765199  3.594594  2.342457  6.381627  6.910024  8.310020  9.093534
 10.482382 11.110009 10.478373  9.088912 12.490007  1.210000  2.095780  0.000000

ATOMIC COORDINATES



X-COORDS
  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000



Y-COORDS
  0.000000  0.000000  1.212435  2.424872  2.424878  1.212446  1.212435  0.147219  0.147219 -1.065221
 -1.065221  0.147214  1.359651  1.359657  0.147214  1.212452  2.260344  0.164565



Z-COORDS
  0.000000  1.400000  2.100002  1.400005  0.000005 -0.700002  3.500002  4.114994  5.514994  6.214986
  7.614986  8.314988  7.614991  6.214991  9.694988 -2.190002 -2.794999 -2.795007



ATOMIC IONISATION POTENTIALS
 11.160000 11.160000 11.160000 11.160000 11.160000 11.160000 14.700000 14.700000 11.160000 11.160000
 11.160000 11.160000 11.160000 11.160000 17.500000 24.800000 21.000000 21.000000



ATOMIC ELECTRON AFFINITIES
  0.030000  0.030000  0.030000  0.030000  0.030000  0.030000  2.300000  2.300000  0.030000  0.030000
  0.030000  0.030000  0.030000  0.030000  7.500000 12.500000  2.500000  2.500000



ATOMIC VIRTUAL CHARGES
  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
  1.000000  1.000000  1.000000  1.000000  2.000000  2.000000  1.000000  1.000000

HUCKEL APPROXIMATION



EIGENVALUES
 -5.596207 -5.322593 -4.722517 -3.940727 -2.899303 -2.400000 -2.400000 -1.610379 -0.000000 -0.000000
  1.610379  2.400000  2.400000  2.899303  3.940727  4.722517  5.322593  5.596207



EIGENVECTOR
  0.230398  0.248885  0.349941  0.248885  0.230398  0.288346  0.307940  0.294981  0.305543  0.203819
  0.169712  0.191907  0.169712  0.203819  0.094304  0.253867  0.138360  0.138360
 -0.208157 -0.142763 -0.108455 -0.142763 -0.208157 -0.318878  0.043549  0.172676  0.319675  0.265263
  0.268611  0.330449  0.268611  0.265263  0.170732 -0.349050 -0.200016 -0.200016
 -0.013983 -0.201021 -0.381570 -0.201021 -0.013983  0.173507 -0.337527 -0.223340 -0.030604  0.085283
  0.198416  0.305143  0.198416  0.085283  0.177690  0.443254  0.286272  0.286272
 -0.194455 -0.216332 -0.160756 -0.216332 -0.194455 -0.102957  0.163266  0.359331  0.380062  0.126371
 -0.172565 -0.409717 -0.172565  0.126371 -0.285918  0.263829  0.204195  0.204195
  0.304441  0.005742 -0.297504  0.005742  0.304441  0.362035 -0.358918 -0.104414  0.297634  0.233725
 -0.015285 -0.252189 -0.015285  0.233725 -0.239202 -0.205833 -0.216531 -0.216531
```

```
 -0.000104 -0.000104 -0.000000  0.000104  0.000104  0.000000 -0.000000  0.000000 -0.000000 -0.500000
 -0.500000 -0.000000  0.500000  0.500000  0.000000  0.000000 -0.000000 -0.000000
 -0.500000 -0.500000  0.000000  0.500000  0.500000 -0.000000  0.000000  0.000000 -0.000000  0.000104
  0.000104  0.000000 -0.000104 -0.000104  0.000000  0.000000  0.000000  0.000000
  0.151311 -0.259330 -0.325319 -0.259330  0.151311  0.360858  0.290684  0.439622 -0.054446 -0.245404
 -0.110218  0.171449 -0.110218 -0.245404  0.292779 -0.072587 -0.137477 -0.137477
 -0.000000  0.162362 -0.000000  0.162362  0.000000 -0.162362 -0.314248  0.000000  0.367468 -0.000000
 -0.367468  0.000000 -0.367468 -0.000000  0.641398  0.000000  0.051354  0.055113
 -0.000000 -0.000432 -0.000000 -0.000432 -0.000000  0.000432  0.000835 -0.000000 -0.000977 -0.000000
  0.000977 -0.000000  0.000977 -0.000000 -0.001705 -0.000000 -0.707246  0.706963
  0.151311  0.259330 -0.325319  0.259330  0.151311 -0.360858 -0.290684  0.439622  0.054446 -0.245404
  0.110218  0.171449  0.110218 -0.245404 -0.292779 -0.072587  0.137477  0.137477
 -0.478438  0.478438  0.000000 -0.478438  0.478438  0.000000 -0.000000  0.000000  0.000000 -0.145249
  0.145249  0.000000 -0.145249  0.145249 -0.000000  0.000000 -0.000000 -0.000000
  0.145249 -0.145249  0.000000  0.145249 -0.145249 -0.000000 -0.000000  0.000000  0.000000 -0.478438
  0.478438  0.000000 -0.478438  0.478438 -0.000000 -0.000000  0.000000  0.000000
  0.304441 -0.005742 -0.297504 -0.005742  0.304441 -0.362035  0.358918 -0.104414 -0.297634  0.233725
  0.015285 -0.252189  0.015285  0.233725  0.239202 -0.205833  0.216531  0.216531
 -0.194455  0.216332 -0.160756  0.216332 -0.194455  0.102957 -0.163266  0.359331 -0.380062  0.126371
  0.172565 -0.409717  0.172565  0.126371  0.285918  0.263829 -0.204195 -0.204195
  0.013983 -0.201021  0.381570 -0.201021  0.013983  0.173507 -0.337527  0.223340 -0.030604 -0.085283
  0.198416 -0.305143  0.198416 -0.085283  0.177690 -0.443254  0.286272  0.286272
  0.208157 -0.142763  0.108455 -0.142763  0.208157 -0.318878  0.043549 -0.172676  0.319675 -0.265263
  0.268611 -0.330449  0.268611 -0.265263  0.170732  0.349050 -0.200016 -0.200016
  0.230398 -0.248885  0.349941 -0.248885  0.230398 -0.288346 -0.307940  0.294981 -0.305543  0.203819
 -0.169712  0.191907 -0.169712  0.203819 -0.094304  0.253867 -0.138360 -0.138360



BOND-ORDER MATRIX
  1.000000  0.688892 -0.000000 -0.311108  0.000000  0.630451 -0.060860  0.000000  0.025501 -0.000000
 -0.014722  0.000000 -0.014722 -0.000000  0.021559 -0.000000 -0.113839 -0.113839
  0.688892  1.026361  0.593431  0.026361 -0.311108 -0.026361 -0.051022 -0.197361  0.059663  0.066718
 -0.059663 -0.036057 -0.059663  0.066718  0.104139 -0.031042  0.008643  0.008643
 -0.000000  0.593431  1.000000  0.593431  0.000000 -0.278534  0.435593  0.000000 -0.096006 -0.000000
  0.045383 -0.000000  0.045383 -0.000000 -0.062874  0.000000  0.074390  0.074390
 -0.311108  0.026361  0.593431  1.026361  0.688892 -0.026361 -0.051022 -0.197361  0.059663  0.066718
 -0.059663 -0.036057 -0.059663  0.066718  0.104139 -0.031042  0.008643  0.008643
  0.000000 -0.311108  0.000000  0.688892  1.000000  0.630451 -0.060860 -0.000000  0.025501  0.000000
 -0.014722  0.000000 -0.014722 -0.000000  0.021559  0.000000 -0.113839 -0.113839
  0.630451 -0.026361 -0.278534 -0.026361  0.630451  1.026361  0.051022  0.150173 -0.059663 -0.055939
  0.059663  0.031317  0.059663 -0.055939 -0.104139  0.267076 -0.008643 -0.008643
 -0.060860 -0.051022  0.435593 -0.051022 -0.060860  0.051022  1.098753  0.795347 -0.115477 -0.178121
  0.115477  0.087905  0.115477 -0.178121 -0.201560  0.018432 -0.016729 -0.016729
  0.000000 -0.197361  0.000000 -0.197361 -0.000000  0.150173  0.795347  1.000000  0.467440 -0.000000
 -0.113471 -0.000000 -0.113471  0.000000  0.137127 -0.000000 -0.044231 -0.044231
  0.025501  0.059663 -0.096006  0.059663  0.025501 -0.059663 -0.115477  0.467440  1.135034  0.550836
 -0.135034 -0.170358 -0.135034  0.550836  0.235695 -0.009239  0.019562  0.019562
 -0.000000  0.066718 -0.000000  0.066718  0.000000 -0.055939 -0.178121 -0.000000  0.550836  1.000000
  0.748866  0.000000 -0.251134  0.000000 -0.168450 -0.000000  0.016982  0.016982
 -0.014722 -0.059663  0.045383 -0.059663 -0.014722  0.059663  0.115477 -0.113471 -0.135034  0.748866
  1.135034  0.475075  0.135034 -0.251134 -0.235695  0.005786 -0.019562 -0.019562
  0.000000 -0.036057 -0.000000 -0.036057  0.000000  0.031317  0.087905 -0.000000 -0.170358  0.000000
  0.475075  1.000000  0.475075 -0.000000  0.712806 -0.000000 -0.009629 -0.009629
 -0.014722 -0.059663  0.045383 -0.059663 -0.014722  0.059663  0.115477 -0.113471 -0.135034 -0.251134
  0.135034  0.475075  1.135034  0.748866 -0.235695  0.005786 -0.019562 -0.019562
 -0.000000  0.066718 -0.000000  0.066718 -0.000000 -0.055939 -0.178121  0.000000  0.550836  0.000000
 -0.251134 -0.000000  0.748866  1.000000 -0.168450  0.000000  0.016982  0.016982
  0.021559  0.104139 -0.062874  0.104139  0.021559 -0.104139 -0.201560  0.137127  0.235695 -0.168450
 -0.235695  0.712806 -0.235695 -0.168450  1.411395 -0.008682  0.034144  0.034144
 -0.000000 -0.031042  0.000000 -0.031042  0.000000  0.267076  0.018432 -0.000000 -0.009239 -0.000000
  0.005786 -0.000000  0.005786  0.000000 -0.008682  1.000000  0.680506  0.680506
 -0.113839  0.008643  0.074390  0.008643 -0.113839 -0.008643 -0.016729 -0.044231  0.019562  0.016982
 -0.019562 -0.009629 -0.019562  0.016982  0.034144  0.680506  1.502834 -0.497166
 -0.113839  0.008643  0.074390  0.008643 -0.113839 -0.008643 -0.016729 -0.044231  0.019562  0.016982
 -0.019562 -0.009629 -0.019562  0.016982  0.034144  0.680506 -0.497166  1.502834

BOND MATRIX CONVERGED TO REQUIRED EXTENT,NUMBER OF ITERATIONS  8



EIGENVALUES
-18.288590-14.950464-13.871443-13.125362-12.083648-11.515615-10.382217-10.310264-10.079001 -8.031576
 -3.241340 -2.327818 -0.804084 -0.660811 -0.154175  0.610665  2.409586  2.736366



EIGENVECTOR
  0.057461  0.017973  0.008346  0.018027  0.057445  0.189157  0.003505  0.001998  0.000442  0.000068
  0.000067  0.000070  0.000064  0.000041 -0.000026  0.753135  0.441406  0.441397
  0.090110  0.157612  0.323688  0.162826  0.092442  0.066353  0.558163  0.562861  0.316001  0.164903
  0.109224  0.116231  0.107032  0.158694  0.062256 -0.018839 -0.023205 -0.023418
 -0.129851 -0.160342 -0.223427 -0.162143 -0.130894 -0.118001 -0.192317 -0.049980  0.174864  0.239357
  0.351219  0.540154  0.348951  0.237877  0.355615  0.018936  0.035408  0.035515
  0.366366  0.308887  0.230265  0.307087  0.365666  0.390633 -0.160956 -0.325125 -0.184636 -0.032549
  0.116809  0.267059  0.117451 -0.030035  0.209987 -0.039366 -0.111152 -0.110957
 -0.010236 -0.006282 -0.000004  0.006312  0.010240  0.000022 -0.000025  0.000017  0.000239  0.000204
 -0.000006 -0.000176 -0.000034  0.000114 -0.000163  0.000030 -0.707029  0.706981
  0.200716 -0.041935 -0.257988 -0.043788  0.199167  0.324164 -0.311844  0.028230  0.435490  0.321349
  0.043455 -0.285233  0.040850  0.319942 -0.387719 -0.000555 -0.089682 -0.090121
 -0.500820 -0.499397 -0.012891  0.488122  0.509603  0.009458 -0.002709  0.008394 -0.002693 -0.021571
 -0.019136  0.002804  0.013403  0.011016  0.007319  0.000472  0.009034 -0.014385
  0.019293  0.012634 -0.006246 -0.019622 -0.014332  0.006065 -0.000074  0.010560  0.004447 -0.494712
 -0.510215  0.002870  0.504456  0.488954  0.006650  0.000394 -0.002193 -0.001336
  0.172504 -0.273569 -0.432957 -0.294616  0.148100  0.435769  0.133679  0.326150 -0.077265 -0.195727
 -0.136893  0.092220 -0.153524 -0.212978  0.332338  0.033747 -0.128895 -0.128164
 -0.008823  0.149702  0.076057  0.148810 -0.009134 -0.145512 -0.291748  0.017726  0.401007  0.078229
 -0.355103 -0.162890 -0.361685  0.075613  0.616778 -0.030220  0.052357  0.052274
  0.213088  0.150056 -0.249967  0.151915  0.203551 -0.198615 -0.262536  0.364796 -0.006669 -0.179966
  0.049242  0.156750  0.039983 -0.176527 -0.158704 -0.417997  0.368352  0.368583
  0.106507 -0.186011 -0.004205 -0.193091  0.119177  0.135668  0.408017 -0.382320 -0.079799  0.218601
 -0.026111 -0.206528 -0.009143  0.208516  0.178540 -0.427825  0.328348  0.328214
  0.492671 -0.507049  0.001376  0.504035 -0.495259  0.002949  0.002218 -0.003726 -0.006470 -0.006844
  0.013990 -0.007966 -0.010187  0.017657  0.005410 -0.002116 -0.001298  0.004004
 -0.016197  0.005479  0.011220 -0.019780  0.007571  0.011976  0.003344 -0.003041  0.001147 -0.506670
```

```
  0.493879 -0.004426 -0.489899  0.508155  0.002473 -0.007146  0.004323  0.004248
 -0.213008 -0.170164  0.417852 -0.163788 -0.217059  0.440857 -0.154787 -0.060839  0.334077 -0.155994
 -0.144678  0.357185 -0.132910 -0.171765 -0.218754 -0.215502  0.120825  0.120827
  0.219617 -0.002090 -0.230265  0.007672  0.212441 -0.329818  0.325247 -0.354135  0.340570 -0.059839
 -0.238420  0.436811 -0.249245 -0.048392 -0.239159  0.127577 -0.064875 -0.064892
 -0.318535  0.356366 -0.413597  0.354548 -0.317613  0.312398  0.139501  0.005608 -0.204390  0.197841
 -0.193137  0.205207 -0.196170  0.202229 -0.089570 -0.082465  0.033758  0.033745
 -0.145835  0.186831 -0.266273  0.188750 -0.146700  0.135237  0.201704 -0.242695  0.450770 -0.342878
  0.285240 -0.281405  0.286730 -0.344638  0.118779 -0.033797  0.013316  0.013288



BOND-ORDER MATRIX
  0.967853  0.685415  0.044431 -0.313120 -0.054802  0.624372 -0.038203 -0.008039  0.020251  0.006321
 -0.009969 -0.006146 -0.009413  0.006272  0.013789  0.060890 -0.120148 -0.125453
  0.685415  0.989783  0.610250  0.014996 -0.310870 -0.011595  0.006679 -0.190953  0.058100  0.067720
 -0.034880 -0.049626 -0.033961  0.068872  0.063518 -0.037186  0.022055  0.027334
  0.044431  0.610250  0.935569  0.607590  0.042337 -0.288313  0.374053 -0.057616 -0.055375  0.007118
  0.016528 -0.000702  0.017648  0.007056 -0.016074 -0.059766  0.090985  0.091051
 -0.313120  0.014996  0.607590  0.993959  0.689968 -0.012859  0.004474 -0.181701  0.056754  0.064920
 -0.034070 -0.048506 -0.033640  0.067639  0.062498 -0.037685  0.027975  0.022527
 -0.054802 -0.310870  0.042337  0.689968  0.968761  0.620898 -0.045820 -0.004617  0.018058  0.004831
 -0.007947 -0.005154 -0.009055  0.005299  0.011977  0.060095 -0.124203 -0.119021
  0.624372 -0.011595 -0.288313 -0.012859  0.620898  1.045956 -0.005782  0.130920 -0.045113 -0.051427
  0.028549  0.039559  0.027948 -0.052586 -0.052621  0.285058 -0.116889 -0.116787
 -0.038203  0.006679  0.374053  0.004474 -0.045820 -0.005782  1.149382  0.811436 -0.181298 -0.195707
  0.092917  0.133604  0.091826 -0.205410 -0.164141  0.016637 -0.009740 -0.009506
 -0.008039 -0.190953 -0.057616 -0.181701 -0.004617  0.130920  0.811436  1.065373  0.446764  0.065308
 -0.098634 -0.058421 -0.090547  0.066728  0.115015  0.026434 -0.042825 -0.043081
  0.020251  0.058100 -0.055375  0.056754  0.018058 -0.045113 -0.181298  0.446764  1.041960  0.568540
 -0.081504 -0.229565 -0.080047  0.571086  0.191805 -0.020015  0.022544  0.022623
  0.006321  0.067720  0.007118  0.064920  0.004831 -0.051427 -0.195707  0.065308  0.568540  0.956886
  0.728153  0.031663 -0.275234 -0.015261 -0.112577 -0.013188  0.019095  0.019220
 -0.009969 -0.034880  0.016528 -0.034070 -0.007947  0.028549  0.092917 -0.098634 -0.081504  0.728153
  1.112682  0.529817  0.083114 -0.272206 -0.257338  0.011845 -0.013893 -0.013994
 -0.006146 -0.049626 -0.000702 -0.048506 -0.005154  0.039559  0.133604 -0.058421 -0.229565  0.031663
  0.529817  0.986016  0.533769  0.034266  0.592425  0.011547 -0.015833 -0.015874
 -0.009413 -0.033961  0.017648 -0.033640 -0.009055  0.027948  0.091826 -0.090547 -0.080047 -0.275234
  0.083114  0.533769  1.115456  0.723375 -0.262136  0.011896 -0.013856 -0.013839
  0.006272  0.068872  0.007056  0.067639  0.005299 -0.052586 -0.205410  0.066728  0.571086 -0.015261
 -0.272206  0.034266  0.723375  0.950618 -0.113388 -0.013448  0.019522  0.019534
  0.013789  0.063518 -0.016074  0.062498  0.011977 -0.052621 -0.164141  0.115015  0.191805 -0.112577
 -0.257338  0.592425 -0.262136 -0.113388  1.631440 -0.019855  0.024379  0.024440
  0.060890 -0.037186 -0.059766 -0.037685  0.060095  0.285058  0.016637  0.026434 -0.020015 -0.013188
  0.011845  0.011547  0.011896 -0.013448 -0.019855  1.143058  0.664044  0.664145
 -0.120148  0.022055  0.090985  0.027975 -0.124203 -0.116889 -0.009740 -0.042825  0.022544  0.019095
 -0.013893 -0.015833 -0.013856  0.019522  0.024379  0.664044  1.472720 -0.527349
 -0.125453  0.027334  0.091051  0.022527 -0.119021 -0.116787 -0.009506 -0.043081  0.022623  0.019220
 -0.013994 -0.015874 -0.013839  0.019534  0.024440  0.664145 -0.527349  1.472526



SINGLE ELECTRON EXCITATIONS

TRANSITIONS BEFORE CI

TRANS.  SINGLET  TRIPLET  TRANS. DIPOLE  ALPHA  BETA  OSC. STRENGTH  ABSORPTION


 8,11    4.9736   4.7629      0.0602    268.36  0.00      0.0262      249.3158
 8,12    5.6674   5.3567      0.1131     84.97  0.00      0.0561      218.7946
 8,13    7.6323   7.6268      0.0035    177.28  0.00      0.0023      162.4670
 9,11    4.3860   3.4144      1.3191    348.67  0.00      0.5063      282.7192
 9,12    5.1474   4.3887      0.0595     88.18  0.00      0.0268      240.8970
 9,13    6.3023   5.3541      0.5818    267.63  0.00      0.3209      196.7548
10,11    2.9732   2.4263      4.1523    172.20  0.00      1.0805      417.0530
10,12    3.7983   3.0443      1.4558    348.49  0.00      0.4839      326.4576
10,13    5.2900   5.1178      0.0845     84.36  0.00      0.0391      234.4060

NUMBER OF STATES USED IN CI 9

TRANSITIONS AFTER CI

TRANS.  SINGLET  TRIPLET  TRANS. DIPOLE  ALPHA  BETA  OSC. STRENGTH  ABSORPTION


  1      2.7504   1.7212      6.3014    171.60  0.00      1.5168      450.8404
  2      3.8487   3.1549      0.1715    336.84  0.00      0.0578      322.1852
  3      4.4468   3.6164      0.3074      6.03  0.00      0.1196      278.8521
  4      4.5072   4.0140      0.2606    313.06  0.00      0.1028      275.1127
  5      5.1151   4.3993      0.2830     92.58  0.00      0.1267      242.4200
  6      5.2433   4.7804      0.0908     75.04  0.00      0.0417      236.4915
  7      6.1477   6.0720      0.0213     86.62  0.00      0.0115      201.7020
  8      6.4785   6.1061      0.3900    268.85  0.00      0.2211      191.4022
  9      7.6328   7.6275      0.0039    181.87  0.00      0.0026      162.4568



SINGLET CONFIGURATION VECTORS
  0.001486 -0.004633 -0.001258 -0.212717 -0.036936  0.001969  0.920589 -0.325325 -0.006151
 -0.018218  0.009761  0.000060 -0.103950 -0.239553 -0.003482  0.291606  0.919918  0.009276
 -0.446393  0.293653  0.003522  0.817195 -0.112212 -0.008660  0.184031 -0.007302  0.009710
  0.711713 -0.450523 -0.006839  0.517857 -0.026133 -0.042534  0.126197  0.029874  0.054421
 -0.036412  0.020003 -0.005120 -0.056067 -0.148236 -0.354167 -0.028606 -0.047409  0.919038
 -0.047832  0.019727  0.003774  0.067835  0.951462 -0.033571  0.129859  0.211398  0.157311
  0.538732  0.842145  0.010481 -0.007801  0.008209  0.014666  0.002684  0.002095  0.009765
  0.004216 -0.022664 -0.004248  0.012530 -0.025193  0.933445  0.000377 -0.005004  0.356810
  0.000808 -0.013019  0.999885 -0.000006 -0.004359  0.001867  0.000693 -0.001319  0.005856
```

```
TRIPLET CONFIGURATION VECTORS
 -0.002184  0.000476 -0.001010 -0.201399  0.064843 -0.001962  0.812537 -0.543108 -0.006471
 -0.001844 -0.006333 -0.001099 -0.762333 -0.018853 -0.003681  0.219323  0.608464  0.010165
 -0.018748  0.012039  0.002562  0.505149 -0.570108  0.005912  0.468989  0.446396 -0.006554
  0.800681 -0.597986 -0.008920  0.015971 -0.003854  0.018389  0.014246  0.011344 -0.017435
  0.020110 -0.014437 -0.007268  0.017495  0.008490 -0.654855  0.009527  0.002070  0.755001
 -0.006476  0.009441  0.001468  0.350018  0.818699  0.017357  0.267268  0.367850 -0.006276
  0.103999  0.143145  0.001744 -0.002408 -0.007412  0.743398  0.001585 -0.008286  0.644917
  0.589311  0.788190  0.010467 -0.005082 -0.002705 -0.133461  0.001595  0.004116 -0.116166
  0.000992 -0.013991  0.999872 -0.002522  0.000372 -0.004542 -0.000355 -0.001476  0.005454


ELECTRON DENSITY CHANGES


      ROWS USED =    10,   11


  0.045329  0.000106  0.056699  0.000934  0.041350  0.018274 -0.016192  0.132762
 -0.160762  0.026268 -0.123674 -0.001963 -0.129217  0.025444 -0.355229  0.173808
  0.132942  0.133121


TOTAL ENERGY =   -822.01734


PI-CONTRIBUTION TO DIPOLE MOMENT


X-MOMENT=     0.00     Y-MOMENT =    -0.72     Z-MOMENT =    11.81


TOTAL MOMENT =   139.91     ALPHA =   356.49     BETA =     0.00
```

7.0 Generalised PPP Parameters.

Group or Atom Type	Atoms X-Y	Core Charge Y	β_{X-Y} (eV)	$VSIP_Y$ (eV)	Electron Affinity A_Y (eV)	Bond Length (A)
Carbon - Carbon						
Aromatic	C=C	1	-2.4	11.16	0.03	1.40
Olefinic	C=C	1	-2.6	11.16	0.03	1.35
Olefinic	C-C=	1	-2.3	11.16	0.03	1.45
Halogenated	C=CCl	1	-2.6	12.00	0.61	1.35
Chloro	C-Cl	2	-1.36	23.3	12.5	1.34
Carbonyl						
General	C=O	1	-2.46	18.0	2.5	1.22
Free	C=O	1	-2.46	17.7	2.47	1.22
H-Bonded	C=O	1	-2.46	15.0	0.71	1.22
Imine						
Acyclic	C=N	1	-2.8	15.0	0.97	1.26
Cyclic	C=N	1	-2.4	16.0	2.5	1.40
Sulphur Systems	C=N	1	-2.00	12.0	0.50	1.33
Cyano	C≡N	1	-2.67	14.2	4.5	1.15
	C-CN	1	-2.3	11.2	0.1	1.40
Azo	N=N	1	-2.9	14.7	2.3	1.23
	C-N=	1	-2.48	14.7	2.3	1.40
Azonium	$N=N^+H$	2	-2.9	22.0	12.5	1.40
	$C-N^+H-$	2	-2.75	22.0	12.5	1.40
Azo (H-bonded)	N=N	1	-2.9	17.0	2.6	1.23
Diazide	$CN^+=N^-$	1	-3.0	15.0	2.5	1.15
	$C=N_2$	2	-2.0	24.0	12.0	1.40
Nitro	N-O	1	-3.05	21.0	2.5	1.21
	C-N<	2	-2.0	24.8	12.5	1.49
Sulphonyl	$C-SO_2-$	1	-2.8	18.0	3.4	1.80

Group or Atom Type	Atoms X-Y	Core Charge Y	β_{X-Y} (eV)	$VSIP_Y$ (eV)	Electron Affinity A_Y (eV)	Bond Length (A)
Heterocyclics						
π-equivalent	C=N	1	-2.6	16.0	2.5	1.33
π-equivalent	C-N=	1	-2.4	16.0	2.5	1.38
π-equivalent	C-N<	2	-2.4	18.0	2.9	1.35
Thiazole C=N	C=N	1	-2.4	12.0	0.5	1.33
π-excessive	·· C-N	2	-2.4	21.0	10.0	1.35
π-excessive	·· C-O	2	-2.4	40.0	14.5	1.35
π-excessive	·· C-S	2	-1.0	20.0	10.0	1.71
Improved	·· C-S	2	-1.0	24.0	8.2	1.71
Pyrazolone	C-NH	2	-2.4	21.0	12.0	1.40
Azo dyes	C=N	1	-2.6	14.0	2.0	1.40
(Hydrazone Form)	C=O	1	-2.46	15.0	0.71	1.22
	N-N=	1	-2.3	14.0	2.0	1.40
	N=C	1	-2.6	10.0	0.75	1.40
Hydrazone	C=N	1	-2.48	15.0	0.97	1.33
Tautomers	=N-NH	2	-2.42	18.0	8.50	1.35
(Azonaphthols)	NH-C	1	-2.75	11.16	0.03	1.40
	C=O	1	-2.46	17.7	2.47	1.22
Electron Donors						
Hydroxy (free)	C-OH	2	-2.60	32.9	11.4	1.36
Hydroxy (H-bd)	C-OH	2	-2.60	28.0	10.0	1.36
Methoxy	C-OMe	2	-2.60	32.9	11.4	1.36
Phenoxide	$C-O^-$	1	-2.60	17.7	2.47	1.36
Hydrazone (free)	=N-NH	2	-2.42	21.0	9.26	1.35
Hydrazone anion	$=N-N^-$	1	-2.42	10.0	0.05	1.35

Group or Atom Type	Atoms X-Y	Core Charge Y	β_{X-Y} (eV)	$VSIP_Y$ (eV)	Electron Affinity A_Y (eV)	Bond Length (A)
Electron Donors						
C-NH_2 (Free)	C-N ..	2	-2.75	21.0	9.5	1.38
C-NH_2 (H-Bonded)	C-N ..	2	-2.75	18.8	8.7	1.38
C-NHMe (H-Bonded)	C-N ..	2	-2.75	15.0	8.6	1.38
C-NMe_2	C-N ..	2	-2.75	18.0	8.0	1.38
C-NEt_2	C-N ..	2	-2.75	17.5	7.5	1.38
Amino groups attached directly to Quinone 2,3-double bond.						
C-NH_2 (Free)	C-N ..	2	-2.75	22.55	10.8	1.38
C-NHMe	C-N ..	2	-2.75	21.9	10.15	1.38
C-NHEt	C-N ..	2	-2.75	21.9	10.15	1.38
C-NMe_2	C-N ..	2	-2.75	21.2	9.45	1.38
C-NEt_2	C-N ..	2	-2.75	21.0	9.25	1.38
C-OMe	C-N .. C-O	2	-2.60	37.0	15.53	1.36
Note: These values may also be appropriate to amide and ester groups, But this has not been confirmed.						
Di- and Tri-arylmethane Dyes.						
C-NH_2 (Auramine)	C-N ..	2	-2.75	15.0	6.0	1.40
C-NMe_2 (Di-)	C-N ..	2	-2.75	12.7	6.62	1.40
C-NMe_2 (Tri-)	C-N ..	2	-2.75	13.2	7.12	1.40
C-N (Julolidine)	C-N ..	2	-2.75	11.0	5.0	1.40
C-OMe	C-N .. C-O	2	-2.60	32.9	21.47	1.36
Nitro	N-O	1	-3.05	16.3	1.8	1.21
	C-N<	2	-2.0	24.8	12.5	1.49