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Software Review: PISYSTEM for Windows Version 3.1. A Program for the Calculation of Excited State Properties Including Colour of π Electron-Based Molecules

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ABSTRACT

PISYSTEM for Windows is a commercial program based on a modified PPP SCF-CI-MO model for the rapid and convenient calculation of excited state properties, especially colour, of π-conjugated systems such as dyes. The use and performance of the program is reviewed.

Two of the main activities of colour chemists are discovering new chromogens and extending basic understanding of older ones. Achievement of these aims has been immeasurably expedited by the advent of rapid computer-based procedures for calculation of excited state properties via molecular orbital (MO) theory, especially when the results are rapidly accessible following a few minutes work on a desk-top computer. A new addition to the software available for such studies is the package PISYSTEM for Windows,[1,2] designed for the calculation of excited state properties of π-electron molecules. This article is a review of the use and performance of this system, mounted on an IBM PC clone and a COMPAQ ProLinea 4/33, each based on 486/33DX processors.[2]

PISYSTEM is a privately sold Windows package designed to run on a 386 or more powerful PC with a maths co-processor. The package is supplied on a single diskette with minimal but sufficient documentation to allow rapid and trouble-free mounting. As supplied, it is security protected ('dongled') so that although it is possible to mount the package on several machines at once, only one version can be live at any one time. Activation is passed from one installation to another by means of the original diskette, which cannot be copied. While understandable, this is

at least a nuisance for the user, and in the case of damage or loss of the diskette, is a terminal weakness. However, at 50% higher cost a double application version is available.

PISYSTEM comprises three separate modules, covering molecule input, SCF-CI-MO calculation, and result output. Each has to be called separately from the Windows Program Manager, and it is easy to toggle between one and the others, as well as other applications.

Input is by means of the module PISYSINP. Initial molecule input involves sketching the σ-molecular framework on the screen by means of the mouse. Both ends of each bond must be clicked; no continuous draw mode is possible. The program assumes a π-electron system corresponding to the framework drawn. In the first instance, a planar conformation is assumed. Heteroatoms and nonstandard carbon atoms are selected from a pull-down menu and inserted onto the molecular framework. A wide selection of nitrogen, oxygen, and sulphur types is possible, and planar and pyramidal options are possible for some nitrogen environments. Some other heteroatoms are also allowed. Having input several hundred molecules, we have found most eventualities to be accounted for, but, not unexpectedly, transition metals are not handled. Moreover, there is an option to provide user-selected parameters for heteroatoms. A small weakness is that there is no facility to edit the library of parameters and save permanently for future use—each user-selection must be entered afresh for each molecule.

Before any further processing is possible, the crude structure must be submitted to a simple force field calculation which optimises the bond lengths and angles. Extra optimisation iterations can be called after the default optimisation if the structure still appears to be unsatisfactory—the molecular geometry is continually updated on the screen. On the basis of our experience, it is recommended routinely to submit to 100 extra cycles of structure optimisation. This takes only a matter of seconds on a 486/33 processor even for the largest molecule. The maximum molecule size tolerated is 56 π-atoms with 80 π-bonds, and this is usually ample. Structures can be stored and recalled in the future to act as skeletons for further input. In this way, a library can soon be built up so that it becomes unnecessary to draw molecules from scratch. Once optimised, the structure can be further modified if desirable by rotating about exocyclic bonds one or more units in the molecule with respect to the remainder, thus allowing for steric interaction and subsequent calculation of nonplanar conformations. When the input structure has been finalised, it can be submitted for SCF-MO calculation. Alternatively, further structures may be drawn, each new one being automatically queued for submission to the SCF calculation.

In the event of user error, a message is given on the screen, but in any case the input and optimisation routine is simple and rapid to use, and in our hands has given almost trouble free use. After familiarisation, input of a new molecule and submission for calculation typically takes a few minutes or so. We have encountered only one program crash, during a structure optimisation for a particularly hindered species. Even this could not be repeated. The structure optimisation routine has coped satisfactorily with structures which we have intentionally entered in particularly distorted fashion, and without exception generated realistic geometries. One idiosyncracy is the need to draw nitrile groups more or less linear, otherwise they are 'optimised' to bent structures.

The SCF-MO calculation routine, PISYSCAL, is basically an implementation of the well-known PPP model making allowance for σ-frame polarisation, and appropriate alterations of interaction integrals as well as two-centre repulsion integrals for nonplanar molecules.[3] The CI calculation takes account of the lowest 36 singly excited states. Once called, PISYSCAL processes each molecule submitted in turn in batch mode in the background while other input is prepared or results interrogated. Calculation times are obviously dependent on what other applications are being run. Figure 1 illustrates the times taken for a random selection of six dyes of differing sizes, run in the absence of any other active application. Operation of the SCF routine is transparent, and once started no other

$$\log_{10}(\text{time/secs}) = 3.055\log_{10}(\text{number of atoms}) - 2.017$$
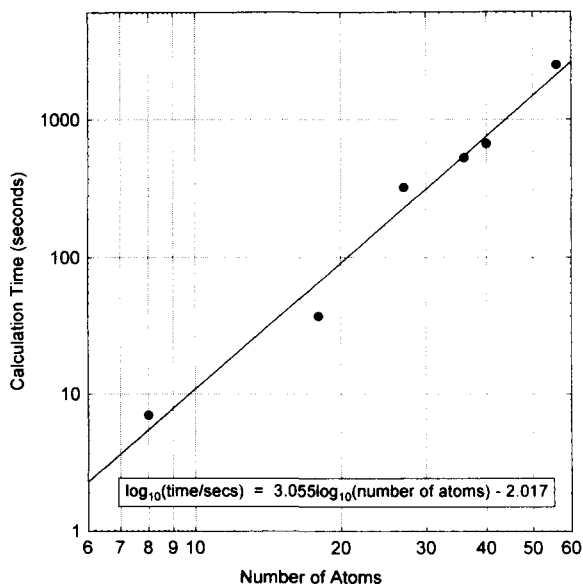
Fig. 1. Log–log plot of time of calculation versus number of atoms for six dyes calculated by PISYSTEM.

manipulation is necessary or possible. Progress of the calculations can be monitored by means of a window which indicates which molecule is being progressed. Once complete, results are written to an output file, and PISYSCAL proceeds to the next molecule for calculation, if any, or else is automatically closed down.

The program is not designed for triplet ground state molecules, or open shell systems. Besides these, we have encountered a few other molecules which PISYSCAL fails to calculate for reasons unclear to us. The only diagnostic is a message in the output module that a faulty output file was generated, and no results are obtained. This has only happened for less than about 5% of those input.

Results are accessed from the third module, PISYSRES. New results are deposited by PISYSCAL in a 'provisional' file, which once selected by the user from a menu can be interrogated in a number of ways. Colour chemists will be particularly interested in the excited state data, which include a diagram of the UV visible spectrum, coloristic data, eigenvectors, electron densities and differences between GS and the first three excited states, bond orders and alterations, net charges, dipole moment and transition moment. Additionally, there are options to access the estimated effects on spectra of electronegativity changes, bond twisting and elongation, substitution with a variety of groups, and ring annelation. In practice, it is more meaningful to resubmit the molecule after structural adjustments have been explicitly built in.

The most useful options are the spectrum and the electron density changes. The spectrum (Fig. 2) may be displayed alongside transition energies, wavelengths, oscillator strengths, and extinction coefficients. Interestingly, PISYSTEM presents more than a simple stick spectrum and attempts to reproduce band shapes based on a published bandwidth procedure.[4] We are unable at this stage to comment on how well these reflect experimental reality. Furthermore, an estimate is given of how the spectrum will respond to polar solvents. However, this only takes account of dipolarity effects, and overlooks any influence due to specific solvent–solute interaction such as H-bonding. Also, if a molecule is centrosymmetric, it assumes no solvatochromism; this is patently incorrect for many molecules. At best, this facility is only a very rough guide to possible solvatochromic behaviour. The electron density changes are given as differently shaded circles on the molecule framework (Fig. 3), the size of the circle representing the degree of electron shift.

Data are also provided for use in reactivity studies of conjugated systems, particularly those dependent on frontier orbitals. HOMO, NHOMO, LUMO and NLUMO are provided, along with charge densities.
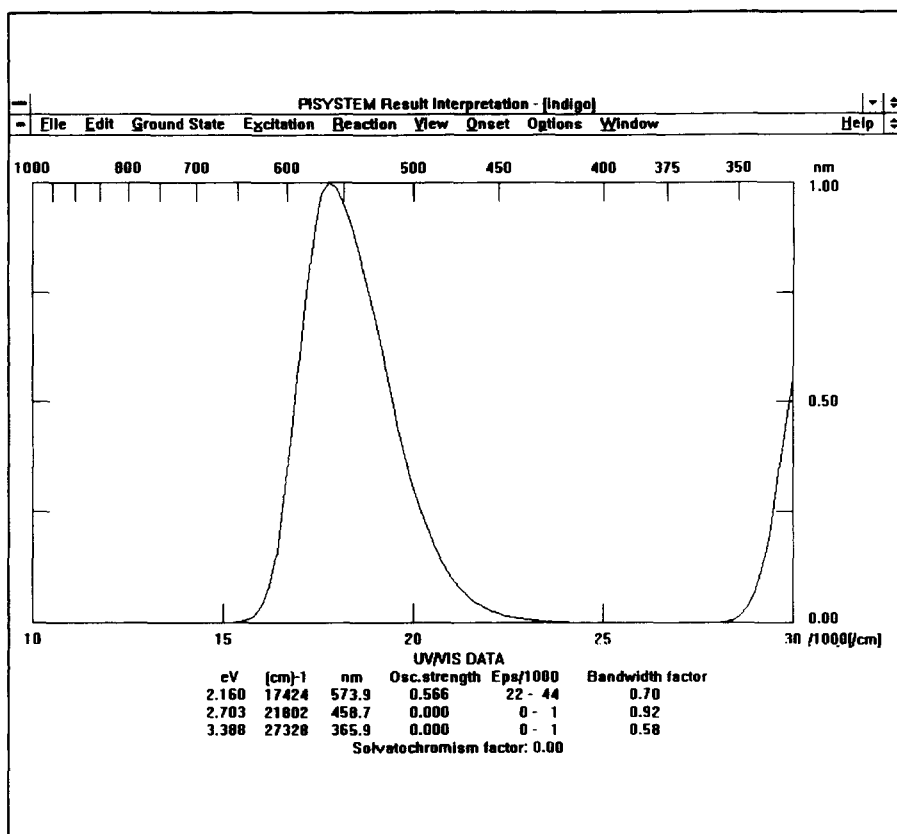
Fig. 2. Screen dump of calculated spectroscopic properties of indigo.

Examination of the results is straightforward and has proven trouble free. The graphical output is attractive and in the main easily interpreted.

Result files can then be stored for future reference. Although the input files are given unique names, these are not carried forward to label the archived data. Thus, when it comes to search such stored results, it is not possible merely to provide a file or molecule name, but rather it is necessary to go through a cumbersome procedure in response to menu questions which enquire how many atoms, how many heteroatoms, and how many rings (ranges can be specified). Only then does the program offer alternatives, identified by their names, from which to select. This is probably the most inconvenient feature of PISYSTEM, and there seems to be no quick way around it.

Help files are accessible from the menu in the output modules, and these are reasonably complete and useful. They addressed most problems we encountered, and provide a 'Questions and Answers' section for
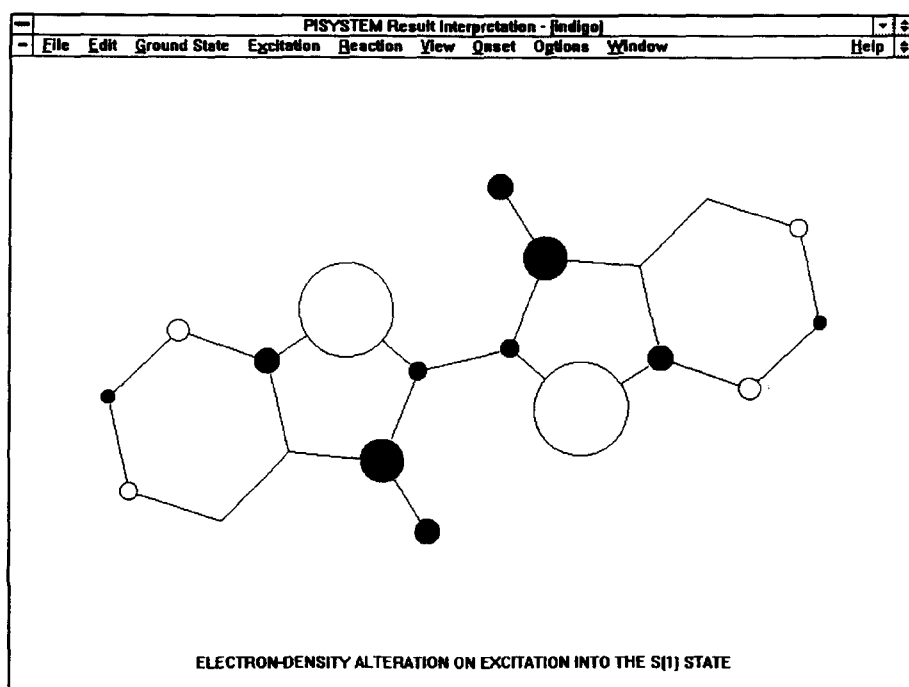
Fig. 3.   Screen dump of calculated electron density change on excitation of indigo to its
first singlet excited state.

common queries. Helpful and relevant literature references are cited.
Overall, these files compensate for the rather restricted documentation
which is provided. The author himself proved very helpful in responding
to queries we sent him.

The accuracy of the results obtained will be discussed in more detail
elsewhere, when PISYSTEM will be compared with other programs
based on higher levels of MO theory. The main conclusions are:

—the trend in experimental absorption maxima for a series of different
chromogens is more-or-less reproduced by the values calculated by
PISYSTEM, but there are some serious outliers; for example, some
macrocyclic molecules such as porphyrins and phthalocyanines are
bad. Underlying reasons for this particular behaviour are unknown;

—for a series of known solvatochromic molecules, it is found that the
calculated absorption maxima do not necessarily correspond to the
least polar situation, as expected, but instead reflect a relatively polar
environment;

—experimentally known solvatochromic shifts correlate only qualitatively
with the calculated 'solvatochromism factor';

—the results of the calculations of the absorption maxima are well in line with those expected on the basis of past experience with PPP-MO calculations.

Overall, PISYSTEM can be strongly recommended to chemists interested in a quick, easy, and foolproof package for the calculation of colour and other excited state properties on a desktop computer, given the usual caveats surrounding the use of approximate MO methods. Chemists normally reluctant to become involved with computers find PISYSTEM very comfortable to use, and acclimatisation takes only a few minutes. While we in Zeneca Specialties already have several systems available for calculation of colour and related properties, PISYSTEM is to be added to this list and made generally accessible to all chemists via their desktop PCs.

Perhaps the strongest testimony we can offer is anecdotal: more often than not, when we have set out to calculate one or two specific molecules, we have ended up running a dozen. Above all, this is because using the program is fun. There are few better reasons for practising science, whether at the bench or on a computer.

REFERENCES

1. PISYSTEM for Windows, Version 3.1 (1994). Available from Dr Rudolf Naef, Im Budler 6, CH-4419 Lupsingen, Switzerland. Price: SFr560; second authorisation SFr280 extra. PISYSTEM is a copyright of the owner.
2. Windows is a trademark of Microsoft Corporation. IBM is a trademark of International Business Machines Corporation. ProLinea is a trademark of Compaq Computer Corporation.
3. Griffiths, J., *Dyes and Pigments*, 3 (1982) 211.
4. McCoy, E. F. & Ross, I. G., *Austr. J. Chem.*, 15 (1962) 573.