On the solvatochromic reversal of merocyanine dyes. Part 2.[1] An experimental and semi-empirical study of the solvatochromism of α- and γ-vinylogous pyridones

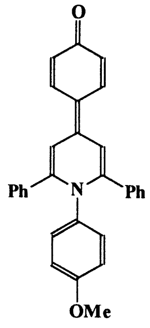
Carolina Aliaga,[a] Juan Soto Galdames[b] and Marcos Caroli Rezende *,[b]

[a] *Facultad de Ciencias, Universidad de Chile, Santiago, Chile*
[b] *Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile*

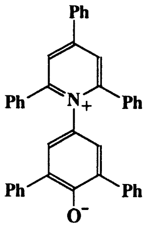
The vinylogous α-pyridone 1,2-dihydro-1-(4-methoxyphenyl)-2-(4-oxocyclohexa-2,4-dienylidene)-4,6-diphenylpyridine 3 was prepared and its solvatochromic behaviour in several solvents recorded and compared to that of its γ-isomer 1. The relative behaviour of these dyes, which differed from that of other solvatochromic vinylogous α/γ-pyridones, could be reproduced by a previously described theoretical model.

Introduction

Some years ago, Reichardt and co-workers synthesized the vinylogous γ-pyridone **1** and compared its solvatochromic behaviour with the widely employed $E_T(30)$ dye **2**.[2] Although **1** behaved very much like the $E_T(30)$ dye, its solvatochromic shifts in a variety of solvents did not span such a wide range of values as its isomer **2**.



1

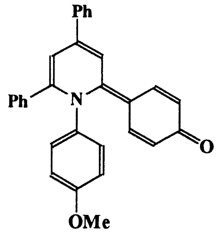


2

We have been concerned with the solvatochromic behaviour of pyridiniophenoxide dyes and on the structural features responsible for relative changes in the magnitude of their spectral shifts. In the preceding paper[1] we turned our attention to vinylogous γ-pyridones and the fact that the introduction of an unsaturated link between the pyridinio acceptor and the phenoxide donor moieties led to a qualitative change in the solvatochromic behaviour of these dyes.

In the present paper, we describe the synthesis and the solvatochromic properties of the vinylogous α-pyridone dye **3** and compare its behaviour with its analogue **1**.

The relative behaviour of these two systems is qualitatively reproduced by means of a simple theoretical model described previously.[1] One possible way of improving this model incorporates configuration interactions into the calculations. An example of this procedure is provided by calculations made on a merocyanine dye previously described by us.[3]



3

Experimental

Melting points were recorded on a Koffler hot-plate apparatus and were not corrected. IR spectra were obtained with a Perkin-Elmer 735B spectrometer. NMR spectra were recorded with a Bruker 200 MHz equipment, utilizing tetramethylsilane as internal reference. UV–VIS spectra of dye **3** were recorded with a Shimadzu UV-160 spectrophotometer. *J* values are given in Hz.

All solvents employed were analytically pure and were redistilled and stored over molecular sieves prior to use. 4-Hydroxyacetophenone, boron trifluoride–diethyl ether and 4-methoxyaniline were purchased from Aldrich.

2,4-Diphenyl-6-(4-hydroxyphenyl)pyrylium fluoroborate

A mixture of 1,3-diphenylprop-2-enone[4] (2.08 g, 10 mmol) and 4-hydroxyacetophenone (0.68 g, 5 mmol) in boron trifluoride–diethyl ether (2 ml, 16.3 mmol) were stirred in a water bath at 80–90 °C for 2 h. The cooled viscous liquid was then poured into diethyl ether (50 ml) and the precipitated brick-red solid filtered, washed with cold ethanol (5 ml) and recrystallized from acetone–diethyl ether to give, after drying, 0.84 g (41% yield) of the 2,4-*diphenyl*-6-(*hydroxyphenyl*)*pyrylium fluoroborate*, mp 236–237 °C. Found: C, 67.15; H, 3.98%. $C_{23}H_{17}BF_4O_2$ requires C, 66.99; H, 4.13%. ν_{max}/cm^{-1} (KBr) 3300 (OH), 1040 (BF_4^-). $\delta_H(CD_3SOCD_3)$ 7.23 (d, 2 H, *J* 8, Hs *ortho* to the OH group), 7.8–7.9 (m, 6 H, Hs at positions 2′ and 6′ of the three phenyl substituents), 8.4–8.6 (m, 6 H, other Hs of the phenyl substituents), 8.95 (s, 1 H, pyrylium H), 9.0 (s, 1 H, pyrylium H), 9.2 (1 H, s, OH).

1-(4-Methoxyphenyl)-2,4-diphenyl-6-(4-hydroxyphenyl)-pyridinium fluoroborate

A solution of 2,4-diphenyl-6-(hydroxyphenyl)pyrylium fluoroborate (1.0 g, 2.4 mmol), 4-methoxyaniline (0.3 g, 2.4 mmol) and triethylamine (0.4 g, 4 mmol) in dichloromethane (30 ml) was allowed to react at 25 °C for 12 h. The organic solution was washed with fluoroboric acid (50%, 5 ml), then with water (10 ml) and dried over anhydrous $MgSO_4$. After concentration in a rotary evaporator, diethyl ether (50 ml) was added and the pale-yellow solid that precipitated was filtered and recrystallized

Table 1 Variation of the longest wavelength band absorption in different solvents of the vinylogous pyridones **1** and **3**

	λ_{max}/nm	
Solvent	γ-Pyridone **1**[a]	α-Pyridone **3**
Water	—	416
2,2,2-Trifluoroethanol	418	—
Propane-1,2,3-triol	—	437.5
Ethane-1,2-diol	—	441
Formamide	458.5	—
Methanol	444	446
Ethanol	463.5	471
Propan-1-ol	469.5	482
Butan-1-ol	—	489
3-Methylbutan-1-ol	—	495
Pentan-2-ol	—	506
Acetonitrile	495	527
Dimethyl sulfoxide	499	532
Dimethylformamide	501	536
Acetone	507	527
Acetophenone	—	525
1,2-Dichloroethane	511.5	—
Chloroform	—	523.5
Hexamethylphosphorictriamide	510	—

[a] Data from ref. 2.

from acetone–diethyl ether to give 0.84 g (65% yield) of the 1-(*4-methoxyphenyl*)-2,4-*diphenyl*-6-(4-*hydroxyphenyl*)*pyridinium fluoroborate*, mp 213–214 °C. Found: C, 69.95; H, 4.32; N, 2.53%. $C_{30}H_{24}BF_4NO_2$ requires C, 69.63; H, 4.64; N, 2.71%. ν_{max}/cm^{-1} (KBr) 3400 (OH), 1040 (BF_4^-). $\delta_H(CD_3SOCD_3)$ 3.7 (s, 3 H, OCH_3), 6.8 (d, 2 H, *J* 8, Hs *ortho* to the OH group), 7.2–7.4 (m, 9 H, other Hs from α-phenyl substituents), 7.7 (m, 3 H, Hs at positions 3′, 4′ and 5′ of the γ-phenyl substituent), 8.3 (m, 2 H, Hs at positions 2′ and 6′ of the γ-phenyl substituent), 8.5 (s, 2 H, pyridinium Hs), 8.6 (s, 1 H, OH).

The corresponding pyridiniophenoxide betaine **3** was generated *in situ* by treatment of solutions of the pyridinium fluoroborate with a pellet of sodium hydroxide. The resulting coloured solutions containing dye **3** were decanted and their spectra immediately recorded at 25 °C.

Theoretical calculations

Geometry optimizations were carried out utilizing the semi-empirical AM1 Hamiltonian of the MOPAC 6.0 package,[5] with the only restraint of constant planarity of the aromatic rings.

Environmental polarity variations were mimicked by positioning a sparkle of charge +2 at a variable distance from the oxygen atom of each phenoxide dye in its most stable conformation. The variable C=O bond distance thus obtained for each dye was a function of the sparkle–oxygen distance. This C=O bond distance was employed for the definition of a normalized ‘polarity’ scale *P* as described before.[1]

For the calculations involving configuration interactions, the molecular geometry of the dye with the +2 point charge, optimized by the AM1 method, was fed into a ZINDO/S-CI program[6] and calculations carried out with all monoelectronic transitions from the thirteen highest occupied to the thirteen lowest unoccupied molecular orbitals, performing a total of 197 interactions.

Results

Dye **3** was generated in solution by treatment of the 1-(4-methoxyphenyl)-2,4-diphenyl-6-(4-hydroxyphenyl)pyridinium fluoroborate with base. The pyridinium fluoroborate was prepared by the route depicted in Scheme 1.

In contrast to the preparation of the analogue **1**,[2] treatment of the 2-(4-hydroxyphenyl)pyrylium salt with 4-methoxyaniline to form the corresponding pyridinium salt did not require previous protection of the hydroxy group by acylation.

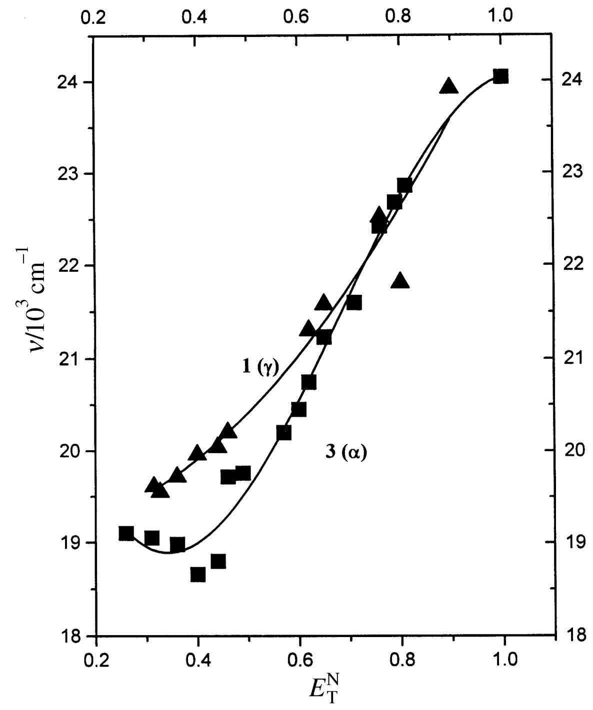
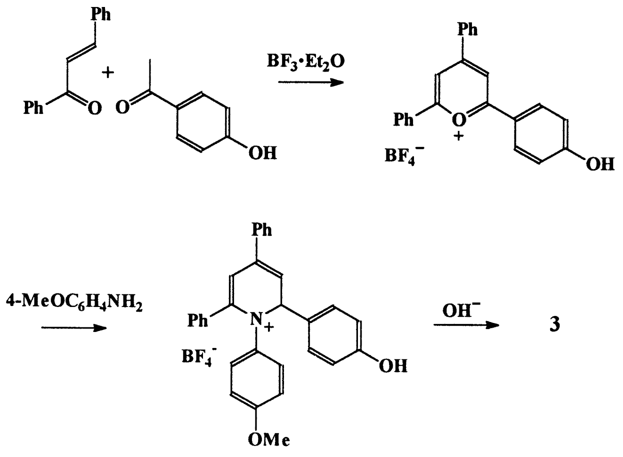


Fig. 1 Variation of the wavenumber values ν of the charge-transfer band of dyes **1** and **3**, as a function of the solvent polarity E_T^N



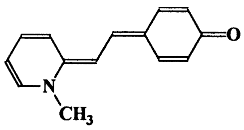
Scheme 1

Table 1 lists the λ_{max} values of the longest-wavelength band in the visible spectrum of dye **3** in various solvents. A comparison of the solvatochromic behaviour of this compound with its analogue **1** is illustrated in Fig. 1, where the wavenumber values of the CT bands of both compounds in several solvents are plotted against the corresponding E_T^N values.

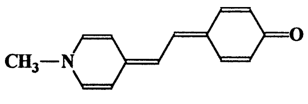
Both **1** and **3** are less sensitive solvatochromic compounds than the $E_T(30)$ dye: changing from acetone to methanol produces a solvatochromic shift of *ca.* 160 nm for solutions of the $E_T(30)$ dye, compared with shifts of 63 and 81 nm for solutions of **1** and **3** respectively. In addition, the data of Table 1 indicate that the vinylogous α-pyridone is more sensitive to medium changes than its solvatochromic γ-isomer. As can be seen from Fig. 1, compound **1** absorbs at higher energies than its isomer **3** in solvents of medium polarity. However, as the solvent polarity is increased, the CT transition energies of both isomers converge to the same value in methanol, reverting their relative positions in more polar media.

Discussion

The relative behaviour of the pair of vinylogous pyridones **1** and **3** is in contrast with that of other analogous pyridones found in the literature. Thus, the pair of isomeric compounds **4**[7]



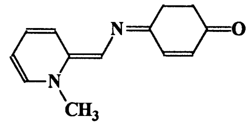
4



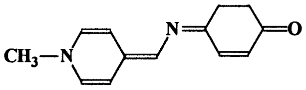
5

and **5**[8] present a similar solvatochromic behaviour and the γ-isomer **5** consistently absorbs at lower energies than its α-analogue **4**.

The same relative behaviour is observed for the pair of iminomerocyanines **6**/**7**,[3] both of which are examples of dyes exhibiting reverse solvatochromism in media of low polarity.



6



7

This variable behaviour, found in a family of related merocyanines with similar donor and acceptor units, offers an interesting opportunity to test the theoretical approach described in the preceding paper.[1] This was based on the assumption that a solvatochromic merocyanine undergoes structural modifications in response to its environment. Experimental evidence for this arises from NMR, X-ray and Raman studies by different authors. ^{13}C NMR spectra of Brooker's merocyanine in deuteriated methanol and dimethyl sulfoxide yielded differences in chemical shifts indicative of a more zwitterionic structure in the former solvent than in the latter.[9] An increase in solvent polarity led to significant changes in the ^1H NMR spectrum of the open form of a spironaphthoxazine.[10] Also, changing solvent polarity resulted in important chemical shifts in ^1H NMR spectra of solvatochromic pyridiniophenoxide dyes.[11] Marder, Perry *et al.* studied the bond-length alternation in donor–acceptor polyenes. Their conclusion, based on X-ray evidence, coupled with Raman spectra of these compounds in the solid state and in a variety of solvents ranging from tetrachloromethane to methanol, was that structural changes in these dyes can be tuned by the surrounding medium.[12]

By polarizing the dye structure in the presence of a variable electric field, one should in principle be able to mimic the solvatochromic behaviour of the dye in media of different polarity. This approach has been followed in different ways in the study of polymethine dyes,[13] and Brooker's merocyanine.[14] The use of sparkles to promote structural and electronic changes in a polarizable dye is a well established technique which has been utilized by Morley in a theoretical study of the spectra of merocyanines.[15] More recently, the same approach has been adopted in a theoretical study of the solvatochromic properties of bipyrazine cations.[16] We have developed this classic procedure to a larger number of calculated points, thus spanning a continuum of media of increasing polarity.[1]

We generate a variable electric field by gradually bringing a charge closer to the phenoxide oxygen of the molecule, along its C–O bond. This is due to the fact that these dyes are strongly sensitive to the microenvironment around the phenoxide oxygen, behaving in general as α-indicators, in Kamlet and Taft's terminology.[17] We next equate the charge-transfer transition energy of the perturbed dye with its HOMO–LUMO energy gap. This approximation is partly validated by the observation, made by different calculations that include configuration interactions on these systems, that the HOMO–LUMO transition is always the major contributor to the calculated $S_0 \rightarrow S_1$ transition.[15,16,18–20] Finally, we define a normalized 'polarity' scale *P* based on the elongation of the C–O bond of the phenoxide dye, as described in the preceding paper.[1]

By plotting the calculated HOMO–LUMO energy gaps ΔE against the corresponding 'polarity' values *P* we obtain a curve which should reproduce the solvatochromic behaviour of the dye in different media.

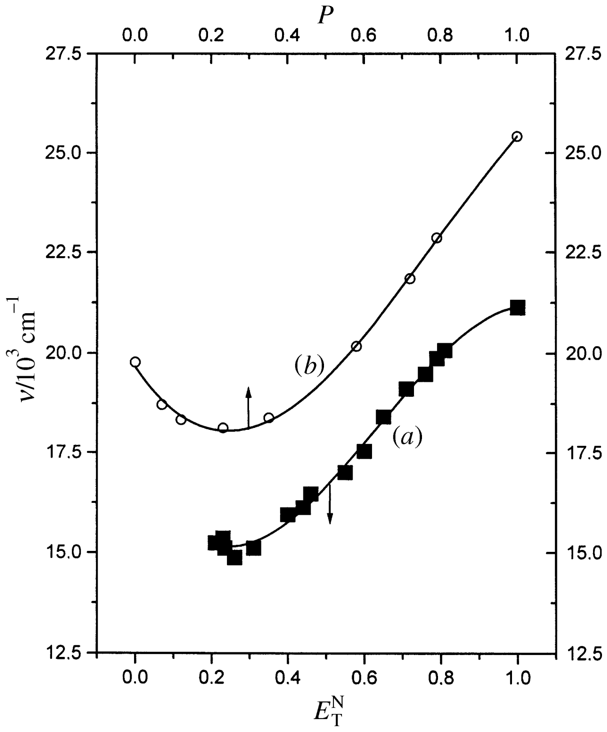


Fig. 2 Variation of the wavenumber values ν of the charge-transfer band of dye **7** with the polarity of the medium. (*a*) Experimental values, as a function of the solvent polarity E_T^N; (*b*) theoretical values, employing a combined AM1//ZINDO/S-CI method, as a function of 'polarity' values *P*.

In spite of all the approximations made, this simple protocol should be useful if it is capable of reproducing the qualitative behaviour of related solvatochromic dyes. One possible way of improving it would be the inclusion of configuration interactions in the calculations. We therefore decided to perform CI calculations on one of the phenoxide dyes and to use a more adequate program, parametrized for the estimation of electronic transition energies. We applied our method to dye **7**. After optimizing the geometry of this molecule in the presence of a +2 sparkle by the AM1 method, the coordinates obtained were fed into a ZINDO/S-CI program[6] and the $S_0 \rightarrow S_1$ transition was calculated after taking into account 197 configurations arising from monoelectronic transitions from the 13 HOMOs to the lowest virtual orbitals. The theoretical curve obtained is shown in Fig. 2, together with the experimental solvatochromic shifts of this compound in a variety of solvents, as a function of $E_T{}^N$ polarity scale. As expected, CI calculations led to transition energies which were much closer to the experimental values: our calculated HOMO–LUMO transition energies, in the range of 6.0–6.5 eV (9.6×10^{-19}–10.4×10^{-19} J), reduced to values in the range of 2.5–3.0 eV (4.0×10^{-19}–4.8×10^{-19} J) when the CI calculation was performed, in closer agreement with the experimental range of 1.9–2.6 eV (3.0×10^{-19}–4.2×10^{-19} J). However, the qualitative behaviour of the theoretical curves was similar, both of them predicting a solvatochromic reversal in media of low polarity and a negative solvatochromism in more polar solvents. This result validates our approximation of considering HOMO–LUMO transition energies in comparing similar systems, especially when one is not interested in the absolute values of their absorptions, but in their relative solvatochromic trends in various media.

This is the case of the pair of dyes **1**/**3**, to which our protocol was applied. The theoretical curves obtained for both dyes are shown in Fig. 3. The curves agree reasonably well with the relative behaviour depicted in Fig. 1. Thus, compound **3** is seen

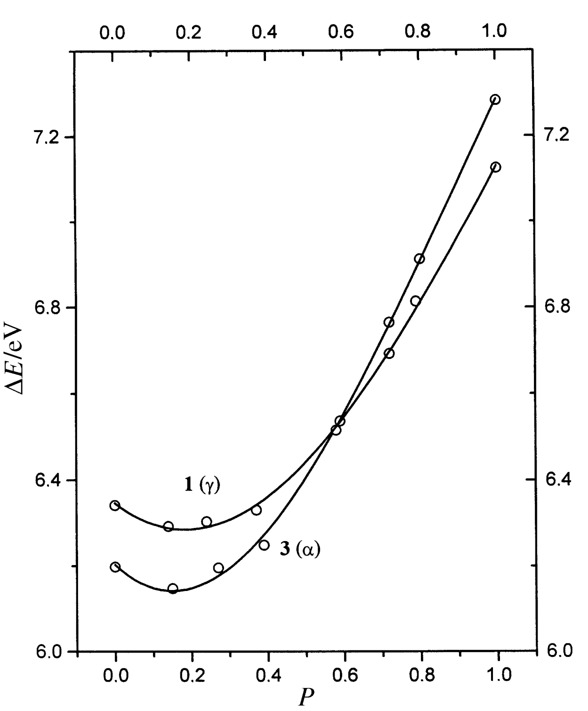


Fig. 3 Calculated solvatochromic shifts, based on HOMO–LUMO energy-gap variations, for systems **1** and **3**, as a function of ‘polarity’ values P

to be more sensitive to polarity changes than its isomer **1**. In addition, the α-pyridone **3** is expected to absorb at lower λ_{max} values (higher energies) than its γ-analogue in media of high polarity ($P > 0.6$), reverting to this behaviour in less polar media.

The different behaviour of the pair **1**/**3**, as compared to dyes **4**/**5**, or **6**/**7**, can be ascribed to steric effects. As far as coplanarity of the donor–acceptor rings is concerned, there should not be a great difference between the vinylogous α- and γ-isomers of bridged pyridiniophenoxides **4**/**5** and **6**/**7**. The situation, however, changes for the pair **1**/**3**. In the α-isomer **3**, the coplanarity of the donor phenoxide and the acceptor pyridinium rings is prevented by steric hindrance by the *N*-aryl substituent, an effect which is absent in the γ-isomer. Consequently, the structure of dye **3** should have a greater zwitterionic character than that of dye **1**, thus rendering the phenoxide oxygen of the former more basic than the donor oxygen of the γ-isomer **1**. This has the effect of providing a greater stabilization of the ground-state HOMO of **3** in polar, hydrogen bond–donor solvents, as compared to the HOMO of the more quinonoid γ-dye **1**.

In conclusion, the data presented by us here point to trends which differ from the relative solvatochromic behaviour of other vinylogous α/γ-pyridones reported in the literature. This behaviour is qualitatively reproduced by application of a classical theoretical model employed previously by us.[1] The model can be refined to include configuration interactions in the calculations, with the result that the transition energies obtained are much closer to the experimental values. However, this is not necessary if one is interested in comparing and predicting, in a qualitative way, the behaviour of related dyes. The model, which only requires a semiempirical package to be run on a microcomputer, should be helpful in providing easy access to the prediction of the relative solvatochromic behaviour of related pyridiniophenoxide merocyanines.

Acknowledgements

This work was supported by the Directoría de Ciencia y Tecnología (DICYT), Universidad de Santiago de Chile.

References

1 Part 1, L. Silva, C. Machado and M. C. Rezende, *J. Chem. Soc., Perkin Trans. 2*, 1995, 483.
2 C. Reichardt, P. Milart and G. Schaefer, *Liebigs Ann. Chem.*, 1990, 441.
3 C. Machado, M. G. Nascimento and M. C. Rezende, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2539.
4 B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, Longman, Essex, 5th edn., 1989, p. 1034.
5 MOPAC 6.0 for IBM-PC, QCEP, University of Bloomington, Indiana, 1990.
6 M. C. Zerner and J. E. Ridley, *Theor. Chim. Acta*, (*a*) 1973, **32**, 111; (*b*) 1976, **42**, 223.
7 S. T. Abdel-Halim, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 55.
8 P. Jacques, *J. Phys. Chem.*, 1986, **90**, 5535.
9 A. Botrel, A. LeBeuze, P. Jacques and H. Strub, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 1235.
10 N. L. Zaichenko, A. V. Lyubimov, V. S. Marevtsev and M. I. Cherkashin, *Isv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1040 (*Engl. transl.* p. 941).
11 C. Runser, A. Fort, M. Barzoukas, C. Combellas, C. Suba, A. Thiébault, R. Graff and J. P. Kintzinger, *Chem. Phys.*, 1995, **193**, 309.
12 S. R. Marder, J. W. Perry, B. G. Tiemann, C. B. Gorman, S. Gilmour, S. L. Biddle and G. Bourhill, *J. Am. Chem. Soc.*, 1993, **115**, 2524.
13 S. R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J. L. Brédas and B. M. Pierce, *Science*, 1994, **265**, 632.
14 V. Luzhkov and A. Warshel, *J. Am. Chem. Soc.*, 1991, **113**, 4491.
15 J. O. Morley, *J. Mol. Struct., Theochem.*, 1994, **304**, 191.
16 L. A. Eriksson, N. Salhi-Benachenhou and O. Goscinski, *Mol. Eng.*, 1995, **4**, 339.
17 M. J. Kamlet, J. L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.
18 J. Catalán, E. Mena, W. Meutermans and J. Elguero, *J. Phys. Chem.*, 1992, **96**, 3615.
19 A. Botrel, B. Aboab, F. Corre and F. Tonnard, *Chem. Phys.*, 1995, **194**, 101.
20 M. Adachi, Y. Murata and S. Nakamura, *J. Org. Chem.*, 1993, **58**, 5238.

Paper 6/05966J
Received 29*th August* 1996
Accepted 14*th January* 1997