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On the Application of Theoretical Methods for the Prediction of Fluorescence Maxima of Organic Dyes

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SUMMARY

Theoretical methods, especially the well established Pariser–Parr–Pople molecular orbital method, have proved to be very useful in colour prediction of organic dye molecules. Because of the increasing importance of highly fluorescent substances for applications as optical brighteners as well as laser dyes there exists a clear need for a theoretical model which allows the prediction of fluorescence maxima with comparable accuracy to that of absorption maxima. It is shown that the simulation of the change of molecular geometry upon excitation by a simple iterative procedure within the framework of the PPP*-method can be used for the calculation of fluorescence maxima with satisfactory accuracy thus allowing reliable predictions for this class of dyes. Therefore the method discussed may prove very helpful in practical and synthetic work on fluorescent organic dyes.*

1. INTRODUCTION

In a recent publication Griffiths[1] has demonstrated the value and economy of theoretical methods, especially the Pariser–Parr–Pople (PPP) method,[2] in the colour prediction of organic dye molecules. As has been convincingly shown in that paper the PPP method allows the calculation of the wavelengths of maximum absorption for any class of dye molecules with reasonable reliability. Furthermore, it was briefly mentioned that this semi-empirical method also may be used to predict

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the Stokes shift for a chromogen and hence the position of its fluorescence maximum. Since the fluorescence properties of organic molecules have become increasingly important, mainly because of the enormous interest in efficient optical brighteners as well as laser dyes, the prediction of the fluorescence maxima of organic dyes by theoretical methods should be as helpful in synthetic dye chemistry as the calculation of λ_{max} values. The present communication deals with such an application of the PPP-method to the prediction of the fluorescence maxima of optical brighteners and laser dyes, especially coumarin derivatives.

2. OUTLINE OF THE METHOD

A priori the results of the PPP calculations are energy differences between ground and excited states. Since according to the Franck–Condon principle the position of the absorption maximum is determined by the ground state geometry the use of experimental geometries (e.g. taken from X-ray data) or standard bond lengths (e.g. those compiled in ref. 1) should yield energy differences corresponding to absorption maxima. On the other hand the position of fluorescence maxima is determined by the geometry of the excited state. Correspondingly, the prediction of fluorescence maxima requires the calculation of the changes of molecular geometry upon excitation. Within the framework of the PPP method the only parameters which depend on the interatomic distances are the resonance integral $\beta_{\mu\nu}$ which usually is treated as a fixed parameter, e.g. those given by Griffiths,[1] corresponding to standard bond lengths and the electron–electron repulsion integral $\gamma_{\mu\nu}$. As has been shown by Fratev *et al.*[3] and successfully applied by other authors[4,5] geometrical changes may be solely simulated by the distance dependence of the resonance integral $\beta_{\mu\nu}$, the variations in $\gamma_{\mu\nu}$ being only negligible corrections.[4] In order to obtain the required geometrical changes upon excitation the well-known bond order ($P_{\mu\nu}$)–bond length ($R_{\mu\nu}$) relationship (1)[3]

$$R_{\mu\nu} = a + bP_{\mu\nu} \tag{1}$$

is used to calculate from excited state bond orders the corresponding bond lengths of the excited state. These bond lengths are then used to evaluate new values for the resonance integrals $\beta_{\mu\nu}$ by means of eqn (2):

$$\beta_{\mu\nu} = -k_1 \exp(-k_2 R_{\mu\nu}) \tag{2}$$

In a second calculation these new values for $\beta_{\mu\nu}$ are used instead of the

TABLE 1
Parameters a, b, k_1 and k_2 for the Various Types of Bonds

Bond	a	b	k_1	k_2
C—C[5]	1·517	−0·18	1 157·0	4·431
C—N[5]	1·451	−0·18	466·728	3·980
C—O[5]	1·410	−0·18	21·149	1·747
C—S	1·831	−0·18	9·257	0·891

standard $\beta_{\mu\nu}$-values, thus simulating the changes in bond lengths accompanying the excitation. In an iterative procedure these calculations are now repeated until convergence of bond lengths or transition energies is achieved. Using a convergence criterion of $\Delta R_{\mu\nu} < 0{\cdot}002$ Å and $\Delta\tilde{\nu} < 100\,\mathrm{cm}^{-1}$, respectively, usually 4–5 such calculations are necessary. A simple example, pyrid-2(1*H*)-one, may serve to illustrate the method outlined above. Using the standard $\beta_{\mu\nu}$-values a transition energy of 31·2 $(10^3\,\mathrm{cm})^{-1}$ to be compared with the experimental absorption maximum of 33·7 $(10^3\,\mathrm{cm})^{-1}$ is obtained. In the second calculation the $\beta_{\mu\nu}$-values calculated via eqns (1) and (2) using the bond orders of the first excited state as obtained by the previous calculation are used as input parameters leading to a lowering of the transition energy to 28·4 $(10^3\,\mathrm{cm})^{-1}$. This process now is repeated until after some four calculations the final value of 27·6 $(10^3\,\mathrm{cm})^{-1}$ (experimental fluorescence maximum = 27·3 $(10^3\,\mathrm{cm})^{-1}$) is obtained.

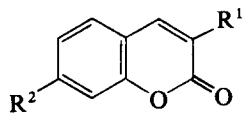
The parameters a, b, k_1 and k_2 of eqns (1) and (2) for the various types of bonds (C—C, C—N, C—O, C—S) are collected in Table 1.

3. RESULTS

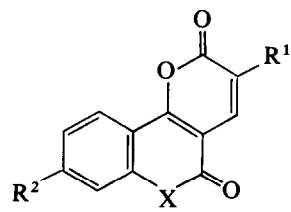
As has been briefly mentioned in the introduction the method outlined above will be applied to a series of coumarin derivatives which according to their high fluorescence efficiency may be useful as potential optical brighteners as well as laser dyes. The structures of the investigated compounds are shown in Fig. 1.

The results of the calculations for compounds **1–14** (wavenumbers of absorption and fluorescence maxima) are collected in Table 2 and compared with the corresponding experimental values.

As can be seen from the data given in Table 2 the simple calculational



Compd	R^1	R^2
1	phenyl	H
2	phenyl	OH
3	*p*-OH-phenyl	H
4	*p*-NH_2-phenyl	H
5	phenyl	NH_2
6	2-benzthiazolyl	OH



Compd	*X*	R^1	R^2	*Compd*	*X*	R^1	R^2
7	O	H	NH_2	**14**	O	CN	H
8	O	phenyl	NH_2	**15**	O	phenyl	OH
9	NH	H	H	**16**	O	3-pyridyl	H
10	NH	H	NH_2	**17**	O	2-benzothiazolyl	H
11	NH	phenyl	NH_2	**18**	O	2-benzothiazolyl	NH_2
12	NH	CN	OH	**19**	NH	phenyl	H
13	NH	CN	NH_2	**20**	NH	2-benzothiazolyl	H

Fig. 1. Structures of the investigated compounds.

procedure outlined above allows the prediction of the fluorescence maxima of organic dyes with an accuracy at least comparable to the prediction of absorption maxima. In both cases (absorption as well as fluorescence) the mean deviation between calculated and experimental values is less than about $400\,cm^{-1}$. Given this accuracy the method should be a reliable and valuable tool in the synthesis of fluorescent dyes. Relatively large deviations occur for the compounds substituted by an amino group in the aromatic ring (compounds **5, 7, 8, 10, 11** and **13**) both in the calculated absorption as well as fluorescence maxima. This effect

TABLE 2
Experimental and Calculated Wavenumbers (in $10^3\,cm^{-1}$) of Absorption and Fluorescence Maxima for Compounds **1–14**[a]

Compound	$\tilde{\nu}_{abs}$		$\tilde{\nu}_{flu}$	
	Exp.	*Calc.*	*Exp.*	*Calc.*
1	30·8 (ref. 6)	30·0	24·0 (ref. 6)	23·7
2	29·8 (ref. 6)	30·2	23·7 (ref. 6)	23·4
3	29·3 (ref. 6)	29·3	21·7 (ref. 6)	21·8
4	27·8 (ref. 6)	27·1	—[b]	—
5	26·3 (ref. 6)	27·4	21·7 (ref. 6)	23·4
6	24·1 (ref. 7)	24·7	21·5 (ref. 7)	22·1
7	24·3 (ref. 8)	26·1	21·1 (ref. 8)	23·2
8	22·7	24·8	19·9 (refs 8, 9)	21·5
9	26·5	27·0	23·4 (ref. 8)	23·6
10	24·6	26·0	21·6 (ref. 8)	23·5
11	23·3	24·8	19·4 (ref. 8)	21·6
12	24·0 (ref. 10)	25·8	22·5 (ref. 10)	21·7
13	22·1 (ref. 10)	25·1	20·7 (ref. 10)	21·3
14	26·4 (ref. 10)	26·7	22·7 (ref. 10)	22·6

[a] Spectra for compounds **12–14** were recorded in toluene; spectra for all other compounds were recorded in ethanol.
[b] No fluorescence.[6]

seems to be rather common in the series of coumarin derivatives.[11] Of course an improvement would be possible by an optimization of the empirical parameters of the amino group used in the PPP calculation, viz. valence state ionization potential, resonance integral and electron repulsion integrals. As has been pointed out by Griffiths[1] such an empirical adjustment of parameters certainly will result in a loss of generality of the method. In order to maintain generality, therefore, no such parameter optimization has been performed in agreement with the proposal of Griffiths.[1] The predictive accuracy of the method described above is further confirmed by a comparison of the experimental and calculated fluorescence maxima of compounds **15–20** shown in Table 3.

Besides an accurate prediction of absorption as well as fluorescence spectra of organic dyes theoretical methods can also be used for an at least semiquantitative explanation of the Stokes shift—a quantity of considerable interest in practical applications of fluorescent compounds. Since the geometrical changes upon excitation leading to the observed

TABLE 3
Experimental and Calculated Fluorescence maxima (in $10^3\,cm^{-1}$) of compounds **15–20**

Compound	$\tilde{\nu}_{flu}$		*Compound*	$\tilde{\nu}_{flu}$	
	Exp.[a]	*Calc.*		*Exp.*[a]	*Calc.*
15	21·8	21·8	**18**	18·2	19·5
16	22·7	22·2	**19**	22·2	22·2
17	20·2	20·2	**20**	20·2	20·3

[a] The experimental values are taken from ref. 9.

differences in the absorption and fluorescence maxima are accompanied by a corresponding change in the electronic structure the magnitude of the Stokes shift may be estimated from the different electron distributions in ground and excited states. A convenient measure for the description of this difference in electronic structure is provided by the Julg index[12] defined by

$$A = A_1 \cdot A_2 \tag{3}$$

$$A_1 = 1 - \frac{225}{n} \sum_{\mu\nu} (1 - R_{\mu\nu}/\bar{R})^2 \tag{4}$$

$$A_2 = \prod_{\mu\nu} [1 - (q_{\mu\nu}/R_{\mu\nu})^2] \tag{5}$$

and which was successfully applied to related problems.[5,13,14] In eqn (4) the quantity $R_{\mu\nu}$ is the bond length between centres μ and ν and $\bar{R}$ is the mean bond length. The summation is over all peripheral bonds, the number of which is denoted by n (cf. eqn (4)). In eqn (5) $q_{\mu\nu}$ denotes the difference of the charge densities of the two centres μ and ν and the product $\prod_{\mu\nu}$ again is over all peripheral bonds. The quantity A_1 (eqn (4)) describes the effect of a bond equalization whereas the quantity A_2 (eqn (5)) is a measure of the charge equalization. Using bond lengths and charge densities of the first excited (S_1) and ground state (S_0), respectively, $A(S_1)$ and $A(S_0)$ were calculated separately. The difference $\Delta A = A(S_1) - A(S_0)$ together with the experimental Stokes shifts for compounds **1–14** (except **4**, for which no fluorescence could be detected[6]) are collected in Table 4.

From these data it can be seen that compounds **1–3** which show an

TABLE 4
Difference ΔA of the Julg Index and Experimental Stokes Shifts $\Delta\tilde{\nu}$ (in $10^3\,cm^{-1}$)

Compound	ΔA	$\Delta\tilde{\nu}$	*Compound*	ΔA	$\Delta\tilde{\nu}$
1	0·208	6·8	**9**	0·099	3·1
2	0·158	6·1	**10**	0·058	3·0
3	0·101	7·6	**11**	0·076	3·9
5	0·027	4·6	**12**	0·017	1·5
6	0·035	2·6	**13**	0·008	1·4
7	0·067	3·2	**14**	0·044	3·7
8	0·082	2·8			

unusually large Stokes shift ($\Delta\tilde{\nu} > 6000\,cm^{-1}$) are characterized by a relatively large value of ΔA (in ref. 13 $\Delta A > 0{\cdot}1$ was considered as critical value for the occurrence of $\Delta\tilde{\nu} > 5000\,cm^{-1}$), whereas compounds **12** and **13** with a rather low magnitude of $\Delta\tilde{\nu}$ (cf. Table 4) show a negligible change in electronic structure upon excitation, as evidenced by the corresponding ΔA values. The remaining molecules listed in Table 4 have Stokes shifts in the intermediate range ($\Delta\tilde{\nu} = 2600$–$4600\,cm^{-1}$). Correspondingly, their ΔA values lie between the two above-mentioned extremes ($\Delta A = 0{\cdot}027$–$0{\cdot}099$). Overall the correlation between $\Delta\tilde{\nu}$ and ΔA is quite reasonable ($r = 0{\cdot}936$).

4. CONCLUSIONS

The PPP-method may be regarded as a routine method for the calculation of absorption maxima of conjugated molecules. As has been demonstrated by Griffiths[1] on a wide variety of organic dye molecules the predictive power of this method may be very helpful in the search for new chromogens. Much less attention has been paid to the calculation of fluorescence maxima. In the foregoing it has been shown that the PPP-method combined with the β-variation procedure of Fratev[3] may equally well be used for the prediction of fluorescence transitions. Due to the increasing interest in efficient optical brighteners as well as laser dyes this method should be quite useful for practical applications in this field of dye chemistry.

REFERENCES

1. J. Griffiths, *Dyes and Pigments*, **3** (1983) 211.
2. R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21** (1953) 466,767; J. A. Pople, *Trans. Faraday Soc.*, **49** (1953) 1375.
3. F. Fratev, G. Hiebaum and A. Gochev, *J. Mol. Struct.*, **23** (1974) 437; F. Fratev, *Z. Naturforsch.*, **30a** (1975) 1691.
4. A. Mehlhorn, B. Schwenzer and K. Schwetlick, *Tetrahedron*, **33** (1977) 1483, 1489.
5. W. Fabian, *Z. Naturforsch.*, **35a** (1980) 428; W. Fabian, *J. Mol. Struct.*, **69** (1980) 227.
6. C. Y. Chen and T. E. Gompf, *Heterocycles*, **7** (1977) 933.
7. O. S. Wolfbeis, *Z. Naturforsch.*, **32a** (1977) 1065.
8. O. S. Wolfbeis, *Monatsh. Chem.*, **113** (1982) 365.
9. A. Knierzinger and O. S. Wolfbeis, *J. Heterocyclic Chem.*, **17** (1980) 225.
10. H.-W. Schmidt, R. Schipfer and H. Junek, *Liebigs Ann. Chem.* (1983) 695.
11. H. Nakazumi and T. Kitao, *8th International Congress of Heterocyclic Chemistry*, Graz, 1981.
12. A. Julg, *The Jerusalem Symposia on Quantum Chemistry and Biochemistry*, **3**, 383, ed. E. Bergmann and B. Pullman. Jerusalem, The Israel Academy of Sciences and Humanities, 1971.
13. P. Nikolov, F. Fratev, S. Stojanov and O. E. Polansky, *Z. Naturforsch.*, **36a** (1981) 191.
14. F. Fratev, V. Monev, O. E. Polansky, S. Stojanov and N. Tyutyulkov, *Z. Naturforsch.*, **32a** (1977) 178.