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A Study on 6-Hydroxyfluorone Using a Modified PPP–CI Method

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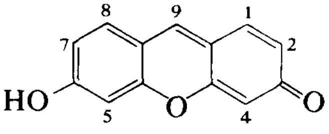
SUMMARY

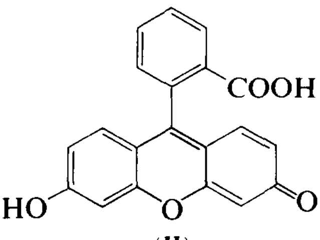
6-Hydroxyfluorone was studied using a modified PPP–CI method and standard parameters. The calculated results of the different states were compared with the experimental data recorded in different solutions. It was found that the spectral data showed very good consistency and that the gas phase data were acceptable. Other data, including those on the first excited state, are also presented.

1 INTRODUCTION

6-Hydroxyfluorone (HF) (**I**) is the basic model system for the xanthene dyes and these compounds are also widely used in, for example, dye lasers,[1] solar energy systems[2–4] and redox reactions.[4–8] In this study, the different states of HF were treated using a modified PPP–CI method. The calculated results were compared with the experimental data from fluorescein (FL) (**II**), a typical xanthene dye. They show good comparability.



(I)



(II)

Dyes and Pigments 0143-7208/87/$03·50

2 COMPUTATION METHOD AND PARAMETERIZATION

For the large conjugated systems present in organic dyes, the PPP–CI method is a most suitable one when using a minicomputer. The Fock matrix elements of the Roothaan equations consist of

$$\begin{aligned} F_{rr} &= H_{rr} + 0{\cdot}5P_{rr}\gamma_{rr} + \sum P_{ss}\gamma_{rs} \\ &= -I_r + 0{\cdot}5P_{rr}(I_r - A_r) + \sum P_{ss}\gamma_{rs} \qquad (1) \end{aligned}$$

$$F_{rs} = H_{rs} - 0{\cdot}5P_{rs}\gamma_{rs} = \beta_{rs} - 0{\cdot}5P_{rs}\gamma_{rs} \qquad (2)$$

where[9]

$$\begin{aligned} \gamma_{rs} &= 14{\cdot}39(\gamma_{rr} + \gamma_{ss})/[(\gamma_{rr} + \gamma_{ss})R_{rs} + 28{\cdot}78] \\ &= 14{\cdot}39(I_r - A_r + I_s - A_s)/[(I_r - A_r + I_s - A_s)R_{rs} + 28{\cdot}78] \qquad (3) \end{aligned}$$

The modification is that the variable atomic distance (R_{rs}) and resonance integral (β_{rs}) participate in the self-consistency of the generalized density matrix (P_{rs}). In HF there are three fused rings, and hence[10]

$$R_{cc} = 1{\cdot}517 - 0{\cdot}18P_{rs}(A) \qquad (4)$$

$$\beta_{cc} = -1{\cdot}84 - 0{\cdot}51P_{rs} \qquad (5)$$

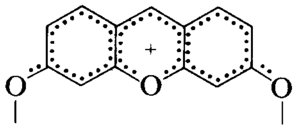
$$R_{co} = 1{\cdot}410 - 0{\cdot}18P_{rs}(A) \qquad (6)$$

$$\beta_{co} = 2{\cdot}20 - 0{\cdot}56P_{rs} \qquad (7)$$

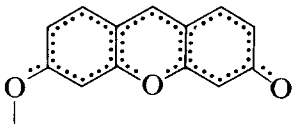
The only parameters which should be carefully chosen are the valence state ionization potential (I_r) and the electron affinity (A_r) of the atoms in the molecule. From the comprehensive references available, almost no difference exists in these values for C in sp^2 hybridization, but different values for other atoms have been recommended by various workers (e.g. refs 11 and 12), most of them being drawn from spectral data. In fact, I_r and A_r are not the properties of the atom in the free state, but the properties of the atom in the valence state in the molecule. Hinze and coworkers have carried out systematic studies based on theoretical foundations[13–16] and the I_r and A_r values calculated by them may be regarded as standard values. Hinze's values also include those for a variety of different atoms and ions in different states. Suitable parameters can be selected provided that the valence state of the atom in the molecule is known. As a semi-empirical method, the values are generally satisfactory for use in semi-quantitative predictions.

3 RESULTS AND DISCUSSION

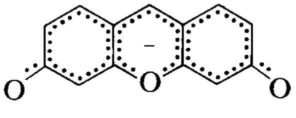
6-Hydroxyfluorone and its derivatives exist in cationic (HFC), neutral (HF) and anionic (HFA) forms in different solutions under various pH conditions.[17–19] The models used for computation are as follows:



(HFC)



(HF)



(HFA)

In fluorescein (FL), the 9-*o*-carboxyphenyl substituent is not coplanar with the chromophore and therefore its influence on the absorption is not significant. The experimental data from FL can thus be used for comparison with the calculated results for HF.

In acidic solution, the hydroxy group cannot be associated and therefore HFC is taken as the model, whilst HFA is the model in basic solution, in which the hydroxy group can associate. Some calculated results and experimental spectral data are shown in Table 1, where 'state' is the form of HF in solutions at different pH values, E_s^{PPP} is the singlet energy calculated by the PPP method, E_s^{CI} is the CI result from 5 × 5 levels, OS_s is the calculated oscillator strength, λ_{max} is the wavelength of maximum absorption of FL in acidic, neutral and basic MeOH solutions measured by us (see Fig. 1) and E_s is the corresponding energy value, and ε is the extinction coefficient.

It is apparent from the data in Table 1 that both the calculated energies and the absorption strengths correspond very well with the experimental values in each state. It is also noted that the CI treatment improves the prediction of the absorption values.

The gas-phase constants IP and EA are defined as

$$\mathrm{IP} = E_{ox} + \Delta E_{solv}^{+} - C \qquad (8)$$

$$\mathrm{EA} = E_{R} - \Delta E_{solv}^{-} - C \qquad (9)$$

in which ΔE_{solv}^{+} and ΔE_{solv}^{-} are the differences in real solvation energies between the oxidized and reduced form of the dye in solution and the original molecule in the gas phase which were found to be *ca* 1·84 and 1·81 eV, respectively. The constant C is related to the reference electrode and the solvent and is −4·51 eV for Ag/AgCl (satd KCl) in MeOH.[20] E_{ox} and E_R were measured by us and found to be 0·90 and −1·13 eV, respectively, and hence

TABLE 1

State	E_s^{PPP} *(eV)*	E_s^{CI} *(eV)*	OS_s	λ_{max} *(nm)*	E_s *(eV)*	$\varepsilon \times 10^{-5}$ *(litre cm^{-1} mol^{-1})*
HFC	3·01	2·77	0·68	441	2·81	0·67
HF	2·74	2·48	0·53	493	2·51	0·46
HFA	2·68	2·47	0·78	494	2·51	0·97

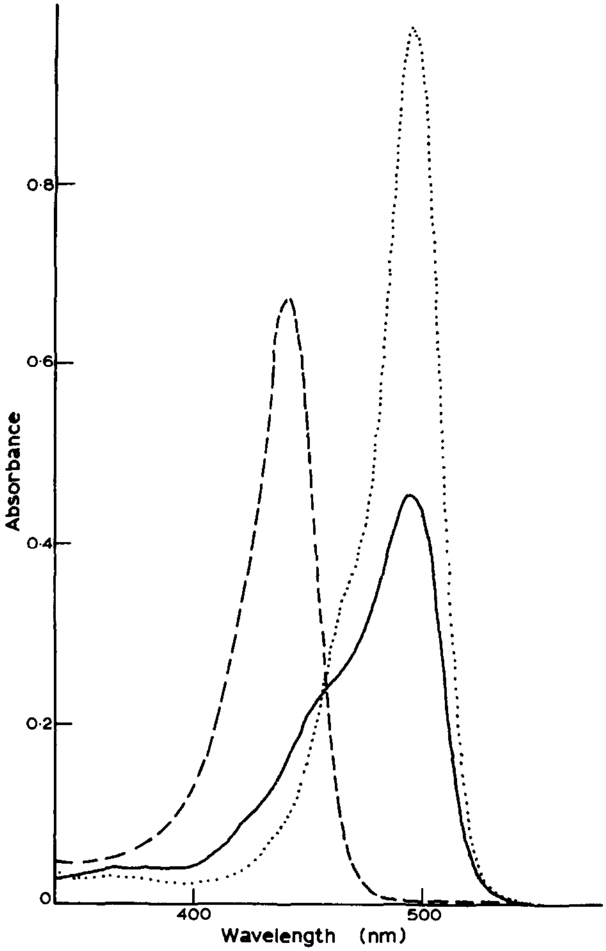


Fig. 1. The absorption spectra of FL in neutral solution (——), in acidic solution (– – –) and in basic solution (···).

IP = 7·25 eV and EA = 1·57 eV. Considering the uncertainty of the ionization potential and the electron affinity in both experimental and calculated measurements,[21] the calculated IP and EA values of 7·94 and 2·82 eV, respectively, by this method are acceptably close to the measured values.

Other data to be checked are listed in Table 2, where E_{pi} represents the total π-electron energy (eV), $E_{\mathrm{T}}^{\mathrm{PPP}}$ is the triplet energy calculated by the PPP method (eV), $E_{\mathrm{T}}^{\mathrm{CI}}$ is the CI result of triplet energy (eV), OS_{T} is the oscillator strength of the triplet transition, and α_{s} and α_{T} are the angles of singlet and triplet transition vectors to the x- (long) axis, respectively.

On the basis of the assumption that the conformation of the molecule remains the same as in the ground state, some first excited state

TABLE 2

State	$-E_{pi}$ *(eV)*	E_T^{PPP} *(eV)*	E_T^{CI} *(eV)*	OS_T	α_s *(deg.)*	α_T *(deg.)*
HFC	264·0	1·85	1·39	0·81	0	0
HF	254·3	1·45	1·06	0·58	178	−170
HFA	242·5	1·54	1·29	0·86	180	180

characteristics were computed and are compared with the ground state values in Table 3. P_{max}, P_{min} and P_{FV} are the positions possessing the maximum and minimum electron density and the highest free valence, respectively, and therefore should be the possible substitution positions for electrophilic, nucleophilic and radical reactions, respectively; μ is the dipole moment (D), α_μ the angle of the dipole moment to the x-axis, and the symbol * refers to the excited state.

TABLE 3

State	P_{max}	P^*_{max}	P_{min}	P^*_{min}	P_{FV}	P^*_{FV}	μ *(D)*	μ^* *(D)*	α_μ *(deg.)*	α^*_μ *(deg.)*
HFC	4, 5	9	9	2, 7	4, 5	9	5·44	9·36	−90	−90
HF	4	4	9	5	5	5	13·48	8·47	−1	−37
HFA	4, 5	9	9	2, 7	4, 5	9	5·30	1·14	90	90

It can be deduced from Table 3 that in HFC(acidic), HF(neutral) and HFA(basic solution) the positions having the highest π-electron density and free valence are the 4- and 5-positions, followed by positions 2 and 7. These positions would therefore be expected to be attacked first by electrophilic reagents and free radicals. That is in fact observed in the halogenation of fluorescein. Position 9, on the other hand, is the most electron-deficient, and hence nucleophilic substitution should occur at this position. On the same basis, this also implies that pH should not affect the positions of substitution in HF.

It may also be seen from the data above that, in general, there exist differences in density distributions between the ground state and excited states, and changes also take place in the positions which have the highest free valence. Both the magnitude and the direction of the dipole moments of the excited states are different from those of the ground state. It can therefore be expected that the photochemical behaviour in the excited states will be different from the general chemical reactions which occur in the ground state.

4 EXPERIMENTAL

The 6-hydroxyfluorone used was of analytical grade from Beijing Chemical Works.

Absorption data were recorded on a Model 557 spectrophotometer (Hitachi Co. Ltd, Japan) in neutral (10^{-5} M-FL in MeOH), acidic (adding *ca* 0·5 M-HCl) and basic (adding *ca* 0·5 M-NaOH) solution.

Potentials were obtained using a cyclic voltammeter Model 79-1 (Jinan Electronic Factory IV, China) using 10^{-3} M-sample in MeOH with 0·1 M-LiCl as electrolyte.

REFERENCES

1. K. H. Drexhage, in: *Dye lasers*, 2nd revised edn, ed. F. P. Schafer, pp. 144–93. New York, Springer-Verlag (1977).
2. M. S. Chan and J. R. Bolton, *Solar Energy*, **24**, 561 (1980).
3. H. Misawa, H. Sakuragi, Y. Usui and K. Tokumaru, *Chemistry Letters*, 1021 (1983).
4. T. Shen, *Huaxue Tongbao (Chemistry)*, (6), 34 (1984).
5. K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).
6. Y. Usui and H. Enokido, *Bull. Chem. Soc. Japan*, **46**, 2741 (1973).
7. H. J. Xu and S. Y. Shen, *Acta Chim. Sinica*, (2), 148 (1985).
8. H. J. Xu and S. Y. Shen, *Huaxue Xuebao*, **43**, 757 (1985).
9. K. Nishimoto and N. Mataga, *Z. Physik. Chem. (Frankfurt)*, **12**, 335 (1957).
10. K. Nishimoto and L. Forster, *Theor. Chim. Acta (Berlin)*, **4**, 155 (1966).
11. J. Kuthan, I. Danihel and V. Skala, *Coll. Czech. Chem. Commun.*, **43**, 447 (1978).
12. J. Griffiths, *Dyes and Pigments*, **3**, 211 (1982).
13. J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962).
14. J. Hinze, M. A. Whitehead and H. H. Jaffe, *J. Amer. Chem. Soc.*, **85**, 148 (1963).
15. J. Hinze and H. H. Jaffe, *Can. J. Chem.*, **41**, 1315 (1963).
16. J. Hinze and H. H. Jaffe, *J. Phys. Chem.*, **67**, 1501 (1963).
17. K. K. Rohatgi, *J. Indian Chem. Soc.*, **42**, 737 (1965).
18. F. M. Abdel-Halim, R. M. Issa and A. A. Hasanein, *UAR J. Chem.*, **14**, 275 (1971).
19. M. M. Martin and L. Lindavist, *J. Luminesc.*, **10**, 381 (1975).
20. R. O. Loutfy and J. H. Sharp, *Photogr. Sci. Eng.*, **20**, 165 (1976).
21. H. A. Hammond, *Theor. Chim. Acta (Berlin)* **18**, 239 (1970).