Dyes and Pigments, Vol. 35, No. 1, pp. 31–44, 1997
© 1997 Elsevier Science Ltd. All rights reserved
Printed in Great Britain
PII: S0143-7208(96)00092-7 0143-7208/97 $17.00+0.00

Structure and Properties of Fluorescent Reactive Dyes: Electronic Structure and Spectra of Some Benzanthrone Derivatives

M. Nepraš,[a] O. Machalický,[a] M. Šeps,[a] R. Hrdina,[a] P. Kapusta[b]* & V. Fidler[b]

[a]Department of Organic Technology, University of Pardubice, Pardubice, Czech Republic
[b]Department of Physical Electronics, Czech Technical University in Prague, Prague, Czech Republic

(Received 2 August 1996; accepted 10 September 1996)

ABSTRACT

Absorption and fluorescence spectra of N-(disubstituted-1,3,5-triazinyl)-3-aminobenzanthrones, 3-acetylaminobenzanthrone and 3-methoxybenzanthrone have been investigated. Excitation energies and the character of the first absorption band have been calculated by the PPP-MO method. Some data on substituent and solvent effects on fluorescence spectral position and quantum yields are reported. The connection between electron density distribution in the electronic ground and excited state, and spectroscopic properties of those compounds, is explained. © 1997 Elsevier Science Ltd

Keywords: benzanthrone derivatives, fluorescence and absorption spectroscopy, PPP-MO calculations, electron density alterations.

INTRODUCTION

Reactive organic dyes contain a reactive chemical group capable of forming a covalent bond with a substrate. This chemical bonding provides a strong fixation of a dye to a substrate material. Due to their specific colouristic and fluorescence properties, such dyes are of a great importance in both scientific and industrial uses. There is a widespread application of reactive fluorescent

---

*Corresponding author.

dyes in analytical chemistry and biochemistry; the dyes are used as fluorescent probes in molecular and cell biology (and recently for fluorescence lifetime imaging), [1, 2] etc.

The linkage of a reactive group to a chromophoric system can change the spectral, photochemical, and photophysical properties of the original chromophore. On the basis of structure–colour relationship, the influence of the reactive group on colouristic data (steady state absorption) can be predicted reasonably well. The situation becomes more complicated when the main interest is on fluorescence properties, e.g. when a reactive dye is to be used as a fluorescent probe, pigment or optical brightening agent. Then, the understanding of the reactive group influence on the chromophore–substrate fluorescence properties is essential. Many experimental data indicate that fluorescence emission characteristics (lifetimes and quantum yields) are more sensitive to the presence of reactive chemical group. Their theoretical predictions are rather difficult and not very reliable so far. It is therefore important to study them experimentally.

We have been interested in polynuclear aromatic systems coupled with more or less selective reactive groups (for example 1,3,5-triazinyl-, isothiocyanato-, maleimidyl- and photoreactive azido-groups), and in a subsequent study of their reactivity, spectral, photophysical, and photochemical properties. These dyes serve as model compounds, and some of them are intended to be used as fluorescence labels and/or crosslinking reactive fluorescent dyes. In particular, here we are dealing with N-(dichloro-, chloromethoxy-, and dimethoxy-triazinyl)-3-aminobenzanthrones (*ABaTC2*, *ABaTCM* and *ABaTM2*, respectively). For comparison, the properties of unsubstituted 3-aminobenzanthrone (*ABa*), N-acetyl-3-aminobenzanthrone (*ABaAc*) and 3-methoxybenzanthrone (*BaM*) are also discussed (Fig. 1).

Only a few papers on the absorption and luminescence properties of substituted benzanthrones have been published. Krasovitskii and Bolotin [3] referred to the work of Levtschenko [4] on dyeing of polyamide with the products of the condensation of *ABa* with epichlorhydrin and with cyanuric chloride, the former dyeing the polyamide red, and the latter yellow. Bentley *et al.* [5] studied the absorption and luminescence characteristics of benzanthrone and its amino- and hydroxy-derivatives, but 3-aminobenzanthrone (*ABa*) is not mentioned in their work. He explained the solvent effect on the fluorescence quantum yield with respect to a change of the sequence of excited states of different configuration and multiplicity [6]. The interpretation of the dramatic decrease in the fluorescence quantum yields of N-phenyl-aminobenzanthrones in polar solvents was based on a hypothesis that the excited state decays from a planar CT form, mainly by nonradiative deactivation within the singlet manifold, in analogy with Kosower's model for 2-N-arylamino-6-naphthalenesulfonates [7].

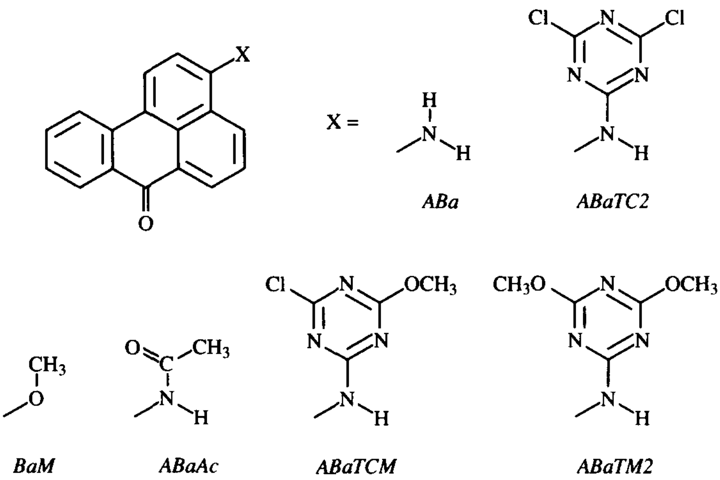

Fig. 1. Structure of compounds studied.

Ayyangar et al. [8] prepared *ABaTC2* by condensation of *ABa* with cyanuric chloride in chlorobenzene at 140°C. Substituting both chlorines with alkoxy and amino groups, bright yellow disperse dyes for synthetic fibres were obtained. Absorption, NMR, and mass spectra of the dyes were measured and interpreted, but no fluorescence properties were mentioned.

Bushtchuk *et al.* [9] investigated the influence of intramolecular hydrogen-bonding on the absorption and fluorescence spectra of *ABa* and N-cyclohexyl-3-aminobenzanthrone. Deviations from linear dependence of absorption and emission maxima on solvent polarity in alcoholic solvents were analysed, and strengths of the H-bond in the ground and first excited states were estimated.

Afanasiadi *et al.* [10] discussed the influence of amino group in positions 2, 3, or 4 on the fluorescence of corresponding aminobenzanthrones, without presenting any quantitative data for more solvents. They stated that acylation of the amino group results in a strong decrease of fluorescence intensity, in comparison with corresponding amines.

In this work we present the synthesis and the explanation of the spectral properties of selected benzanthrone derivatives substituted in position 3. This paper is the first of a series devoted to the experimental and theoretical studies of the spectral and photophysical characteristics of reactive fluorescent dyes.

EXPERIMENTAL

Syntheses

ABa was prepared by reduction of 3-nitrobenzanthrone in a solution of sodium sulphide in water. Under stirring, the mixture was heated and kept boiling for 2 h. The crude product was washed with hot water, dried and crystallised from 80% ethanol.

3-Nitrobenzanthrone was prepared by nitration of benzanthrone with 87% nitric acid in nitrobenzene at 50°C for 2 h. The reaction mixture was cooled and diluted with ethanol. The precipitated crude product was filtered, washed with ethanol and water and crystallised from acetic acid.

ABaAc was prepared by acetylation of *ABa* with acetic anhydride by standard procedures. The product was recrystallised from ethanol.

ABaTC2 was prepared from *ABa* and cyanuric chloride in acetone containing a small amount of water and sodium hydrogencarbonate by stirring at 15–20°C for 90 min. The crude product was washed with ethanol and water, dried and recrystallised from toluene.

ABaTCM was prepared from *ABa* and dichloromethoxy-1,3,5-triazine in acetone in the presence of aqueous sodium hydroxide by stirring at 45–50°C for 90 min. The crude product was precipitated from the reaction mixture by addition of water, and was filtered, washed with water, dried and recrystallised from toluene.

ABaTM2 was prepared by dissolving *ABaTC2* in DMI (1,3-dimethyl-2-imidazolidinone) and adding 30% sodium methanolate. The reaction mixture was stirred at room temperature for 12 h. The mixture was than poured into water. The separated crude product was washed with water, dried and recrystallised from toluene.

BaM was isolated from C.I. Disperse Yellow 13, C.I. No. 58900 [11] and crystallised from ethanol.

The purity of all substances was checked by TL and HPL chromatography. The physical properties of the compounds are summarised in Table 1.

Spectra

Absorption spectra were measured on a Perkin–Elmer 555 spectrophotometer. Typical concentrations were of the order of 10^{-5} M, which yielded optical density ≈ 0.5 at the main absorption maximum in a 1 cm cuvette.

Steady-state fluorescence spectra were measured using a Hitachi Perkin–Elmer LS 5 spectrofluorometer. The instrument provides corrected excitation spectra directly; the fluorescence emission spectra were corrected for the characteristics of the emission monochromator and the photomultiplier response. During fluorescence measurements, very weakly absorbing solutions (optical density ≈ 0.05 at the exciting wavelength in 1 cm cuvette) were used. The fluorescence quantum yields were measured using quinine sulphate ($q_{Fl.} = 0.54$ in 0.1 N H_2SO_4) [12] or perylene ($q_{Fl.} = 0.89$ in benzene) [12] as standards. Deoxygenation of the samples by bubbling through N_2 or Ar did

TABLE 1
Melting Points (m.p.) and Results of Elemental Analyses

	Literature *Experimental*	*Calculated* *Experimental*			
	m.p. (°C)	*%C*	*%H*	*%N*	*%Cl*
ABa	240 [ref. [18]]	83.25	4.52	5.71	
	240	*83.31*	*4.44*	*5.80*	
ABaTC2	340 [ref. [8]]	61.09	2.56	14.25	18.03
	>320	*61.17*	*2.61*	*14.16*	*17.94*
ABaTCM	—	64.87	3.37	14.41	9.12
	234–236	*64.92*	*3.29*	*14.49*	*9.00*
ABaTM2	205 [ref. [8]]	68.74	4.20	14.58	
	204	*68.68*	*4.11*	*14.66*	
ABaAc	280 [ref. [19]]	79.43	4.56	4.87	
	279	*79.51*	*4.61*	*4.80*	
BaM	173 [ref. [17]]	83.06	4.65		
	172	*82.99*	*4.59*		
3-Nitro-benz-	244 [ref. [18]]	74.18	3.30	5.09	
anthrone	*244–245*	*74.13*	*3.21*	*5.15*	

not make any difference in spectra and quantum yield recorded, and therefore the reported data correspond to aerated solutions.

The samples for fluorescence measurements were prepared by preparative TL chromatography on silica gel. All solvents used were of spectral grade and were checked for their own fluorescence under relevant conditions.

Semi-empirical calculations

Semi-empirical calculations were performed on a PC compatible computer using the software package PISYSTEM. The core of this package is an SCF-MO calculation routine based on PPP approximation, comprising CI calculation of 36 singly excited states [13, 14]. Application of PPP method for the calculation of electronic structure and spectra of conjugated molecules has proved to be fruitful and more accurate than many recent NDO based methods [15, 16].

RESULTS AND DISCUSSION

Parent fluorophore

Compound *ABa*, 3-aminobenzanthrone, is an aromatic molecule containing an electron-donating amino group and an electron-accepting carbonyl group in mutual conjugation. The steady-state absorption and fluorescence emission spectra in two solvents of different polarity are shown in Fig. 2 . The two solvents—dibuthylether (DBE) and acetonitrile (ACN)—were chosen for the following reasons: (a) they differ in polarity sufficiently, (b) both are aprotic and non-aromatic in order to avoid possible effects of H-bond formation, and/or π-π solute–solvent interactions, (c) dibuthylether is the least polar of all solvents in which all the compounds studied were sufficiently soluble.

The first absorption band in the absorption spectrum corresponds to the $S_0 \rightarrow S_1$ transition with a partial charge transfer (CT) character. The spectra in Fig. 2 support this conclusion: both absorption and emission bands are broad and structureless. The absorption maximum is shifted by 910 cm^{-1} to the red with increasing solvent polarity, and the emission maximum shows a 1574 cm^{-1} bathochromic shift with the same polarity change. Corresponding Stokes shifts are 3776 cm^{-1} and 4440 cm^{-1}, respectively.

$S_0 \rightarrow S_1$ transition energies, calculated for a completely nonpolar environment are 22,460 cm^{-1} for planar, and 24,496 cm^{-1} for pyramidal amino nitrogen, respectively. The experimental value is 21,320 cm^{-1} in dibutylether. Taking into account the polarity influence mentioned above, the agreement of the theoretical value, supposing planar nitrogen, and the experimental value in the low-polarity DBE, can be considered as quantitative. This fact allows us to discuss even further data calculated in this way for a structure with planar sp^2 nitrogen. Electron density alterations on excitation for *ABa* and of benzanthrone itself are depicted on Fig. 3.

Increase of the electron density on excitation takes place on the carbonyl group and carbon atoms in position 5 and 7, that effectively act as an

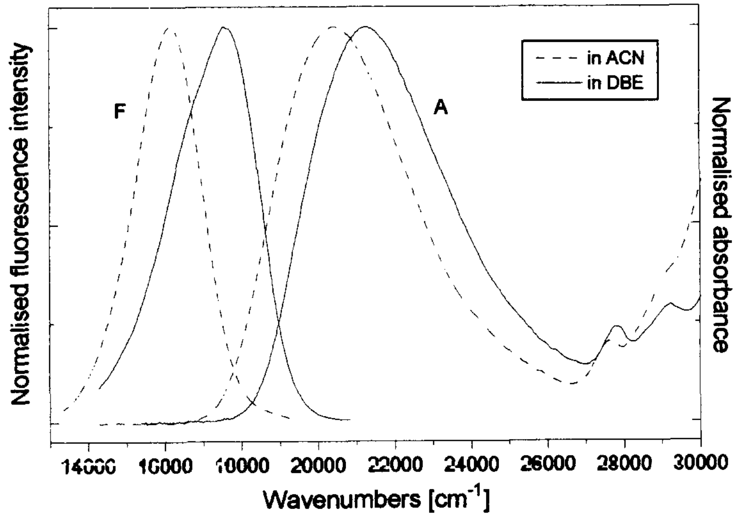

Fig. 2. Steady-state absorption (A) and fluorescence emission (F) spectra of *ABa* in acetonitrile (ACN) and in dibuthylether (DBE).

acceptor site of the molecule. An important difference can be seen on the donor sites of the two molecules; while in the case of benzanthrone the electron density is supplied from 'top side' carbon atoms (at positions 2, 3, 12, 14, 16), then there exists one main source of electron density in the case of *ABa*, and that is the amino nitrogen (with some contributions from carbons 2 and 16 only).

We can therefore say, that the charge redistribution described above is the main photophysical process taking place on excitation, and the property of a substituent on position 3 controls this process. Consequently, it is to be expected that any change of the electron donating properties of the substituent (e.g. chemical substitution of amino hydrogen, etc.) will significantly influence photophysical characteristics.

Triazine-substituted 3-aminobenzanthrones

Three compounds (*ABaTC2*, *ABaTCM*, and *ABaTM2*) were studied: they differ in the functional groups attached to the triazine moiety. Steady-state absorption and fluorescence emission spectra of *ABaTCM* in (low-polar) DBE and (polar) ACN are depicted on Fig. 4.

It is interesting to note that the *ABaTCM* absorption band is blueshifted by 3430 cm^{-1} in DBE, and by 4160 cm^{-1} in ACN, in comparison with that of *ABa* in the same solvents. Moreover, the absorption maxima positions do not depend on solvent polarity. Fluorescence emission behaviour is different; the emission band shows a considerable bathochromic shift with increasing solvent polarity, indicating that the molecular dipole moment increases on excitation. The other two substances, *ABaTC2* and *ABaTM2* behave in a similar way (see spectral data summarised in Table 2).

Bearing in mind the photophysics of *ABa* suggested previously, we can explain the main features of the steady-state spectroscopic data in the

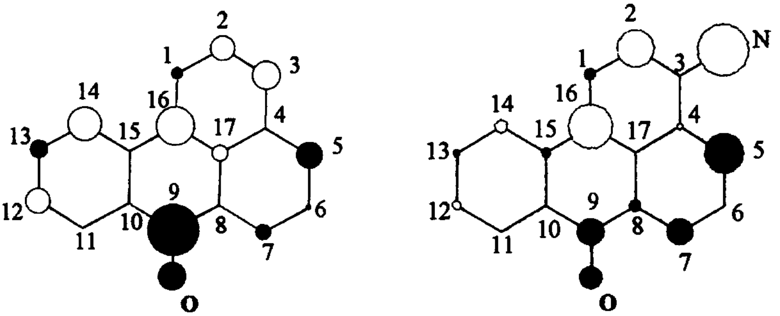

Fig. 3. Electron density alterations on excitation into the S_1 state of benzanthrone and the parent fluorophore *ABa*. White/black circles indicate decrease/increase of electron density. The size of the circles is normalised in each scheme separately.

following way: attachment of an electronegative triazine moiety leads to competition between this substituent and the acceptor site of the molecule mentioned above, and consequently to a new electron density distribution in the ground state. What will this competition cause in the excited state? The hypsochromic shift of the absorption band and low sensitivity of the absorption maxima to solvent polarity suggest a decrease of the CT character of the $S_0 \rightarrow S_1$ transition. Calculated electron density alteration on excitation for *ABaTC2* is depicted on Fig. 5. The pattern is nearly identical to that of *ABa* (see Fig. 3); there is no noticeable electron density change on the triazine moiety. This implies that the main process controlling the photophysical properties, even in substituted aminobenzanthrone derivatives, is the electron density transfer from the amino nitrogen to benzanthrone ring, the extent of which can also depend on the triazine substituents.

As chlorine is electronegative, while the methoxy group is an electron donor, it could be expected that the magnitude of the CT from the amino nitrogen to the benzanthrone skeleton increases in the order *ABaTC2* < *ABaTCM* < *ABaTM2*. Experimental steady-state spectroscopic data support that conclusion: stepwise substitution of chlorine for a methoxy group leads to a red shift of both absorption and emission bands (see Table 2).

Further analogues: *ABaAc* and *BaM*

As far as the above description of the photophysics of triazine-substituted *ABa* derivatives is correct, the spectroscopic properties of *ABaAc* could be

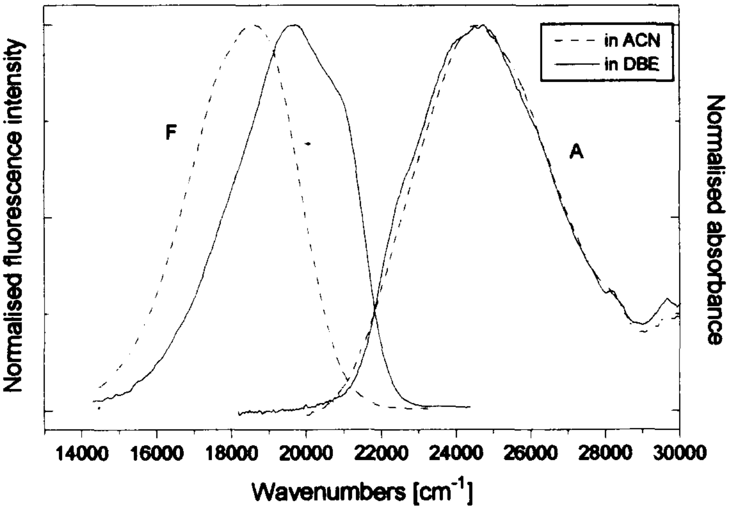

Fig. 4. Steady-state absorption (A) and fluorescence emission (F) spectra of *ABaTCM* in acetonitrile (ACN) and in dibuthylether (DBE).

TABLE 2
Steady-state Absorption Maxima ($\tilde{\nu}_{Abs.}$), Fluorescence Emission Maxima $\tilde{\nu}_{Fl.}$), Fluorescence Stokes Shifts ($\Delta\tilde{\nu}$), and Fluorescence Quantum Yields (q_{Fl}.) of the Compounds Studied in dibutylether (DBE) and in acetonitrile (ACN)

		ABa	*ABaTC2*	*ABaTCM*	*ABaTM2*	*ABaAc*	*BaM*
$\tilde{\nu}_{Abs.}$ (cm^{-1})	DBE	21,320	24,940	24,750	23,700	23,810	24,270
	ACN	20,410	24,810	24,570	24,160	24,100	23,470
$\tilde{\nu}_{Fl.}$ (cm^{-1})	DBE	17,540	20,160	19,720	19,380	19,720	20,530
	ACN	15,970	18,980	18,590	18,050	18,520	18,980
$\Delta\tilde{\nu}$ (cm^{-1})	DBE	3780	4780	5030	4320	4090	3740
	ACN	4440	5830	5980	6110	5580	4490
q_{Fl}.	DBE	0.34	0.015	0.055	0.22	0.065	0.010
	ACN	0.09	0.43	0.52	0.59	0.59	0.62

explained just by considering the acyl group as a different electronegative substituent on the amino nitrogen. There is an even broader analogy which should hold, namely, if we suppose that the property controlling the extent of charge redistribution to the benzanthrone skeleton is the electron donating strength of the amino nitrogen, then benzanthrone derivatives having another monocentric π-electron-donor substituent on position 3 should exhibit spectroscopic properties according to their electronegativity, comparing to that of the original amino group. As an example of such a compound, we studied 3-methoxybenzanthrone, *BaM*. The methoxy group is a weaker electron-donor than an unsubstituted amino group and therefore one could expect spectroscopic properties rather similar to those of the triazine substituted compounds mentioned previously. Relevant steady-state spectra are depicted on Fig. 6, and the main spectroscopic data are included in Table 2. As can be seen, not only are the spectral positions and bandshapes very similar, but trends in polarity dependencies for such different substances are also the same (compare Fig. 4 and Fig. 6). We take this consistency as evidence for the basic soundness of the mechanism suggested in this paper for benzanthrone derivatives substituted in position 3.

Theoretical results and general considerations

PISYSTEM allows the calculation of molecular parameters using either planar or pyramidal sp^2 amino nitrogen configuration, without the possibility of its optimisation. Values summarised in Table 3 correspond to the planar configuration. Though the absolute values of those parameters depend, to some extent, on the particular configuration chosen, it is to be stressed that trends of all parameters dependencies on the substituent are the same, independent of the N-configuration.

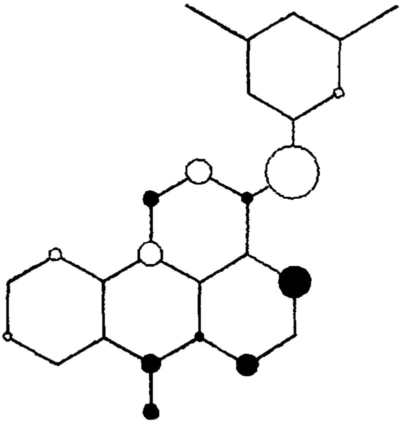

Fig. 5. Electron density alterations on excitation into the S_1 state of *ABaTC2*.

Calculated $S_0 \rightarrow S_1$ transition energies agree well with the experimental ones. Nevertheless, by using the planar configuration of amino nitrogen for all substances, the spectral position of the first absorption band for *ABa*

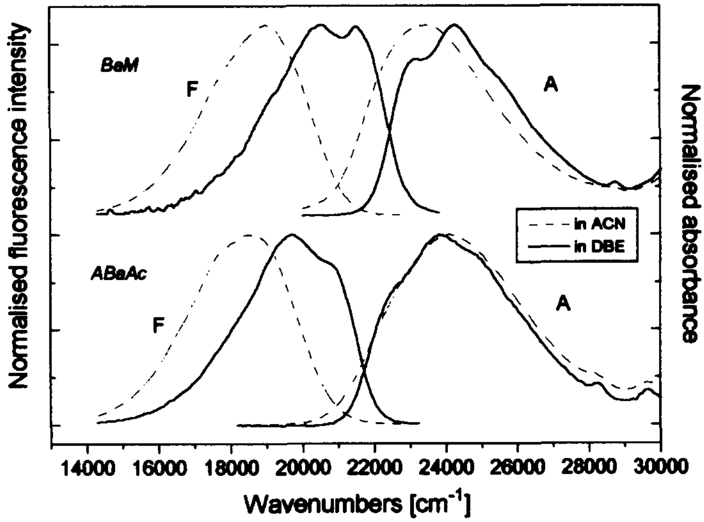

Fig. 6. Steady-state absorption and fluorescence emission spectra of *BaM* (top) and *ABaAc* (bottom) in acetonitrile (ACN) and in dibuthylether (DBE).

TABLE 3

Theoretical Spectral Position of the First Electronic Transition, π-Electron Densities and π-Bond Orders

		ABa	*ABaTC2*	*ABaTCM*	*ABaTM2*	*ABaAc*	*BaM*
$\tilde{\nu}(S_0 \rightarrow S_1)$ (cm^{-1})		22,460	23,211	23,053	22,909	23,816	24,823
Qπ (e$^-$)	Gr.	1.78	1.62	1.62	1.62	1.61	1.87
	Exc.	1.60	1.43	1.43	1.43	1.45	1.76
ΔQ(benz) (e$^-$)	Gr.	0.22	0.14	0.15	0.16	0.12	0.13
	Exc.	0.40	0.39	0.40	0.46	0.32	0.24
ΔQ(subst) (e$^-$)	Gr.	—	0.24	0.23	0.22	0.27	—
	Exc.	—	0.18	0.17	0.11	0.23	—
B.o.(benz)	Gr.	0.47	0.38	0.39	0.40	0.35	0.36
	Exc.	0.55	0.47	0.47	0.47	0.45	0.45
B.o.(subst)	Gr.	—	0.52	0.51	0.50	0.54	—
	Exc.	—	0.52	0.51	0.50	0.54	—

The abbreviations 'Gr.' and 'Exc.' denote the electronic ground and excited state, respectively. Qπ represents the π-electron density on donor atom, e.g. methoxy oxygen in case of *BaM*, amino nitrogen for other compounds; ΔQ(benz) represents the π-electron density transferred from the donor atom to the benzanthrone moiety; ΔQ(subst) represents the π-electron density transferred from the donor atom to the triazine or acyl group; B.o.(benz) represents the π-bond order between the donor atom and the benzanthrone carbon; B.o.(subst) represents the π-bond order between the amino nitrogen and the triazine (or acyl) carbon.

is predicted somewhat hypsochromicly, and for the other compounds somewhat bathochromicly. This could be explained by the fact that *ABa* has the highest CT character of the first transition.

As the N-substituent electronegativity increases, the amount of π-electron density transferred from the amino nitrogen to the N-substituent increases, and consequently, that transferred to the benzanthrone moiety decreases as clear indication of such behaviour is a trend in the calculated ΔQ(subst) and Q(benz) values of triazine substituted *ABa* derivatives; with the number of Cl atoms on triazinyl ring, ΔQ(subst) increases, and ΔQ(benz) decreases. This is noticeable in the electronic ground state, and is pronounced in the excited state.

The π-bond order was calculated for the bond between the donor atom (amino nitrogen or methoxy oxygen) and the benzanthrone carbon, which reveals the degree of conjugation between them. This bond order depends on the electron donating strength of the donor atom, and its substituent. On excitation, the conjugation between the donor atom and the benzanthrone carbon increases for all compounds, while that between the donor atom and its substituent remains unchanged.

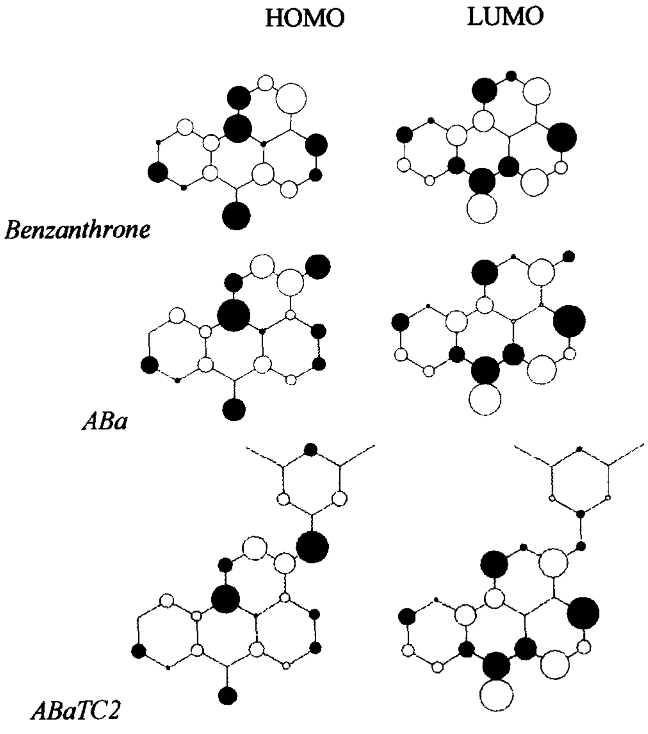

Fig. 7. Comparison of HOMO and LUMO orbitals of benzanthron, *ABa*, and *ABaTC2*.

The first electronic transition is almost a 'pure' 1,1′ transition and corresponds mainly (with 95% weight) to the electron transition from HOMO to LUMO for all substances under study, whereas the LUMO of all compounds corresponds practically to the LUMO of benzanthrone. The important contribution to HOMO of *ABa* and its derivatives is made by the 2pπ MO of amino nitrogen (Fig. 7).

Although there does not exist any simple and straightforward relation between the solute structure, its fluorescence quantum yield, and solvent polarity in general, the experimental data summarised in Table 2 indicate some general features. In spite of the fact that *ABa* is considered as a parent compound, spectroscopically it behaves very differently from any other substance of this family. For all the other compounds studied, the following observations hold:

1. fluorescence quantum yields differ (significantly) in polar and non-polar environment; going from dibuthylether to acetonitrile the $q_{Fl.}$ always increases
2. in polar acetonitrile (solvent with large dipole moment, medium dielectric constant and medium polarisibility) the $q_{Fl.}$ values of compounds having very different substituents at position 3, are high and close to each other (0.43–0.62)
3. in low polar dibuthylether (solvent with small dipole moment and dielectric constant, and with medium polarisibility) the $q_{Fl.}$ values are low and differing significantly (0.015–0.22).

Rigorous explanation of these interesting features of the fluorescence properties requires a more detailed discussion of the character and the energy of molecular states, as well as the microenvironment influence on the relative order of these states. Such discussion, supported by a broad range of photophysical data for various solvents, and accompanied by higher level quantum chemical calculations, will be reported later.

ACKNOWLEDGEMENTS

This work was supported by Research Grants No. 301/93/1100 and No. 104/95/1226 of the Grant Agency of the Czech Republic.

REFERENCES

1. Haugland, R. P., *Handbook of Fluorescent Probes and Research Chemicals*. Molecular Probes, Inc., 5th Ed., Eugene, OR, U.S.A. (1992–4).
2. Gadella, T. W., Jovin, T. M. and Clegg, R. M., *Biophysical Chemistry*, **48** (1993).

3. Krasovitskii, B. M. and Bolotin, B. M., Organic Luminophores. *Khimia, Moskva* (in Russian) (1984), 189.
4. Leftchenko, N. F., Afanasiadi, L. Sh. and Ostis, L. L., In *Scintillatory in Org. Luminophory* (in Russian). Kharkov (1972), pp. 17–23.
5. Bentley, P., McKellar, J. F. and Phillips, G. O., *Journal of the Chemical Society, Perkin Transactions II,* (1974) 523.
6. Bentley, P. and McKellar, J. F., *Journal of the Chemical Society, Perkin Transactions II,* (1976) 1850.
7. Kosower, E. M., Dodiuk, H., Tanizawa, K., Oholenghi, M. and Orbach, N., *Journal of the American Chemistry Society*, **97** (1975) 2167.
8. Ayyangar, N. R., Lahoti, R. J. and Wagle, D. R., *Indian Journal of Chemistry*, **16B** (1978) 106.
9. Bushtchuk, B. A., Rudinov, A. N. and Berutov, A. L., *Zhur. prikl. spektroskopii*, **54** (1991) 565.
10. Afanasiadi, L. Sh., Vineckaya, Yu. M., Leftchenko, N. F., Pereyaslova, D. G. and Shvorina, A. L., *Zhur. prikl. spektroskopii*, **21** (1974) 258.
11. Colour Index, Soc. of Dyers Colourists, 3rd edition, Vol. 4 (1971), 4522.
12. Birks, J. B. and Dyson, D. J., *Proceedings of the Royal Society*, **A275** (1963) 135.
13. Hutchings, M. G., *Dyes and Pigments*, **29** (1995) 95.
14. PISYSTEM for Windows, Version 3.1 (1994). Available from Dr Rudolf Naef, Im Budler 6, CH-4419 Lupsingen, Switzerland.
15. Parr, R. G., *Quantum Theory of Molecular Electronic Structure*. Benjamin, New York (1963).
16. Adachi, M. and Nakamura, S., *Dyes and Pigments*, **17** (1991) 187.
17. I. G. Farbenindustrie, D.R.P. 459 366; Frdl. **16**, 1447.
18. Luttringhaus, A. and Neresheimer, H., *Justus Liebigs Annals of Chemistry*, **473** (1929) 259.
19. Baddar, F. G., *Journal of the Chemistry Society* (1948) 1088.