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Application of fluorescence to elucidate the ground state electronic structure of boron, zinc and aluminum complexes of 3,5-di-tert-butylsalicylic acid

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Abstract

The ground state electronic structure of boron, zinc and aluminum complexes of 3,5-di-tert-butylsalicylic acid (t-BSA) was studied by fluorescence spectroscopy. These compounds are negative charge control additives (CCAs) commercially known as LR120, Bontron E84 and Bontron E88 respectively. They are synthesized by condensing the corresponding metal salts with t-BSA and are primarily characterized by elemental analysis. Spectroscopic analysis, by IR and ^{13}C nuclear magnetic resonance (NMR), fails to provide adequate structural information on these materials. Are they salts or chelate complexes? Previous studies in our laboratory have shown that lithium 3,5-di-tert-butylsalicylate (Lit-BSA) exhibits a characteristic, long-wavelength fluorescence. The Stokes shift (from peak to peak) is approximately 9300 cm^{-1}. In this work, we use the fluorescence of Lit-BSA as a probe of the ionicity of the dibutylsalicylato groups in LR120, Bontron E84 and Bontron E88 (in the ground state). Comparison of the fluorescence spectra reveals that the dibutylsalicylato groups in LR120 are not ionic. In fact, they resemble an ester. We conclude that LR120 is a cyclic boron ester and that the B–O bond is covalent. The comparison also reveals that the dibutylsalicylato groups in Bontron E84 and Bontron E88 are ionic in both polar and non-polar solvents. The strong ionic character in non-polar solvents, which differs from that of Lit-BSA, suggests that Bontron E84 and Bontron E88 are chelate complexes and that the di-tert-butylsalicylato groups are bidentate ligands for the Zn^{2+} and Al^{3+} ions respectively. The technological implications of the results obtained on the toner charging mechanism are discussed. © 1997 Elsevier Science S.A.

Keywords: Boron, zinc and aluminum complexes of 3,5-di-tert-butylsalicylic acid; Fluorescence; Ground state electronic structure

1. Introduction

Charge control additives (CCAs) are additives which are used in dry xerographic toners to maintain and regulate the charge level of a toner in the developer [1]. For negative black toner applications, acidified carbon blacks have been found to serve a dual function in toners [2]. They are the black colorants as well as the negative CCAs. The requirements for CCAs in color toner applications are more stringent. In addition to the charging function, which is already challenging due to the charging effect often exhibited by the colorant, the CCA has to be visibly transparent. Many organic and organometallic compounds are known to impart negative charging in toners. Of the many classes of CCAs studied, Macholdt and Sieber [3,4] showed that azo pigments and their metal complexes, particularly chromium complexes, are potent negative CCAs for toners. Cr–azo complexes are intensely absorbing in the visible region. Some of them even have a black appearance as powders. The visible absorption, which inevitably interferes with the appearance of the intended color toner, has hindered the use of these complexes as CCAs in color toners [5]. Recent efforts have focused on colorless compounds. A tremendous amount of attention has been paid to 3,5-di-tert-butylsalicylic acid (t-BSA), its metal salts such as lithium 3,5-di-tert-butylsalicylate (Lit-BSA) [6] and its boron [7], zinc [8] and aluminum [9] complexes. The trade names of the last three compounds are LR120, Bontron E84 and Bontron E88 respectively. These compounds are synthesized by condensing t-BSA with the corresponding metal salts. They can exist as a salt or a chelate complex in the ground state and routine spectroscopic analysis, such as IR and nuclear magnetic resonance (NMR) spectroscopy, fails to differentiate these possibilities. We felt that an understanding of the ground state structure is essential because it probably has an effect on the charging properties when used in toners. In this paper, we report the use of fluorescence spectroscopy to elucidate the ground state electronic structures of LR120, Bontron E84 and Bontron E88.

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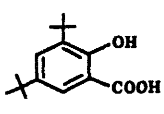
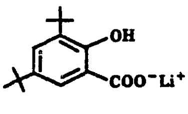
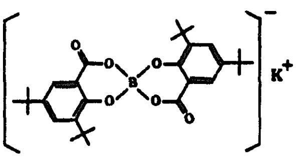
Our spectroscopic data show that LR120 is a cyclic boron ester and Bontron E84 and Bontron E88 are chelate complexes in the ground state. The technological implications are discussed.



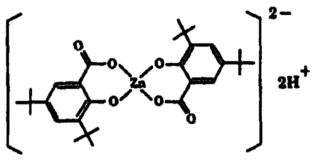
t-BSA



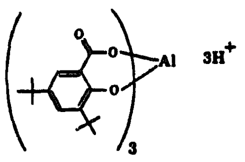
Li tBSA



LR 120



Bontron E84



Bontron E88

2. Experimental details

2.1. Materials

t-BSA was purchased from TCI America and was recrystallized from heptane three times before use. Lit-BSA was synthesized by neutralizing t-BSA with an equivalent amount of LiOH in methanol. The synthesized Lit-BSA was recrystallized twice from heptane. LR120 was prepared by reacting boric acid with two equivalents of t-BSA in an aqueous KOH solution [7]. Bontron E84 and Bontron E88 were prepared by complexing t-BSA with zinc sulfate and aluminum sulfate respectively [8,9]. Satisfactory elemental analyses and spectroscopic data (IR and ^{13}C NMR) were obtained for all the compounds synthesized in this work. Ethyl acetate was spectroanalyzed grade from Fisher. It was purified by stirring with K_2CO_3, followed by simple distillation. Cyclohexane (spectra), chloroform (high performance liquid chromatography (HPLC), pentene stabilized) and tetrahydrofuran (spectroanalyzed grade) were also from Fisher. Ethanol was 200 proof from Quantum Chemical Corporation. All the solvents were routinely stored over 3 Å molecular sieves.

2.2. General techniques

The absorption spectra were recorded on a Hewlett Packard 8451A diode array spectrophotometer. The fluorescence spectra were taken on a Perkin–Elmer MPF-66 fluorescence spectrophotometer, which was interfaced with a professional computer (model 7700) from Perkin–Elmer. All the solutions were purged with dry N_2 for 30 min before use. The spectral data were corrected using the quantum counter method with the RhB 101 solution supplied by Perkin–Elmer [10]. The quantum yields were determined in a corrected mode by comparison with the emission of 9,10-diphenylanthracene in cyclohexane ($\phi_f = 0.93$) [11]. A refractive index correction was made for each solution [12]. The fluorescence lifetimes were determined using the time-correlated single-photon counting technique on an LS-100-04 Fluorescence Lifetime System from Photon Technology Incorporated (PTI). The data were analyzed on an NEC personal computer using the software programs provided by PTI.

3. Results

3.1. Absorption spectra

The absorption spectral data of LR120, Bontron E84 and Bontron E88 in different solvents are summarized in Table 1. The data of t-BSA and Lit-BSA are included as references [13]. LR120, Bontron E84 and Bontron E88 form aggregates at concentrations higher than 10^{-4} M. In this work, the

Table 1
Effect of solvent on the absorption of t-BSA, Lit-BSA, LR120, Bontron E84 and Bontron E88

Solvent	D [c]	λ_{max} [a] ($\log \epsilon_{max}$) [b]				
		t-BSA	Lit-BSA	LR120	E84	E88
Cyclohexane	2.02	324.0 (3.66)	322.0 (3.17)	[d]	[d]	325.6 (4.09)
Chloroform	4.80	323.0 (3.65)		~326 [e]	~326 [e]	326.0 (4.20)
Ethyl acetate	6.02	316.5 (3.66)	316.1 (3.58)	314.3 (3.92)	315.9 (3.99)	316.4 (3.99)
Tetrahydrofuran	7.58	317.6 (3.66)		314.4 (4.10)	313.9 (4.03)	321.3 (4.15)
Ethanol	24.55	307.0 (3.63)	307.8 (3.52)	317.6 (4.02)	308.6 (4.02)	312.8 (4.05)

[a] Absorption maximum (nm) (± 1 nm).
[b] Absorption coefficient (cm^{-1} M^{-1}).
[c] Dielectric constant.
[d] LR120 and Bontron E84 are insoluble in cyclohexane.
[e] These ϵ_{max} values could not be determined accurately due to the low solubility in chloroform.

absorption of each compound was examined at varying concentrations and Beer's law was shown to be obeyed at concentrations ranging from 10^{-5} to 10^{-6} M. The λ_{max} and ϵ_{max} values obtained in this concentration range are given in Table 1.

Similar to t-BSA and Lit-BSA, the λ_{max} values of LR120, Bontron E84 and Bontron E88 all shift to shorter wavelengths as the dielectric constant of the solvent increases. The hypsochromic shifts indicate that the energy of solvation in the ground state is larger than that of the excited state. This phenomenon is quite common for ketones [14] and suggests that $n \rightarrow \pi^*$ electronic transitions are involved in these compounds.

The molar extinction coefficients of LR120 and Bontron E84 are about twofold higher than that of t-BSA. From the λ_{max} and ϵ_{max} values, we conclude that the absorbing chromophores in these compounds are the dibutylsalicylato groups. The molar extinction coefficient of Bontron E88 is approximately 10 000 cm^{-1} M^{-1} and is smaller than that expected from three dibutylsalicylato groups. However, examination of the absorption bandwidths of Bontron E88 in different solvents indicates that they are approximately 30% broader than those of t-BSA. Therefore we conclude that the absorbing chromophore in Bontron E88 is the dibutylsalicylato group and that ϵ_{max} is additive.

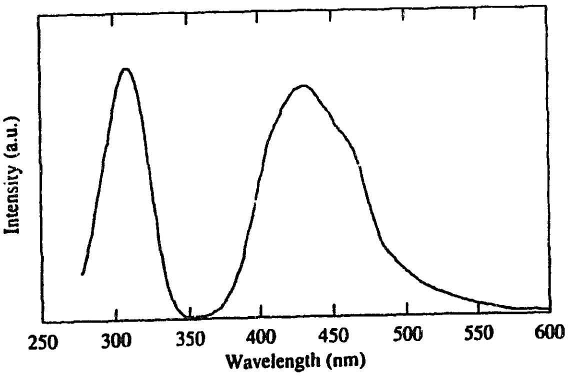


Fig. 1. Fluorescence excitation and emission spectra of t-BSA in ethanol (approximately 5×10^{-6} M).

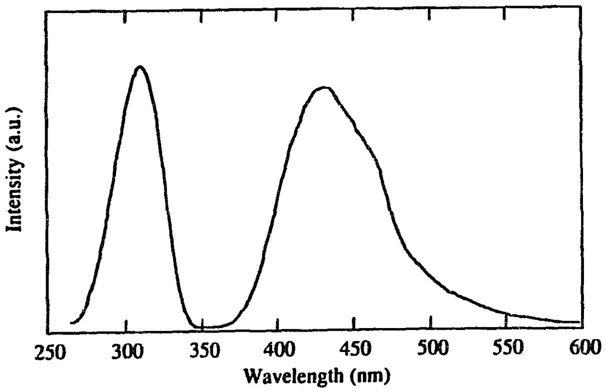


Fig. 2. Fluorescence excitation and emission spectra of Lit-BSA in ethanol (approximately 5×10^{-6} M).

3.2. Fluorescence spectra

3.2.1. Emission spectra

The corrected fluorescence excitation and emission spectra of t-BSA, Lit-BSA, LR120, Bontron E84 and Bontron E88 in ethanol are given in Figs. 1–5 respectively. The fluorescence maximum (λ_F) and the quantum yield (ϕ_f) data are summarized in Table 2. The λ_F values of t-BSA and Lit-BSA are at 432 and 431 nm respectively. The entire emission spectra of t-BSA and Lit-BSA are essentially superimposable. The most important observation involves the emission wavelengths of t-BSA and Lit-BSA. The emission bands are at anomalously long wavelengths and show no overlap with the

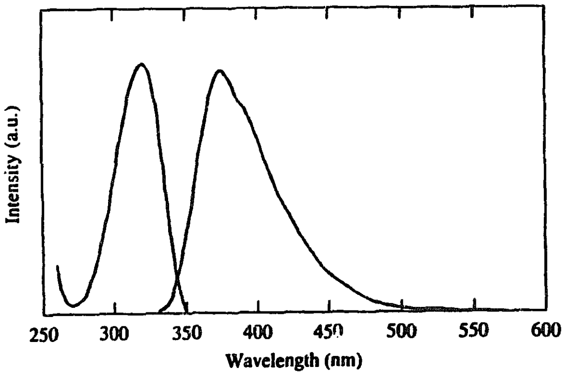


Fig. 3. Fluorescence excitation and emission spectra of LR120 in ethanol (approximately 3×10^{-6} M).

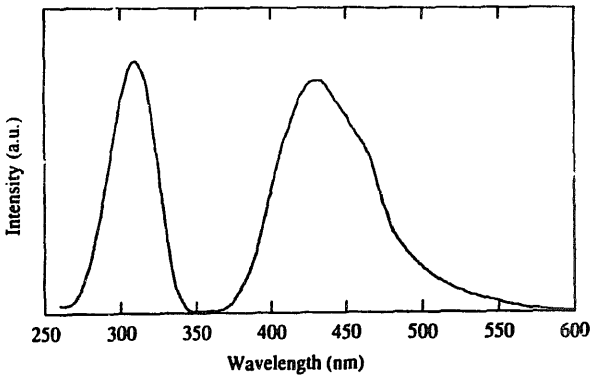


Fig. 4. Fluorescence excitation and emission spectra of Bontron E84 in ethanol (approximately 3×10^{-6} M).

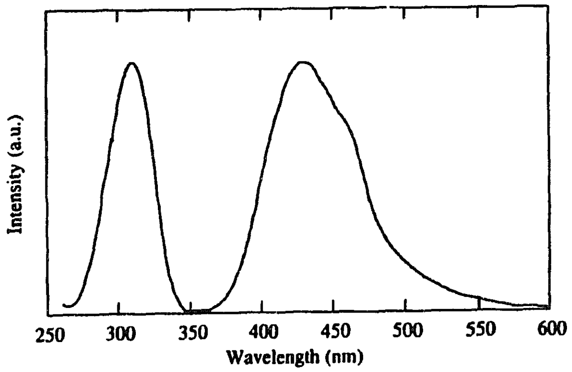


Fig. 5. Fluorescence excitation and emission spectra of Bontron E88 in ethanol (approximately 1×10^{-6} M).

Table 2
Effect of solvent on the fluorescence emission of t-BSA, Lit-BSA, LR120, Bontron E84 and Bontron E88

Solvent	t-BSA [a]		Lit-BSA [a]		LR120		E84		E88	
	λ_F [b]	ϕ_f [c]	λ_F [b]	ϕ_f [c]	λ_F [b]	ϕ_f [c]	λ_F [b]	ϕ_f [c]	λ_F [b]	ϕ_f [c]
Cyclohexane	~466	0.009	~466	0.006					426	0.20
Chloroform	~467	[d]			373	0.057	401	0.14	400	0.18
Ethyl acetate	434	0.15	434	0.23	368	0.13	431	0.18	428	0.22
Tetrahydrofuran	~466				367	0.087	442	0.27	412	0.20
Ethanol	432	0.56	431	0.67	374	0.18	431	0.64	430	0.64
Lifetime in ethanol (ns)	6.8		7.0		2.3		7.1		6.6	

[a] Data from Ref. [13].
[b] Fluorescence maximum (nm) (±2 nm).
[c] Fluorescence quantum yield (±10%).
[d] ϕ_f could not be determined accurately due to interference by fluorescing impurities.

absorption bands. The Stokes shifts are approximately 9300 cm^{-1} (from λ_{max} to λ_F).

The fluorescence emission of LR120 is different from that of t-BSA and Lit-BSA. The emission band is relatively narrow and forms a mirror-image relationship with the absorption band. The Stokes shift of the emission band is approximately 4700 cm^{-1}.

The emission spectra of Bontron E84 and Bontron E88 are very similar to those of t-BSA and Lit-BSA in terms of λ_F, ϕ_f, the shape of the emission band and the Stokes shift (approximately 9100 cm^{-1}).

3.2.2. Solvent effect

Fig. 6 shows the effect of the solvent on the emission spectrum of t-BSA. In cyclohexane, the fluorescence spectrum is broad and the intensity is relatively weak. As the solvent polarity is increased, such as in ethanol, the fluorescence spectrum becomes narrower and a spectral blue shift is observed. The blue shift is accompanied by an increase in the fluorescence intensity. The λ_F and ϕ_f data are summarized in Table 2. A very similar solvent effect is also observed for Lit-BSA.

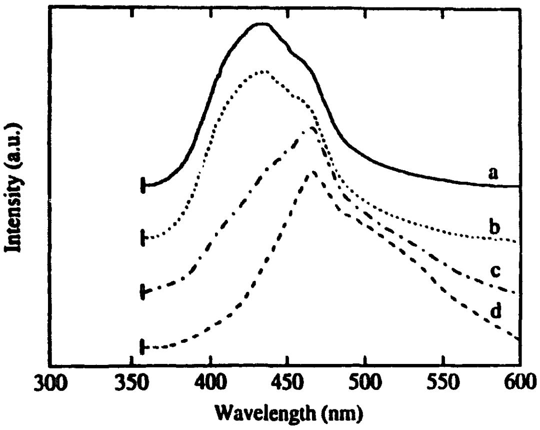


Fig. 6. Effect of solvent on the fluorescence emission of t-BSA (approximately 5×10^{-6} M): (a) ethanol; (b) ethyl acetate; (c) chloroform; (d) cyclohexane.

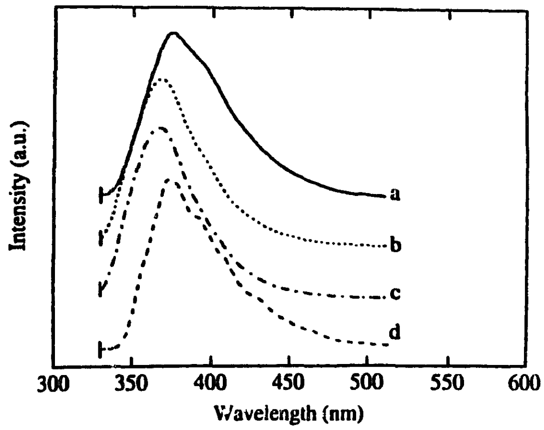


Fig. 7. Effect of solvent on the fluorescence emission of LR120 (approximately 3×10^{-6} M): (a) ethanol; (b) ethyl acetate; (c) tetrahydrofuran; (d) chloroform.

The solvent-dependent emission spectra of LR120 are given in Fig. 7 and the data are shown in Table 2. The spectral results show that both the shape of the emission bands and the ϕ_f values are far less sensitive to solvent changes compared with t-BSA. Vibronic structures are seen in the emission spectrum in chloroform and this observation distinguishes LR120 from t-BSA and Lit-BSA, as well as from Bontron E84 and Bontron E88.

The solvent effects on the emission spectra of Bontron E84 and Bontron E88 are very similar. The data are given in Table 2 and the typical spectral changes are shown in Fig. 8. Although the emission spectra of Bontron E84 and Bontron E88 in ethanol and ethyl acetate are similar to those of t-BSA and Lit-BSA, different results are obtained in non-polar solvents. Namely, the emission spectra in cyclohexane and chloroform are still narrow and at long wavelengths relative to the absorption spectra. Moreover, the decrease in ϕ_f from ethanol to non-polar solvents is only a factor of 4.5, whereas ϕ_f of t-BSA decreases by a factor of 62 in the same solvent range.

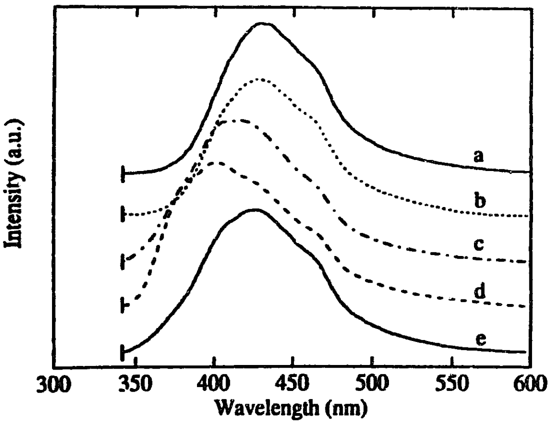


Fig. 8. Effect of solvent on the fluorescence emission of Bontron E88 (approximately 1×10^{-6} M): (a) ethanol; (b) ethyl acetate; (c) tetrahydrofuran; (d) chloroform; (e) cyclohexane.

3.2.3. Fluorescence lifetimes

The fluorescence lifetimes of t-BSA, Lit-BSA, LR120, Bontron E84 and Bontron E88 were determined in ethanol (Table 2). The lifetime of LR120 is 2.3 ns and is distinctly shorter than those of the other five compounds (6.8 ± 0.3 ns).

4. Discussion

4.1. The ground state structure of LR120

The absorption data suggest that there are two dibutylsalicylato groups in LR120. The fluorescence emission band of LR120 forms a mirror-image relationship with the excitation band (Fig. 3). The Stokes shift of the emission band is approximately 4700 cm^{-1}. The small Stokes shift distinguishes LR120 from t-BSA, Lit-BSA, Bontron E84 and Bontron E88, whose Stokes shifts are 9000 cm^{-1} or more. As shown later, the dibutylsalicylato groups in the last four compounds (in the ground state) are essentially anionic in character. In other words, the results imply that the butylsalicylato groups in LR120 possess very little ionic character. We conclude that LR120 is a cyclic boron ester condensed from t-BSA and boric acid. The B–O bond is covalent. This conclusion is supported by the fluorescence lifetime measurements. The singlet lifetime for LR120 of 2.3 ns in ethanol is significantly shorter than those of t-BSA and Lit-BSA (approximately 6.8 ns), whose fluorescences are dominated by the dibutylsalicylate anion [13].

In a previous study of the photophysics of t-BSA, we investigated methyl *o*-methoxybenzoate as a model compound [13]. The λ_F value of methyl *o*-methoxybenzoate in ethanol is at 348 nm and the Stokes shift is approximately 5200 cm^{-1}. The fluorescence is not sensitive to the solvent. The dibutylsalicylato groups in LR120 appear to be spectrally similar to that in methyl *o*-methoxybenzoate. The singlet lifetime of methyl *o*-methoxybenzoate is 1.2 ns in ethanol and is shorter than that of LR120. It is conceivable that the increase in lifetime in LR120 is due to the rigid cyclic dibutylsalicylato structure. The lifetime data are consistent with the conclusion that LR120 is a cyclic boron ester.

4.2. The ground state structures of Bontron E84 and Bontron E88

We reported previously that the fluorescence of t-BSA and Lit-BSA is derived from the dibutylsalicylate anion [13]. The intention of this work is to compare the spectral characteristics of Bontron E84 and Bontron E88 with those of Lit-BSA and t-BSA. If they are identical, we can conclude that these compounds are essentially organic salts.

In ethanol, the fluorescence spectra and lifetimes of Bontron E84 and Bontron E88 are similar to those of t-BSA and Lit-BSA in terms of λ_F and ϕ_f. The data suggest that the dibutylsalicylato groups in these compounds are ionic in ethanol. Further insight into the ground state structure comes from the solvent effect data in Figs. 6, 8 and Table 2. In cyclohexane, the emission spectrum of t-BSA is broad and the ϕ_f value is 62 times smaller than that in ethanol. The solvent effects on the emission spectra of Bontron E84 and Bontron E88 are less dramatic relative to those of t-BSA. In fact, we observe a narrow, blue-shifted spectrum for Bontron E88 in cyclohexane (Fig. 8, spectrum e). Since we established previously that the narrow, intense fluorescence is the signature of the dibutylsalicylate anion hydrogen bonded with the solvent molecules [13], our solvent effect data seem to suggest that this "bonding" situation occurs for Bontron E88 even in cyclohexane. The results suggest that the dibutylsalicylato groups in Bontron E84 and Bontron E88 are ionic over the entire solvent range investigated, implying that the acidic protons in these compounds are not localized at the oxygen atoms. They are either very labile or very delocalized. The only ground state structure which fits this description is a chelate complex structure in which the dibutylsalicylato group bears two negative charges and coordinates to the central metal ion (Zn^{2+} in E84 and Al^{3+} in E88).

In 1948, Clark and Kao [15] reported the X-ray crystal structure of bis(salicylato)zinc, the unsubstituted analog of Bontron E84. As with most X-ray crystal structures, the locations of the protons are not resolvable. Nevertheless, bond length data suggest that the Zn–O bond in bis(salicylato)zinc is slightly longer than that of a covalent Zn–O bond. It was concluded that bis(salicylato)zinc is a Zn chelate complex in the ground state. In this work, we arrive at the same conclusion based on fluorescence measurements. We demonstrate that fluorescence can be a useful tool in investigating the ground state structure of salicylato "complexes". This is especially important when the structure is not accessible by X-ray crystallography.

5. Summary and technological implications

By comparing the fluorescence characteristics of t-BSA and Lit-BSA with LR120, Bontron E84 and Bontron E88, this work demonstrates that fluorescence can be a useful tool in obtaining structural information. Structurally, t-BSA is an acid and Lit-BSA is a salt. The spectroscopic data in this work show that LR120 is a cyclic boron ester and Bontron E84 and Bontron E88 are chelate complexes. Despite the differences in their electronic structures, all of these compounds are effective in imparting negative charges in dry toners [6–9]. The only common structural component in these compounds, as a whole, is that they all have a mobile cation which is significantly smaller in size than the bulky anion, e.g. the dibutylsalicylate anion in t-BSA and Lit-BSA, the bis(dibutylsalicylato)boron anion in LR120, the bis(dibutylsalicylato)zinc anion in Bontron E84 and the tris(dibutylsalicylato)aluminum anion in Bontron E88. The ability of these materials to impart negative charges suggests that their tribocharging mechanism in dry toners may be by transfer of the cations. Indeed, recent results reveal that the ion transfer mechanism occurs in toners containing t-BSA and its alkaline salts [16,17].

References

[1] R.J. Gruber, P.C. Julien, in: A.S. Diamond (Ed.), Handbook of Imaging Materials, Dekker, New York, 1991.

[2] P.C. Julien, in: E.K. Sichel (Ed.), Carbon Black–Polymer Composites, Dekker, New York, 1982.

[3] H.T. Macholdt, A. Sieber, J. Imaging Technol. 14 (1988) 89.

[4] H.T. Macholdt, A. Sieber, Dyes Pigm. 9 (1988) 119.

[5] K.Y. Law, I.W. Tarnawskyj, P.T. Lubberts, J. Imaging Sci. Technol. 38 (1994) 81.

[6] Y. Normura, N. Ide, K. Ohtaki, M. Tomita, H. Tosaka, T. Nanya, M. Orihara, S. Chiba, S. Inone, Y. Asahina, H. Fushimi, US Patent 4 762 763, 1988.

[7] K. Hashimoto, M. Maruta, H. Soyama, Y. Ishii, US Patent 4 767 688, 1988.

[8] Y. Kawagishi, S. Narita, T. Kiriu, K. Uomoto, US Patent 4 656 112, 1987.

[9] T. Kiriu, M. Arakawa, US Patent 4 845 003, 1989.

[10] W.H. Melhuish, J. Res. Natl. Bur. Stand. Sect. A 76 (1972) 547.

[11] S.R. Meech, D. Phillips, J. Photochem. 23 (1983) 193.

[12] J.N. Demas, G.A. Grosby, J. Phys. Chem. 75 (1975) 991.

[13] K.Y. Law, J. Shoham, J. Phys. Chem. 99 (1995) 12 103.

[14] J.G. Calvert, J.N. Pitts, Photochemistry, Wiley, New York, 1966, p. 257.

[15] G.L. Clark, H. Kao, J. Am. Chem. Soc. 70 (1948) 2153.

[16] K.Y. Law, I.W. Tarnawskyj, D. Salamida, T. Debies, Chem. Mater. 7 (1995) 2090.

[17] K.Y. Law, I.W. Tarnawskyj, D. Salamida, T. Debies, ACS Polymer Preprints, 37 (1) (1996) 105.