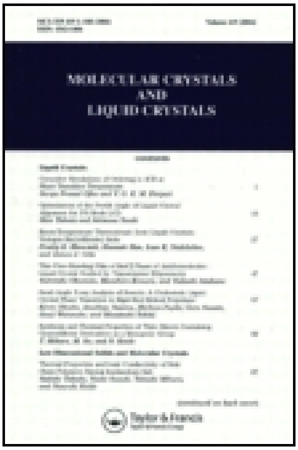

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Absorption and Fluorescence Spectra of Aqueous Solutions of Disodium Cromoglycate

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Absorption and Fluorescence Spectra of Aqueous Solutions of Disodium Cromoglycate

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In the AM1 approximation, we calculated the molecular geometry and energetic structure of an individual molecule of disodium cromoglycate and its conformers as well as measured their absorption and fluorescence spectra in aqueous solutions of different concentrations. The calculation of electron transitions gives the lowest two π-π^* transitions and one n-π^* for the unit aromatic chromophore which is slightly split in a cromoglycate dianion containing two aromatic blocks. These transitions are found to correspond to the low intensive absorption band at 330 nm and fluorescence at 384 nm upon low concentration. It is established that the increase in the concentration leads to the aggregation and hence to the essential splitting of absorption bands and appearance of the fluorescence at 485 nm.

Keywords: AM1 approximation; fluorescence and excitation spectra; lyotropic chromonic liquid crystals absorption; Quantum-chemical calculation

1. INTRODUCTION

Absorption and fluorescent spectra of disodium cromoglycate (other name Cromolyn) molecules is of particular interest because the compound dissolved in water can form lyotropic chromonic liquid crystals (LCLC)–a special class of lyotropic mesophases [1,2]. It is well known that the materials forming LCLCs are composed of plank-like

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molecules with aromatic central core and hydrophilic (or hydrogen-bonding) groups at the periphery. The basic building block of LCLCs is a molecular stack in which the molecules are arranged face-to-face with ionic groups at the water-aggregate interface. In a cromolyn molecule, two acid residues are hydrophilic groups while the aromatic moiety is presented by two aromatic rigid blocks connecting each other by a polymethylene spacer.

Because of a π-conjugated molecular core, many LCLC materials absorb light in the visible and even near IR ranges. This absorption is highly dependent on the orientation of LCLC molecules with respect to the polarization of light. Among many potential applications of LCLCs, the most actively pursued nowadays is the idea to use dye-based LCLCs as light polarizing elements in the liquid crystal display industry [3–7]. Chromonematics with no significant absorption in the visible part of the spectrum can also be used as compensating films in liquid crystal displays [8].

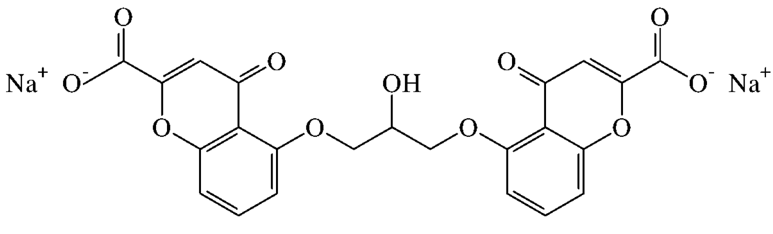
The growing interest to LCLCs, both fundamental and applied, requires a detailed characterization of their optical properties as well as of the electron structure of molecular components of LCLCs. In most research articles, the LCLCs are characterized spectroscopically as anisotropic dyes and not much attention is being paid to their other optical properties.

In this paper, we present the results of spectroscopic investigations of the cromolyn and quantum chemical studies of the features of electron transitions in originated molecules and the dimers and simplest aggregates to explain correctly the absorption and fluorescence spectra.

2. EXPERIMENT

2.1. Materials

Disodium cromoglycate (DSCG), CAS#: 13826-37-6 presented by formula **1** was obtained from Spectrum Chemical Mfg. Corp.



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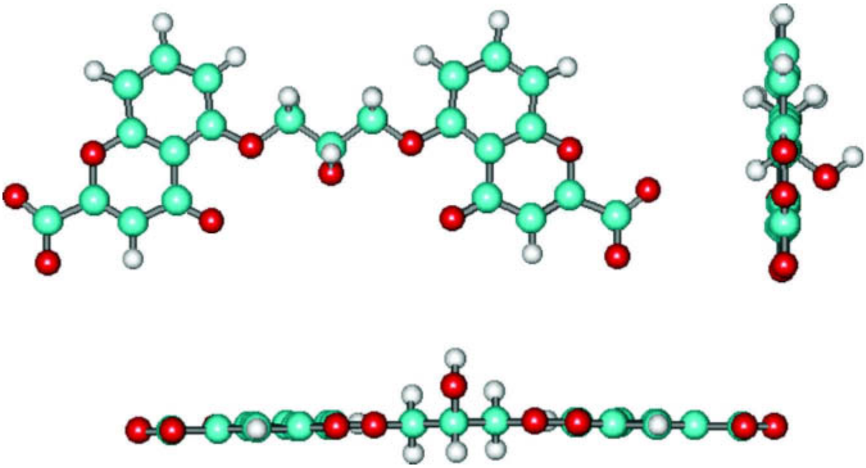


FIGURE 1 Planar spatial conformer of cromolyn.

(Cardena, CA). This material possesses good solubility in water. In the dissociated state, the molecule omits the two sodium cations and is a dicharged anion. The dianion consists of two rigid heterocycles connected with a flexible spacer, which lets the molecule assume many energetically similar conformations. Conformations are limited only by chemical bond lengths and valence angles. The optimized DSCG molecule anion obtained using the AM1 approximation (HyperChem package) is flat (see Fig. 1).

2.2 Spectral Measurements

DSCG is characterized by intensive absorption in the UV region of light. The absorption spectra of the aqueous solution of DSCG as a function of concentration form a family of closely related curves. In Figure 2, the absorption spectra of DSCG in a water solution is plotted for only two concentrations: 3×10^{-6} wt.% (curve a) and 8×10^{-4} wt.% (curve b), since the concentration dependence demonstrates no distinguishing difference in the positions of maximal absorption. For a lower concentration of 3×10^{-6} wt.%, the spectra of DSCG demonstrate the intensive absorption bands near 228 nm and 276 nm (Fig. 2a) and the additional peak at 330 nm. The peaks grow with concentration while the position of the peak at 276 nm shifts to the shorter wavelength region, 262 nm (Fig. 2b), which may be attributed to the molecular aggregation. Curve c (Fig. 2) represents the absorption of

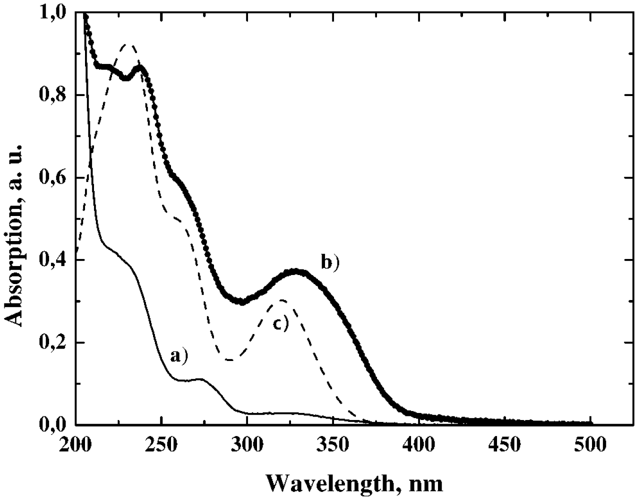


FIGURE 2 Concentration dependence for the absorption of DSCG in water at T = 293 K: a) $3 \times 10^{-6}\%$; b) $8 \times 10^{-4}\%$ and in methanol c) $5^{*}10^{-6}\%$.

DSCG in a methanol solution for a concentration of $5^{*}10^{-6}$ wt.% and the position of peaks.

The fluorescence spectra for the aqueous solution of DSCG are shown in Figure 3. The dilute water solution, its concentration is

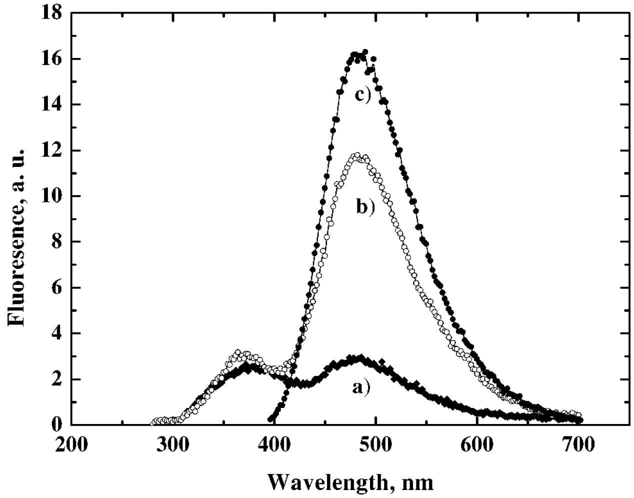


FIGURE 3 Concentration dependence for the fluorescence of DSCG in water at T = 293 K: a) $3^{*}10^{-6}\%$; b) $2.5^{*}10^{-5}\%$; c) $3^{*}10^{-4}\%$.

about 3×10^{-6} wt.%, demonstrates two similar wide bands in the emission spectra at 384 and 485 nm, Figure 3a. The further increase in concentration leads to a remarkable change in the emission spectra. The emission at 384 nm is diminished, whereas a maximum of fluorescence appears around 485 nm as a wide nonstructural band. This emission band was observed for all higher concentrations we measured. A transformation of the emission spectra occurs at a concentration of about 2.5×10^{-5} wt.%, which actually corresponds to the blue-shift of the 330 nm band in absorption spectra. However, for the dilute water solution, we were able to detect the source of emission by measuring the excitation spectra.

The excitation spectra for a low DSCG concentration are shown in Figure 4 by curves b and c. Curve a represents the fluorescence demonstrating two bands as in Figure 3. The obtained excitation spectra for the emission bands of 384 nm and 485 nm are independent. Curve c corresponds to the 384-nm emission maximum, and curve b corresponds to the 485-nm emission maximum. By comparing the excitation spectra with absorption ones, one can see that curve c in Figure 4 fits the absorption band (Fig. 2 curve a) with maximum at 276 nm which also appears only for very low concentrations. The excitation curve b in Figure 4 exactly corresponds to the absorption of higher concentrated DSCG water solutions with the absorption band at 330 nm, curve b in Figure 2. It can thus be concluded that the 384-nm emission

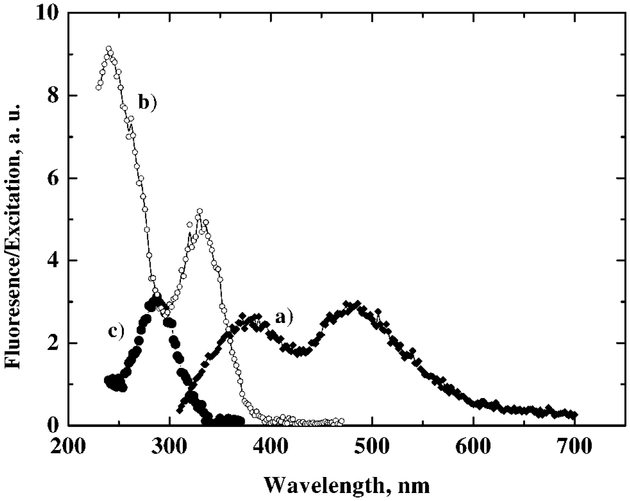


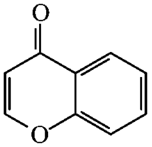
FIGURE 4 Fluorescence a) and excitation spectra for the emission bands b) 485 nm and c) 384 nm for a low concentration ($3^{*}10^{-6}$%).

originates most probably from the molecular form of DSCG, while the shape, position, and concentration dependence of the 485-nm emission indicate the formation of molecular aggregates and are related to intermolecular charge transfer [9,10].

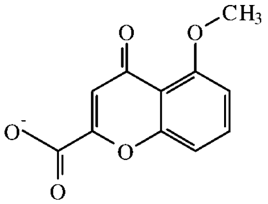
3. DISCUSSION

To explain correctly the obtained spectral data, the electron properties of DSCG molecule **1**, first at all, a dianion, are to be previously considered.

*Model (**2**) and unit (**3**) chromophore/fluorophore.* As a unit or elementary cromophore, the heterocycle moiety should be selected. This chromophore includes the main π-electron system and the lone electron pairs of the two-coordined oxygen atoms which connect the heterocycles each with other by a spacer; as well as the π-systems of the acid residues, COO^-. The calculation have shown that the conjugation between a COO^- substituent and the main heterocycle is practically absent because the length of the corresponding CC-bond is equal to 1.54 Å and hence the rotation barrier for the COO^- residue is negligibly small.

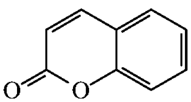


2 (Model chromophor)



3 (Elementary or unit chromophor)

It was shown earlier [11] that two $\pi\rightarrow\pi^*$-transitions and one $n\rightarrow\pi^*$-transition correspond to the longwavelength band in the spectrum of the related chromon-2 **4**.



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For the model compound **2**, the calculation in the AM1 approximation (using 25 lowest single excited configurations) gives the

TABLE 1 Calculated Transition Wavelength (nm) and Oscillator Strength

Model [z = 0]	Unit [z = −1]	DSCG 1 [z = −2]
326 (0.028)	337 (0.044)	337 (0.086)
		336 (0.003)
307 (0.020)	318 (0.044)	319 (0.020)
		318 (0.062)
323* (0.000)	311* (0.000)	305* (0.000)
		305* (0.000)
250 (0.256)	263 (0.052)	265 (0.001)
	257 (0.184)	263 (0.106)
		257 (0.399)
		256 (0.002)

n→π-transition; z-charge.

similar results: 326, 307, and 323 nm, correspondingly (Table 1). As seen from the calculated data, introducing the anionic COO^- group causes a bathochromic shift of the both $\pi \rightarrow \pi^*$-transitions and the opposite effect for the $n \rightarrow \pi^*$-transition. The next $\pi \rightarrow \pi^*$-transitions should appear in the shorter spectral region (250 nm for the model chromophore **2** and 363 and 257 nm for the elementary chromophore **3**); their oscillator strengths (f) are greater, as one can see from Table 1.

Monomer. The dicharged DSCG contains two elementary (unit) chromophores, the distance between which depends on the conformational constitution of the flexible spacer, $\text{-OCH}_2\text{COHCH}_2\text{O-}$. In the ideal case of a totally flat conformer (Fig. 1), the limiting distance between the carbon atoms in every heterocycle connected with spacer is equal to 7.27 Å. As follows from calculations (see Table 1), the interaction of two unit chromophores causes a very slight splitting of the electron transitions simultaneously with a small change of their energies, while the oscillator strength of the whole system remains constant: $f_1 + f_2 \approx 2f_{el}$, where f_{el} is value for a unit chromophore. It is seen from Table 1 that the practically whole intensity of the first transition (337 nm for the elementary chromophore) upon the interaction is concentrated in that split transition which is of the lower energy. On the contrast, the interaction of the next transitions of every unit chromophore (318 nm) which are polarized perpendicularly to the first transitions leads the shortwavelength split transition (318 nm) to be more intensive ($f = 0.062$) in respect to another split one (319 nm; $f = 0.020$). Of course, one would expect that the values of splitting ($\Delta\lambda$) of the interacting transitions and the ratio of the resulting intensities could change for other possible conformers. The analysis of the calculations has shown that the deviations of $\Delta\lambda$ and f_1/f_2 from the "ideal" case are minimal, because the distance between both unit chromophores in the monomer is too long for the interaction to be appreciable.

Thus, we may propose that two groups of the calculated split $\pi \rightarrow \pi^*$-transitions (337, 336 and 319, 318 nm) and the pair of the split practically degenerated $n \rightarrow \pi^*$-transitions (305, 305 nm) correspond to the longwavelength absorption band with the maximum at 320 nm in methanol (Fig. 2c) and 324 nm in water upon low concentrations (Fig. 2a).

Then we can conclude that the spectral band with the maximum at 384 nm in the fluorescence spectrum (Fig. 3a) is connected with emission from the lowest $\pi \rightarrow \pi^*$-transition: the calculated value is 337 nm and the experimental one is 324 nm. The measurement of the excitation of fluorescence (at 384 nm) (Fig. 4c) confirms this conclusion. The maximum of fluorescence proves out to be shifted hypsochromically (<300 nm) in respect to the position of the absorption band (324 nm), which is caused by a change in the equilibrium molecular geometry in the relaxed excited state.

We propose also that the group of split higher $\pi \rightarrow \pi^*$-transitions (265 nm and lower) corresponds to the shoulder (at approximately 250 nm) of the short-wavelength absorption band (Fig. 2).

The observed changes in the absorption spectra upon increasing the concentration of DSCG are likely to be caused by aggregation.

Aggregation. Despite a DSCG molecule is assumed to be preferably flat, we have found that the stable molecular aggregates consist of the conformers with a non-planar constitution of the spacer. Modeling the possible constitution of the aggregates, one should take into consideration that the stable molecular assemblies must give the minimum area of contact with water, i.e. occupy the minimum cavity in the water environment, as well as the distance between the negatively charged COO^- groups must be maximum. In addition, the distance between interacted π-electron molecules is found to be 3.4 Å. In Figure 5, two possible molecular assemblies are presented: an "ideal" totally flat aggregate (TF) and a compact flat one (CF) with antiparallel chromophores. In the last case, the CF aggregate, the bent spacer can additionally fix the molecules in the aggregate stake. Perhaps, the other conformations, similar to the CF structure but with some angle between the planes of both unit chromophores are possible too. However, in this paper, we restrict ourselves by two extreme cases. The calculation has shown that a totally planar monomer is more stable (by 25.51 kcal/mol) than the component of the CF aggregate (see Table 2). An aggregation of the CF-type is more preferable because the energy difference between both types of the molecular assemblies increases progressively upon a growth of the aggregate.

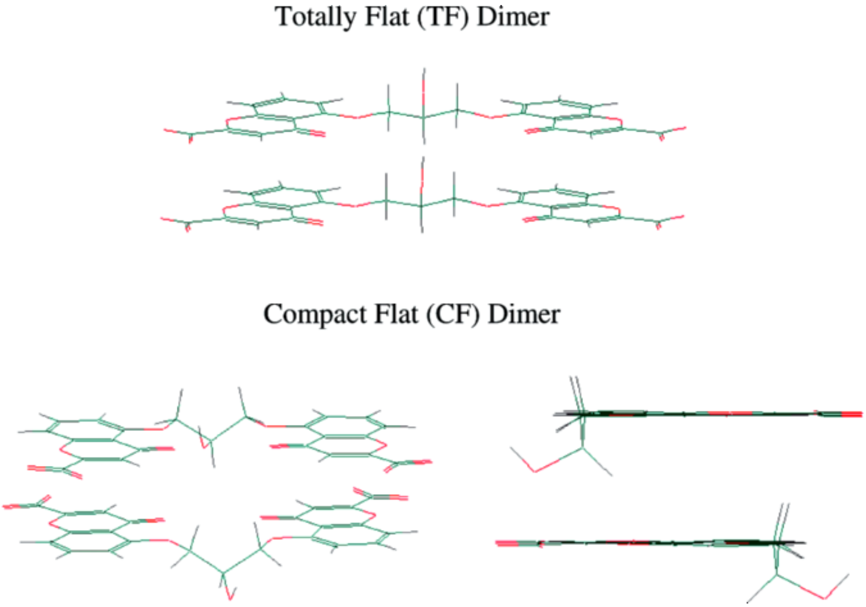

FIGURE 5 Dimers of cromolyn.

There are two types of the interaction of unit chromophores in the aggregates: between two unit chromophores in every DSCG molecule considered above and between the chromophores of different molecules (the stake interaction). The distance between molecules in an aggregate is approximately equal to 3.4 Å similarly to the distance between molecules in other aggregates of conjugated systems [12]. Then the stake interaction should be noticeably greater than the interaction between two chromophores in a monomer. Increasing the

TABLE 2 Calculated (AM1) Energies (Kcal/mol) of a Cromolyn Molecule and its Aggregates

	Conformation		
Number of molecules	Totally flat	Compact flat	ΔE
1	−5669.00	−5643.49	−25.51
2	−11004.20	−11167.65	160.45
4	−21402.59	−21830.68	428.09
6	−31167.22	−32167.24	1000.02

Remark: $\Delta E = E(CF) - E(TF)$.

concentration leads to decreasing the intensity of the fluorescence band at 384 nm and simultaneously increasing the intensity of the band displaced more bathochromically, at 485 nm. Such a considerable shift of the fluorescence band ($\approx$100 nm) could testify to a change of the nature of the fluorescence: instead of the innermolecular fluorescence upon a low concentration, the fluorescence of excimers in high concentration solution is observed. A similar change of the fluorescence nature seems to be connected with that the lowest split state in the aggregate is not fluorescent (is forbidden) which agrees with the practically parallel spatial arrangement of the dipole transition moments of unit chromophores in the aggregates (see, for example, the octamer presented in Fig. 6).

To summarize, we conclude that the water solutions of cromolyn upon low concentrations exhibit the absorption spectra which are

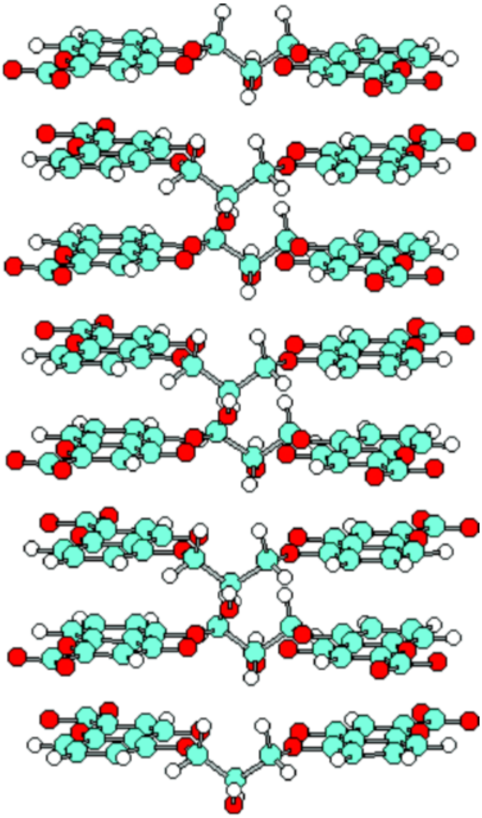

FIGURE 6 Compact flat octamer.

similar to those of the organic solution (methanol): the wide and low intensive band at 300–350 nm which is connected with two π-π^* transitions and one n-π^* electron one (per each unit chromophore); the interaction between both the aromatic systems in a monomer molecule is comparative small. Increasing the concentration of the water solution is accompanied by forming the aggregates which are mainly of a compact flat type. The relatively considerable stake interaction between the parallel unit chromophores in such aggregates causes the splitting of electron transitions so that the energetically higher split transition should be intensive while the lower transition proves out to be practically forbidden. As a result, only excimers produce an effective fluorescence, in contrast to the innermolecular fluorecence in low-concentration water solutions.

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