Structuring of tricarbocyanine dye molecules in Langmuir—Blodgett films

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The problems of formation of stable Langmuir monolayers containing N-sulfopropyl substituted thiatricarbocyanine dyes are considered: the effects of the composition of the mixture applied on the surface of an aqueous subphase and of the extent of compression of the monolayer on processes of ordering of molecular structure. Dyes are introduced into complex monolayers at the water—air interface and then are transferred on solid substrates as multilayered Langmuir—Blodgett (LB) films. For the first time the formation of J-aggregates has been observed for two tricarbocyanine dyes. The structure of J-aggregates depends on the composition of the mixture and the value of the constant pressure at which the transfer occurs. LB films of J-aggregated dyes are optically anisotropic, which is related to the fact that they are formed in the monolayer on the surface and there is no interlayer aggregation during the transfer to substrates. Heterodimers are formed in complex monolayers containing oppositely charged ions of dyes.

Key words: Langmuir monolayer, Langmuir—Blodgett film, tricarbocyanine dye, heterodimer, J-aggregate, absorption spectra.

J-Aggregates of cyanine dyes introduced into Langmuir—Blodgett (LB) films are of significant interest from the viewpoint of using them in electronic and optical devices and as media for supercompact optical recording of information.[1] Depending on particular conditions in liquid solutions, cyanine dyes form aggregates of different types, including J-, H-, and H*-aggregates, oligomers, and dimers.[2] J-Aggregates are characterized by an intense narrow absorption band (its half-width is less than 50 nm), which is bathochromically shifted relative to the absorption band of dye monomers. J-Aggregates of cyanine dyes introduced into LB films comprise two-dimensional single ccrystals with a linear size of 1 to 100 μm, whose structure has been studied by the electron diffraction method.[3]

LB films, which contain J-aggregates of cyanine dyes with long alkyl substituents[4] capable of forming Langmuir monolayers at the water—air interface, are studied in detail. Adsorption of molecules with short alkyl substituents on oppositely charged monolayers is an alternative method for introducing J-aggregating dyes into LB films.[5—8]

The formation of J-aggregates in Langmuir monolayers depends to a great extent on the structure of dye molecules. Aggregates of cyanine and carbocyanine dyes can be most easily obtained.[4—6] Only several works,[1,7,8] in which J-aggregates of dicarbocyanine dyes have been studied, are known.

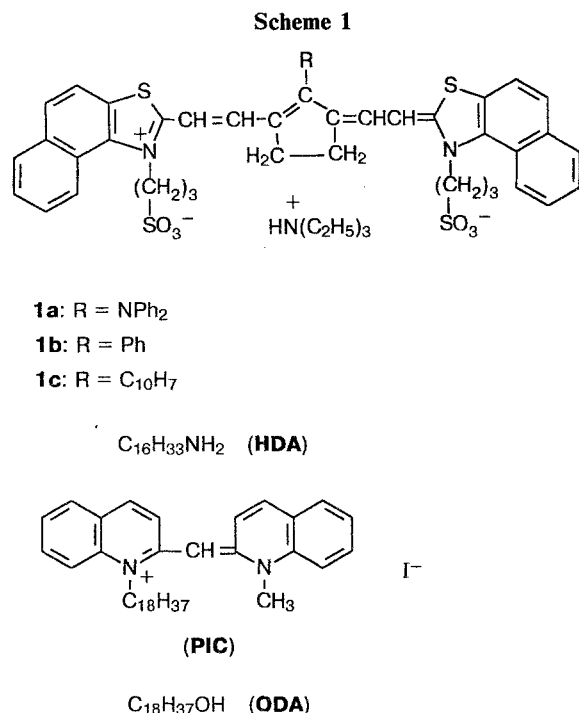The introduction of more than one cyanine dye into LB films results either in the formation of mixed aggregates (in the case when molecules are similar in structure and size) or in the separation of phases when J-aggregates of each of dyes are formed in different regions of a film.[9] The third variant of the combined introduction of two aggregating dyes is also possible. In this case, amphiphilic ions of one dye will form the supporting charged layer on which non-amphiphilic ions of the second dye may be adsorbed. LB films of heterodimers of cyanine dyes can be obtained by this method. It is evident that components of monolayers in such films can exert an effect on aggregation processes of dyes introduced.

LB films containing J-aggregates of dicarbocyanine dyes with a fixed polymethine chain have been studied previously.[7,8] The purpose of this work is determining the conditions of formation of J-aggregates of tricarbocyanine dyes introduced into Langmuir monolayers and studying the spectral properties of LB films.

Experimental

Specially synthesized N-sulfopropyl substituted 4,5,4',5'-dibenzothiatricarbocyanine dyes (**1a—c**) with fixed polymethine chains that differ in structure of meso-substituents (Scheme 1) were studied.

Dyes **1a—c** are water-soluble and cannot form Langmuir monolayers. The introduction of these dyes into monolayers is possible when they are adsorbed on the oppositely charged monolayer. Hexadecylamine (**HDA**) or 1-methyl-1'-octadecyl-2,2'-cyanine iodide (**PIC**) (Scheme 1) were used as am-

Scheme 1

1a: R = NPh$_2$
1b: R = Ph
1c: R = C$_{10}$H$_7$

C$_{16}$H$_{33}$NH$_2$ (HDA)
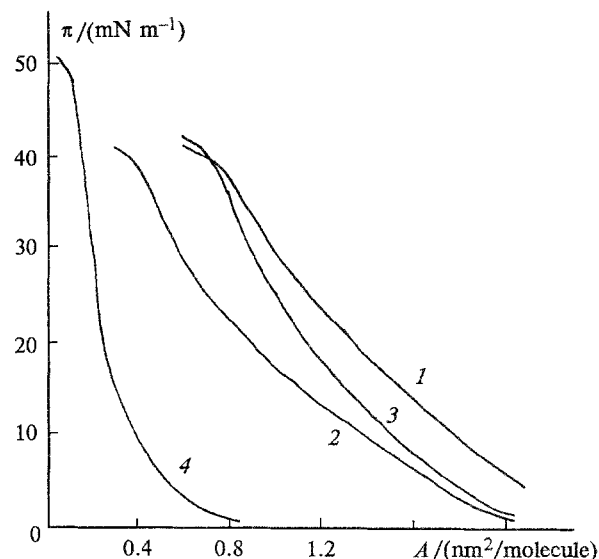
(PIC)

C$_{18}$H$_{37}$OH (ODA)

Fig. 1. Surface pressure—surface area isotherms for dye : **HDA** mixtures with a molar ratio of 1 : 1 containing dyes **1a** (*1*), **1b** (*2*), and **1c** (*3*). The isotherm of pure **HDA** (*4*). 20 °C. To determine the surface area per molecule, the pressure range from 25 to 35 mN m^{-1}, in which the linear dependence π—A of the condensed monolayer is fulfilled, was used.

phiphilic compounds, which form positively charged mono-layers. Octadecyl alcohol (**ODA**) was additionally introduced into supporting monolayers of **PIC** as the stabilizer. Dyes **1a**—**c** and components of supporting monolayers were dissolved in a chloroform—methanol (4 : 1) mixture. All solvents were of chromatographically pure grade.

The method for combined deposition was used to form monolayers of dyes at the water—air interface. A mixture of solutions of a dye and a substance, which forms the supporting monolayer (**HDA** or **PIC**) was applied on the surface of bidistilled water (pH 6.0).

Measurements of isotherms, which relate the surface pressure (π) applied to a monolayer and the surface area (A) per one molecule, and application of Langmuir—Blodgett monolayers on substrates were performed on an installation controlled by an IBM PC/AT. Monolayers were transferred according to the X-type on hydrophobized quartz plates preliminarily covered with two layers of stearic acid. Pressure during the transfer was maintained constant at 30 mN m^{-1} (except specially mentioned cases), and the rate of transfer was 10 mm min^{-1}. Absorption spectra of multilayers on solid substrates and of liquid solutions of **1a**—**c** in water and chloroform were measured on an SDL-2 (LOMO) installation.

Results and Discussion

Mixtures of dyes **1a**—**c** and **HDA** (as well as **PIC**) of 1 : 1 composition form stable Langmuir monolayers at the water—air interface. π-A-Isotherms of the dye : **HDA** (molar ratio 1 : 1) mixtures are presented in Fig. 1. It

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* The addition of octadecyl alcohol as the stabilizer enhances elasticity of the layer (the transfer coefficient of monolayers to substrates becomes equal to unity; alcohol exerts no effect on optical properties of films).

can be seen that the monolayers are compressed to 30 mN m^{-1} and more. The value of the limiting surface area (A_0) per dye molecule can be obtained by extrapolating the linear region of the isotherm, which corresponds to the condensed state of the monolayer, to zero pressure ($\pi{\rightarrow}0$). The A_0 values are 1.4 to 1.8 nm^2 for the dyes studied. Meso-diphenylamino-substituted dye **1a** occupies a larger surface area compared to naphthyl-(**1c**) and phenyl-substituted (**1b**) dyes. Similar diagrams were obtained when **PIC** was used as the main component of the supporting layer.

Optimum conformations of molecules **1a**—**c** were calculated by the molecular mechanics method.[10] Projections of dye molecules on the plane of the water—air interface were determined by computer simulation[11] using van der Waals radii of atoms. The obtained surface areas of model projections were compared to the values of the limiting surface areas A_0 determined from π-A-isotherms. Dye molecules of **1a**—**c** are arranged in the compact Langmuir monolayer in such a way that the plane of a molecule is perpendicular and the long axis is parallel to the surface. This arrangement of molecules in the monolayer favors the formation of the "brickwork" type structure, which is typical of J-aggregates.[12] The differences in surface areas of molecules with different meso-substituents mentioned above are explained by the fact that these substituents are shifted from the plane of the main chromophore fragment of the dye. Therefore, dye molecules with more bulky substituents occupy a larger surface area.

Complex monolayers of the 1 : **HDA** (with ratios from 1 : 1 to 1 : 20) and 1 : **PIC** : **ODA** (with ratios

Table 1. Positions of the maxima of absorption bands of dyes **1a—c** in chloroform and aqueous solutions and in LB films

Dye	λ_{max}/nm		
	Chloroform	Water	LB film
1a	868 [M]	1052 [J]	1034 [J]
1b	746 [M]	732 [M]	738 [M]
		630 [D]	625 [D]
1c	884 [M]	980 [J]	998 [J]

Note. M, D, and J indicate absorption bands of monomers, dimers, and J-aggregates, respectively.

from 1 : 1 : 0 to 1 : 3 : 3) mixtures are transferred to substrates with the transfer coefficient equal to unity. In all of the cases, the optical density at the maximum of the absorption band of the dye increases linearly as the number of transferred monolayers increases.

Maxima of absorption bands of dyes studied in solutions (chloroform and water) and of LB films (the dye : **HDA** mixture with the molar ratio of 1 : 1 transferred at 30 mN m^{-1}) are presented in Table 1.

Dyes **1a—c** exist in the monomeric form in dilute chloroform solutions (10^{-5} mol L^{-1}). An increase in the concentration results in the formation of dimers of dyes. The behavior of these dyes in aqueous solutions can be different. Dyes **1a** and **1c** in aqueous solutions form J-aggregates, while dyes **1b** form dimers.

Since dye molecules exist in the polar aqueous subphase during the formation of Langmuir monolayers, one can expect the formation of the same type molecular aggregates as those in aqueous solutions. As can be seen from the data presented in Table 1, dyes **1a** and **1c** in LB films form J-aggregates like in aqueous solutions. The maximum shift of the J-band relative to the monomeric band is observed for **1a** (the dye : **HDA** molar ratio is equal to 1 : 1). The value of the shift is 166 nm (1850 cm^{-1}). It should be mentioned that a considerable amount of dye monomers is present in the LB film in addition to J-aggregates.

Absorption maxima of J-aggregates in LB films and in aqueous solutions do not coincide. This is explained by basically different conditions of their formation. In water J-aggregates are formed spontaneously under equilibrium conditions. On the contrary, when the Langmuir monolayer is formed and compressed, the formation of J-aggregates occurs under non-equilibrium conditions under the action of the surface pressure, which exerts an effect on the packing density of chromophore fragments in the monolayer. In this case, considerable numbers of non-aggregated molecules can exist. However, LB films are stable in the absence of external action, in particular, absorption spectra remain unchanged during the time of measurements.

It is known[4—6] that the structure of J-aggregates in Langmuir and LB films can depend on the surface pressure and dye concentration in a mixture with a

neutral diluent or stabilizer. For thiadicarbocyanine dyes with fixed polymethine chains adsorbed on monolayers of octadecylpyridinium stabilized by octadecanol, the structure of J-aggregates in a wide concentration range (the molar ratio of the dye : octadecanol mixture ranges from 1 : 1 to 1 : 20) is independent of the concentration of the dye in the mixture applied to the subphase surface,[8] but it is very sensitive to the value of surface pressure at which the transfer occurs.

This is not the case for thiatricarbocyanines adsorbed on **HDA** monolayers. Absorption spectra of LB films of the **1a** : **HDA** (the molar ratio ranges from 1 : 1 to 1 : 20) mixture of 2×20 layers applied at $\pi_{const} = 30$ mN m^{-1} are presented in Fig. 2. The character of the dependence of the shift in the absorption band $\Delta\lambda = \lambda^J_{max} - \lambda^M_{max}$ on the dye concentration is complex. A small shift is observed for the 1 : 10 composition (196 nm or 2120 cm^{-1}). This composition also has the smallest residual absorption of monomers. The intensity of absorption at the maximum of the J-band for the mixture with the 1 : 2 molar ratio is higher than that for 1 : 1, and for 1 : 10 it is higher than for 1 : 5. If the value of the half-width of the band $\Delta W_{1/2}$ is accepted as a measure of perfectness and uniformity of the structure of J-aggregates, it can be stated that the structure of the 1 : 1 composition is the least perfect one ($\Delta W_{1/2} = 1920$ cm^{-1}). Absorption bands of the 1 : 2, 1 : 5, and 1 : 20 compositions are somewhat sharper ($\Delta W_{1/2} = 1200$ cm^{-1}). The LB film of the **1a** : **HDA** mixture with the molar ratio of 1 : 10 ($\Delta W_{1/2} = 860$ cm^{-1}) has the most uniform structure. It is likely that it is this ratio of components at which ordering of adsorbed dye molecules and the formation of the compact **HDA** monolayer occur. Molecules of **1a** adsorbed on the most stable and structurally perfect **HDA** monolayer form more ordered J-aggregates.

The value of fixed pressure at which the transfer occurs affects much stronger the parameters of J-aggregates. At the same ratio of **1a** : **HDA** (the molar ratio of 1 : 1) and the number of monolayers (2×20), a
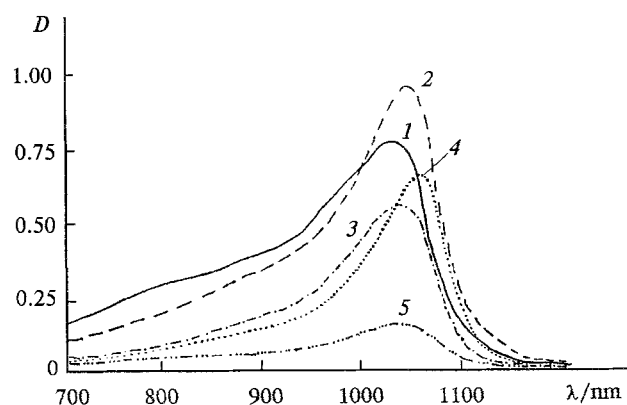

Fig. 2. Absorption spectra of LB films containing **1a** and **HDA** (2×20 monolayers transferred at 30 mN m^{-1}) with a molar ratio of 1 : 1 (*1*), 1 : 2 (*2*), 1 : 5 (*3*), 1 : 10 (*4*), 1 : 20 (*5*).
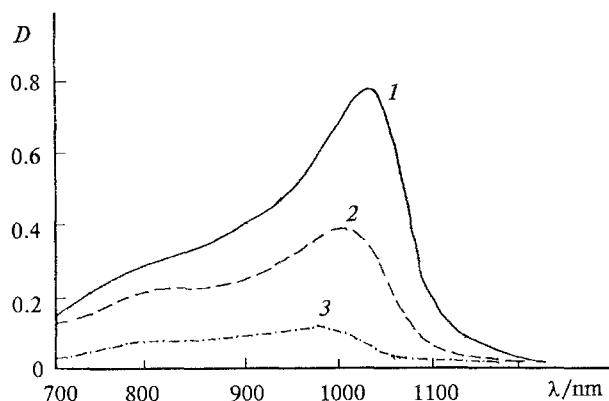
Fig. 3. Absorption spectra of LB films containing **1a** and **HDA** (2×20 monolayers, molar ratio of 1 : 1) transferred at 30 mN m^{-1} (*1*), 25 mN m^{-1} (*2*), 20 mN m^{-1} (*3*).

decrease in π_{const} results in the shift of λ^J_{max} toward lower wavelengths and an increase in $\Delta W_{1/2}$ (Fig. 3). Therefore, the optical density at the maximum of the absorption band decreases correspondingly. No absorption of J-aggregates is observed for LB films transferred at pressures lower than 20 mN m^{-1}. Only the absorption band of monomers (λ_{max} = 870 nm) is present in the absorption spectrum. It is likely that at low values of the surface pressure the plane of the chromophore of the dye molecule is parallel to the surface of the aqueous subphase, which prevents the formation of J-aggregates. This molecular orientation is retained when molecules are transferred to the solid substrate.

LB films of J-aggregated dyes studied in this work are optically anisotropic. The intensity of absorption at the J-band and in the residual M-band decreases as the incident angle of linearly polarized light to the substrate increases. Dipole moments of the transition of J-aggregates of dyes **1a** and **1c** are arranged in the plane of the monolayer. Oscillators of absorption of monomers of these dyes are oriented in a similar way. The anisotropic orientation of J-aggregates is related to the fact that they are formed in the monolayer on the surface and no additional aggregation occurs.[7,8]

Integrals of the interaction between molecules of dye **1a** in the two-dimensional J-aggregate with a **1a** : **HDA** molar ratio equal to 1 : 1 in the LB film transferred at 30 mN m^{-1} were calculated using the model of ordered dipoles.[12] The minimum number of molecules composing such an aggregate is equal to four. The long axes of molecules are parallel to each other and to the plane of the monolayer. The angle α between the line, which connects the centers of molecules (the direction of the moment of the electron transition of the J-aggregate), and the long axes is ~24°. It is likely that the number of molecules composing the J-aggregate is retained as pressure decreases, but the distance between chromophores of individual molecules and the α angle increase. This results in a smaller bathochromic shift in the J-band relative to the M-band. The coexistence of

several types of aggregates is also possible at pressures lower than 30 mN m^{-1}, which results in broadening of the J-band.

PIC can independently form Langmuir monolayers, and chromophore fragments of its molecules are packed in the "brickwork" of J-aggregates, whose structure is well known.[3] When mixtures of dyes **1a—c** and **PIC** are applied on the water—air interface, non-dissociated ion pairs of heterodimers **PIC$^+$ 1$^-$** are formed due to the ion exchange. Since both of the components of such a complex monolayer can form J-aggregates, one should expect that they exert an effect on processes of structuring of dyes. This follows from the difference in geometric dimensions of chromophore fragments of **1a—c** and **PIC**, whose compact packing in the monolayer results in J-aggregation.[12]

Absorption spectra of LB films of heterodimers of dyes **1a** and **PIC** (2×10 layers, π_{const} = 30 mN m^{-1}) are presented in Fig. 4. It can be seen that the predominant aggregation of **1a** (Fig. 4, curve *1*) is observed at the ratio of components of 1 : 1. An increase in the content of **PIC** in the mixture results in a decrease in the intensity of the adsorption band of J-aggregates of **1a** (λ_{max} = 1034 nm), and the absorption of J-aggregates of **PIC** (λ_{max} = 582 nm) increases. No aggregates of **1a** are observed when the **1a** : **PIC** ratio is equal to 1 : 3.

Such a behavior of individual components of the complex monolayer is explained by the difference in geometric sizes of chromophores of non-dissociated ion pairs. According to the results of computer simulation, the surface area occupied by **PIC** on the surface of the aqueous subphase is approximately twice lower than the surface area occupied by **1a**. Therefore, dye **1a** should be aggregated when the ratio of components of heterodimers in the monolayer is equal to 1 : 1, and **PIC** is predominantly aggregated when this ratio is equal to 1 : 3, which is observed experimentally (Fig. 4, curves *1* and *3*, respectively). The intermediate variant (the **1a** : **PIC** ratio is equal to 1 : 2) results in the aggregation of both dyes. This can be explained by the phase separation at which microcrystalline regions with the **1a** : **PIC** ratio equal to 1 : 1 and 1 : 3 can coexist in monolayers. Since the absorption spectrum is the integral parameter of the LB film, the absorption bands of J-aggregates of **1a** and **PIC** are observed simultaneously (Fig. 4, curve *2*). Thus, varying concentrations of components of the Langmuir monolayer of heterodimers makes it possible to suppress J-aggregation of one of dyes.

The *N*-sulfopropyl-substituted thiatricarbocyanine dyes with fixed polymethine chains studied in this work form stable Langmuir monolayers in mixtures with **HDA** and **PIC**. The structure of dye molecules and the nature of the substance that forms the supporting monolayer affect the formation of J-aggregates in monolayers. The structure of J-aggregates of the studied dyes adsorbed on oppositely charged monolayers depends on the dye concentration in the monolayer and is caused to a great
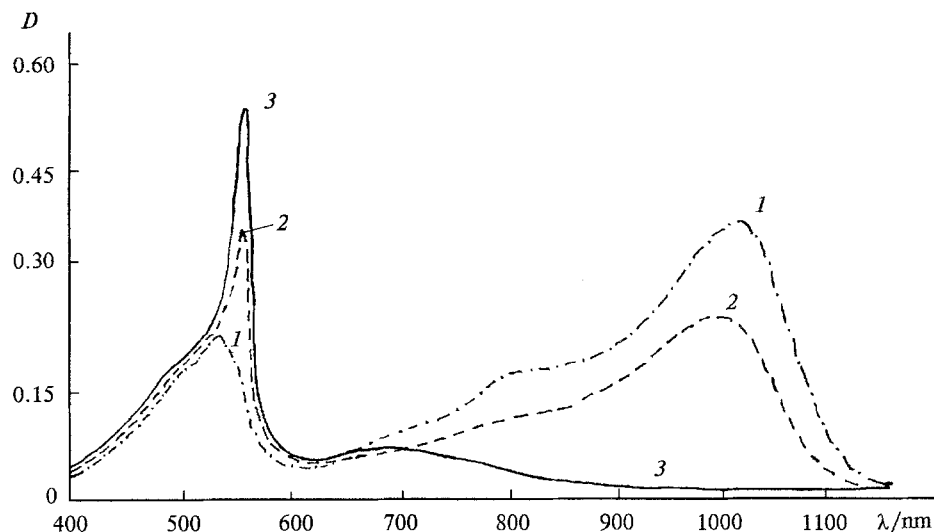
Fig. 4. Absorption spectra of LB films containing **1a, PIC**, and **ODA** (2×10 monolayers transferred at 30 mN m^{-1}) with a molar ratio of 1 : 1 : 2 (*1*), 1 : 2 : 3 (*2*), 1 : 3 : 4 (*3*).

extent by the value of the applied surface pressure at which the transfer occurs.

References

1. C. Ishimoto, H. Tomimuro, and J. Seto, *Appl. Phys. Lett.,* 1986, **49**, 1677.
2. *The Theory of the Photographic Process,* Ed. T. H. James, Macmillan, New York, 1977.
3. C. Duschl, W. Frey, and W. Knoll, *Thin Solid Films,* 1988, **160**, 251.
4. H. Kuhn, D. Moebius, and H. Bucher, in *Physical Methods of Chemistry,* Vol. **1**, Pt. 3B, Eds. A. Weissberger and B. Rossiter, Wiley, New York, 1972, 557.
5. U. Lehmann, *Thin Solid Films,* 1988, **160**, 257.
6. A. Nakano, S. Shimizu, T. Takahashi, H. Nakahara, and H. Fukuda, *Thin Solid Films,* 1988, **160**, 303.
7. V. Tkachev, A. Tolmachev, L. Chernigov, and Yu. Slominsky, *Thin Solid Films,* 1994, **245**, 191.
8. V. A. Tkachev, A. V. Tolmachev, Yu. L. Slominsky, L. V. Chernigov, A. A. Babichenko, A. L. Smirnova, and I. P. Krainov, *Ukr. Khim. Zh.* [*Ukr. Chem. J.*], 1994, **60**, 187 (in Russian).
9. T. L. Penner and D. Moebius, *Thin Solid Films,* 1985, **132**, 185.
10. U. Burkert and N. L. Allinger, *Molecular Mechanics,* ACS, Washington, 1982.
11. J. G. Vinter, A. Davis, and M. R. Saunders, *J. Comp. Aided Molec. Design,* 1987, **1**, 31.
12. V. Czikkely, H. D. Foersterling, and H. Kuhn, *Chem. Phys. Lett.,* 1970, **6**, 207.