

NEW ORGANIC LUMINOPHORES ON THE BASIS OF CYANO- AND DICYANOPYRIDINES

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Absorption and fluorescence spectra of solutions of cyanopyridine derivatives of polyphenylene type, *II–VIII*, were investigated. The spectral characteristics determined are interpreted in relation to the probable conformational structure of the investigated substances in the states S_0 and S_1 . The relationship between the Stokes shift and the solvent effect on the fluorescence spectra is discussed.

Among organic luminophores of heterocyclic structure derivatives of pyridine¹ occur to a relatively low extent. Among them, as a rule, only some derivatives of 2- and 4-pyridone^{1,2} and 2-aminopyridine^{1,3} display more intensive emission electron spectra at room temperature. In compounds containing non-annellated pyridine nucleus fluorescence was observed so far in *para*-substituted 2,4,6-triphenylpyridines *Ia–Ic*, the intensity increase of which can be achieved only by protonation on the heterocyclic nitrogen centre⁴. When looking for new pyridine luminophores we always tried to connect empirically in a single molecular structure a chromophore of type *I* and replace the effect of protonation by introduction of a strongly electronegative cyano group into position 3 with respect to the pyridine nitrogen. The presence of this group has already manifested itself positively in derivatives of 2-pyridone². Moreover, we also investigated the effect of the prolongation of the conjugated system by the *para*-phenylene procedure, proved suitable in other types of luminophores¹.

The subject of this paper is an attempt at the determination of the dependence between the molecular structure, electronic absorption and fluorescence of substances of the type *II–VIII*, in the molecule of which (with the exception of the reference compound *Vc*) 3-cyano- or 3,5-dicyano-4-phenyl fragment is present as the fundamental constructional unit.

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EXPERIMENTAL

The melting points were determined on a Boetius block and they are not corrected. The IR spectra were measured on a Perkin-Elmer 325 instrument and the ^1H NMR spectra on a Varian XL-100 instrument (31°C , internal reference tetramethylsilane). With the exception of compounds *IVa*, *IVb*, and *Vc*, the preparation of the investigated substances is described in our communications⁵⁻⁷. Compounds *IVb*, *VIb*, and *VIc* were prepared by oxidation of corresponding 1,4-dihydropyridines⁸ (2 mmol) with sodium nitrite in acetic acid, in analogy to ref.⁹.

2-(4-Biphenyl)-4,6-diphenyl-3,5-dicyanopyridine (IVb): yield 90%, m.p. $212-214^\circ\text{C}$ (ethanol-benzene). For $\text{C}_{31}\text{H}_{19}\text{N}_3$ (433.5) calculated: 85.88% C, 4.43% H, 9.69% N; found: 85.57% C, 4.35% H, 9.63% N. IR spectrum (chloroform), $\tilde{\nu}_{\text{max}}$ (cm^{-1}): 3 068 w, 3 015 m ($=\text{C}-\text{H}$), 2 230 w ($\text{C}\equiv\text{N}$), 1 610 m, 1 583 w, 1 564 m, 1 535 s, 1 489 s, 1 450 m ($\text{C}=\text{C}$ and the pyridine skeleton). ^1H NMR spectrum (C^2HCl_3), δ (ppm): 7.36-7.68 (m, 13 H, H_{arom}), 7.74 (d, 2 H, $\text{H}_{\text{b,b'}}$), 7.98-8.12 (m, 2 H, $\text{H}_{\text{ortho-phenyl}}$ in position 6), 8.15 (d, 2 H, $\text{H}_{\text{a,a'}}$, $J = 8.2$ Hz).

4,6-Dicyano-5-phenyl-3-methyl-2-aza-1:1',4':1''-terphenyl (IVa): yield 95%, m.p. $206-208^\circ\text{C}$ (ethanol-benzene). For $\text{C}_{26}\text{H}_{17}\text{N}_3$ (371.5) calculated: 84.06% C, 4.62% H, 11.31% N; found: 84.10% C, 4.6% H, 11.16% N. IR spectrum (chloroform), $\tilde{\nu}_{\text{max}}$ (cm^{-1}): 3 068 w, 3 016 m ($=\text{C}-\text{H}$), 2 234 m ($\text{C}\equiv\text{N}$), 1 610 m, 1 602 w, 1 583 w, 1 564 m, 1 545 s, 1 490 m, 1 448 m ($\text{C}=\text{C}$ and $\text{C}\equiv\text{N}$). ^1H NMR spectrum (C^2HCl_3), δ (ppm): 2.92 (s, 3 H, CH_3), 7.27-7.64 (m, 10 H, H_{arom}), 7.70 (d, 2 H, $\text{H}_{\text{b,b'}}$, $J = 8.2$ Hz), 8.03 (d, 2 H, $\text{H}_{\text{a,a'}}$, $J = 8.2$ Hz).

6-Ethoxycarbonyl-5-phenyl-4-cyano-3-methyl-2-aza-1:1',4':1''-terphenyl (Vc): yield 67%, m.p. $129-131^\circ\text{C}$ (ethanol). For $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_2$ (418.5) calculated: 80.35% C, 5.31% H, 6.70% N; found: 79.92% C, 5.22% H, 6.62% N. IR spectrum (chloroform), $\tilde{\nu}_{\text{max}}$ (cm^{-1}): 3 070 w, 3 018 m ($=\text{C}-\text{H}$), 2 232 m ($\text{C}\equiv\text{N}$), 1 782 s ($\text{C}=\text{O}$), 1 610 m, 1 600 w, 1 580 w, 1 564 w, 1 545 s, 1 488 m, 1 446 m ($\text{C}=\text{C}$ and $\text{C}\equiv\text{N}$). ^1H NMR spectrum (C^2HCl_3), δ (ppm): 0.93 (t, 3 H, CH_2CH_3), 2.71 (s, 3 H, CH_3), 4.01 (q, 2 H, OCH_2), 7.25-7.62 (m, 10 H, H_{arom}), 7.68 (d, 2 H, $\text{H}_{\text{b,b'}}$, $J = 8.2$ Hz), 7.98 (d, 2 H, $\text{H}_{\text{a,a'}}$, $J = 8.2$ Hz).

Spectral Measurements

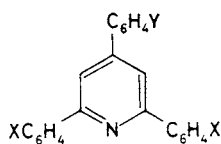
For the study of spectral characteristics preparations of analytical purity were used, which was checked by thin-layer chromatography (Silufol, chloroform as eluent), detection with iodine vapours and in UV light.

The absorption spectra were measured on a Unicam SP 800B instrument in a quartz cell of 10, 5 or 2 mm thickness, the solutions of substances were $1-4 \cdot 10^{-5} \text{ mol l}^{-1}$ in acetonitrile. The fluorescence spectra were measured on an Aminco-Bowman spectrofluorometer. The emission spectra were measured in dilute solutions the absorbance of which did not exceed the value of 0.01 in a 1 cm cell. The spectra were digitalized manually and corrected with a TI-59 calculator. The program for the computation of correction factors utilized the Gauss interpolation formula in values of the logarithms of the correction factors set for 10 nm intervals. The corrected spectrum was standardized per unit area and the wavelengths of the maxima and the functional values of the standardized corrected spectrum ϕ for these wavelengths were determined. For the determination of the quantum yield, solutions of all substances and of quinine sulfate were prepared, the absorbance A of which for the excitation wavelength was about 0.4 in a 1 cm cell. These solutions were diluted 50 times after the measurement of absorbance and the intensity of their emission I was measured in the emission maximum before and after the bubbling through of the solution with nitrogen. Simultaneously the intensity of the excitation radiation was measured. Immediately after the measurement of the solution the same parameters were also measured for

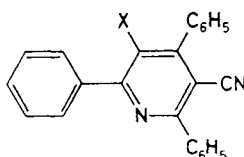
the standard solution of quinine sulfate in 0.5M-H₂SO₄ for which literature^{10,11} gives the quantum yield of fluorescence $q_F = 0.54$.

RESULTS AND DISCUSSION

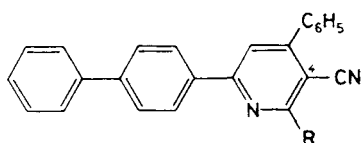
The Dreiding models of the molecules of the substances investigated show that the aromatic and heteroaromatic nuclei cannot be coplanar in the ground electron state S_0 , in consequence of numerous ortho interactions between the hydrogen atomic centres, or between the hydrogen atomic centres and the cyano group. These non-bonding interactions will be of various intensities in individual structural types II–VIII, and will thus participate to various extents in the decrease of the total delocalization energy of π -electrons and thus also affect the relative energies of



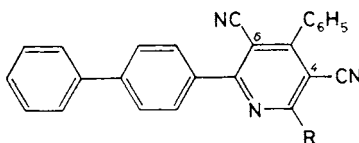
- I a*, X = Y = H
I b, X = *p*-CH₃O, Y = H
I c, X = H, Y = *p*-CH₃O



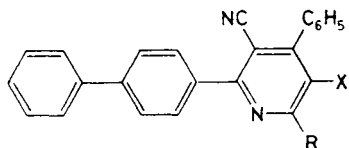
- II a*, X = H
II b, X = CN



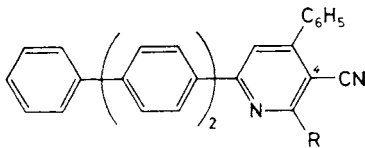
- III a*, R = CH₃
III b, R = C₆H₅
III c, R = *p*-C₆H₅C₆H₄



- IV a*, R = CH₃
IV b, R = C₆H₅
IV c, R = *p*-C₆H₅C₆H₄



- V a*, X = H, R = C₆H₅
V b, X = R = C₆H₅
V c, X = CO₂C₂H₅; R = CH₃



- VI a*, R = C₆H₅
VI b, R = *p*-C₆H₅C₆H₄

the states S_0 in a variable way. Owing to the considerable similarity of the structures of the investigated pyridines *II–VIII* with the compounds of polyphenylene type, their higher degree of planarity may also be expected in the excited state S_1 than in the ground state. For example, *p*-terphenyl, which in consequence of non-bonding *ortho* interactions of the benzene rings has in solution in the state S_0 a non-planar conformation^{12,13}, is in the excited state S_1 most probably coplanar, with a more developed conjugation, and it fluoresces distinctly^{14–16}. The increased resonance interaction in the excited state between the attached benzene rings and the addition of a certain π -character to each coannular bond compels the rings to assume a more planar configuration¹⁷. Analysis of the electron spectra of a large set of organic compounds showed¹⁸ that the effectivity of fluorescence increases with the planarity of the molecules in state S_1 . The authors^{19,20} expressed the assumption that in contrast to the non-radiation energy loss the radiation $S_1 \rightarrow S_0$ transition will be the more preferred the more distinct will be the degree of conjugation of the system in S_1 in comparison with the state S_0 , which can be correlated with the coplanarity of the molecules in states S_0 and S_1 in the case of the compounds *II–VIII* studied. Since a quantitative test of this hypothesis is so far hardly feasible with respect to the molecular dimensions of compounds *II–VII*, we tried to make use of it as a working hypothesis. We tried to check its substantiation mainly in the discussion of the position of the absorption and emission maxima, as well as quantum yields of fluorescence.

Electron absorption spectra. In Table I spectral characteristics of all substances investigated are listed, divided on the basis of these data to types A to G, always on the basis of a common partial chromophore or fluorophore system in the molecule: 4-cyano-2-azabiphenyl type A in compounds *IIa,b*; 4-cyano-2-aza-1 : 1',4' : 1''-terphenyl type B (compound *IVa–c*); 6-cyano-2-aza-1 : 1',4',1''-terphenyl type D (compounds *Va–c*); 4-cyano-2-aza-1 : 1',4' : 1'',4'' : 1'''-quaterphenyl type E (compounds *VIa,b*); 4,6-dicyano-2-aza-1 : 1',4' : 1'', 4'' : 1'''-quaterphenyl type F (compound *VII*) and 4,4'''-dicyano-2,2'''-diaz-1 : 1',4' : 1'',4'' : 1'''-quaterphenyl type G (compounds *VIIIa–VIIIf*).

All the mentioned heterocycles *II–VIII* have certain common spectral features with the polyphenylene hydrocarbons alone, *i.e.* an indistinct vibrational structure of absorption bands, similar values of molar absorption coefficients ($\pi-\pi^*$ transitions). In some cases they also have a similar Stokes shift and quantum yields of fluorescence. The typical appearance of the absorption and emission curves is evident in Figs 1 and 2. The intensity of fluorescence in compounds *II–VIII* is not excessively affected by the presence of oxygen in solution. Its elimination by bubbling through of the measured solution with nitrogen led to an increase in luminescence efficiency by 1.03 to 1.13 times, and only in compound *Vb* 1.24 times. These findings indicate a very short lifetime of the excited states S_1 .

Similarly as in other polyphenylene derivatives²¹, considerable changes of molecular geometry also may be assumed in compounds *II–VIII*, especially of conformational structure, during the transition from states S_0 to states S_1 . The absence of vibrational structure in absorption bands indicates the presence of a number of conformers, under the conditions of the measurement. From Figs 1 and 2 and the data in Table I it is evident that the absorption spectra represent envelopes of a number of close electron absorption bands and that they are not therefore very characteristic of individual types A to G. On increase of the number of π -electrons in the

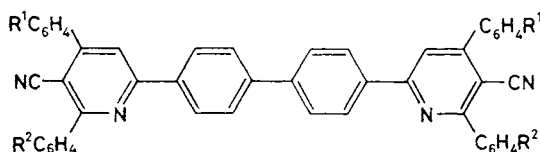
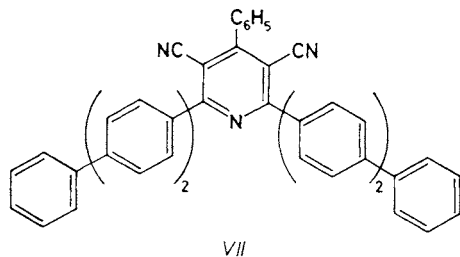
TABLE I

Electronic spectra of solutions of compounds *II–VIII* in acetonitrile (AC), toluene (TL), and cyclohexane (CC)

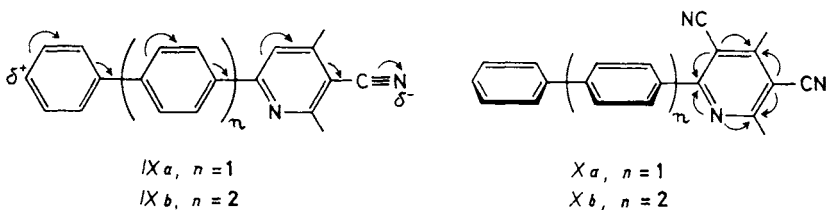
Compound Type ^a	Absorption ^b			Fluorescence ^c				
	λ_{\max} , nm	log ϵ	λ_{\max} , nm			$\phi \cdot 10^3$, nm ⁻¹	q_F^g	
			CC ^d	TL ^d	AC ^e			AC ^f
<i>IIa</i>	A	320	3.98	—	—	367	13.8	0.02
<i>IIb</i>	A	274 ^h	4.60	—	—	—	—	<0.002
<i>IIIa</i>	B	322	4.60	355, 371	(370), 380	399	14.8	0.78
<i>IIIb</i>	B	325	4.59	358, 373	(370), 382	401	14.4	0.73
<i>IIIc</i>	B	300 ^h	4.61	362, 375	(372), 383	401	14.2	0.51
<i>IVa</i>	C	313	4.49	385	401	423	13.6	0.15
<i>IVb</i>	C	285 ^h	4.51	(372), 388	404	434	12.4	0.24
<i>IVc</i>	C	315	4.73	(374), 390	405	441	11.4	0.23
<i>Va</i>	D	280 ^h	4.65	370	384	410	11.8	0.11
<i>Vb</i>	D	286	4.52	<i>i</i>	<i>i</i>	395	14.5	0.004
<i>Vc</i>	D	293	4.53	375	390	402	11.8	0.04
<i>VIa</i>	E	335	4.70	375, 395	390, 403	436	11.3	0.82
<i>VIb</i>	E	332	4.69	376, 395	390, 403	437	11.2	0.80
<i>VII</i>	F	332	4.84	399	430	497	8.7	0.67
<i>VIIIa</i>	G	348	4.82	<i>i</i>	390, 409	409	15.4	0.81, 0.69 ^j
<i>VIIIb</i>	G	345	4.91	<i>i</i>	<i>i</i>	406	15.7	0.83
<i>VIIIc</i>	G	346	4.67	<i>i</i>	<i>i</i>	408	15.5	0.81
<i>VIIId</i>	G	347	4.84	380, 401	390, 409	407	15.6	0.83
<i>VIIIe</i>	G	348	4.73	<i>i</i>	391, 411	407	15.3	0.69 ^j
<i>VIIIf</i>	G	348	4.80	<i>i</i>	390, 410	407	15.4	0.69 ^j

^a For the classification of fluorophores see the text; ^b $c = 1 - 4 \cdot 10^{-5} \text{ mol l}^{-1}$; ^c the data in brackets correspond to inflexions; ^d uncorrected spectra; ^e corrected spectra; ^f maximum intensity of the corrected spectrum standardized per area unit; ^g quantum yield corrected per refractive index; ^h the long-wave band is overlapped with bands of shorter wavelengths; ⁱ not measured; ^j measured in TL.

molecule mostly a bathochromic shift of the long-wave absorption maximum takes place. The spectra of compounds *IIb*, *IIc* and *IV*, in which the long-wave absorption band is evidently overlapped by the shorter-wave more intensive bands are an exception.



- VIII a, $R^1 = R^2 = H$
 VIII b, $R^1 = p-CH_3$; $R^2 = H$
 VIII c, $R^1 = H$; $R^2 = p-CH_3$
 VIII d, $R^1 = R^2 = p-CH_3$
 VIII e, $R^1 = H$; $R^2 = p-C_6H_5$
 VIII f, $R^1 = p-CH_3$; $R^2 = p-C_6H_5$



Fluorescence spectra are more characteristic of individual spectral types A to G and they afford information on the measure of coplanarization of partial fluorophores indicated in formulae *II*–*VIII*. In fluorophore A this planarization is evidently of low level in relation to the size of the molecules which is indicated by the minimal fluorescence of compounds *IIa,b*. In compound *IIa* the Stokes shift is relatively low

(47 nm), showing thus the not very different molecular geometry of the states S_0 and S_1 . In fluorophore B the additional attached phenyl group is distinctly involved in the process of coplanarization during the transition to the state S_1 , which is manifested in compounds *IIIa–IIIc* by an increase of quantum yields (0.51 to 0.78) and a larger Stokes shift (77 or 76 nm in compounds *IIIa* and *IIIb*, respectively). The shift of the emission maximum toward higher wavelengths on transition from solutions in cyclohexane to solutions in acetonitrile (26–28 nm in compounds *IIIa–IIIc*) is remarkable, showing that the state S_1 is more polar in comparison with the state S_0 , probably owing to the shift of the π -electron density indicated in formula *IXa*. In this respect the comparison with the fluorophore C is important in which the 6-cyano group prevents coplanarization of the molecular fragment *Xa* in the S_1 state. The absorption and emission of the electron energy is more connected with the transfer of the π -electron energy in a way approximately indicated in formula *X*, as may be judged on the basis of PPP-calculations of simpler 3,5-dicyanopyridine chromophores²². In agreement with these assumptions, in fluorescence spectra of compounds *IVa–IVc* the solvent shift is more pronounced (47–51 nm), and the Stokes shift is also larger (110 and 126 nm in compounds *IVa,c*). However, the most important argument in favour of the mentioned steric effect of the 6-cyano

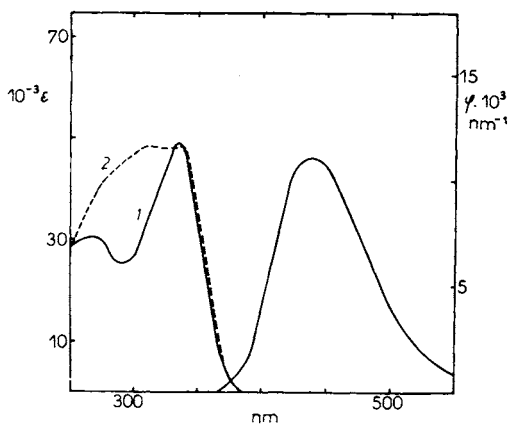


FIG. 1

Electronic spectra of solutions of compounds containing 4-cyano-2-aza-1 : 1', 4' : 1'', 4'' : 1'''-quaterphenyl chromophore (in CH_3CN). 1 Absorption of compound *IVa*; 2 absorption of compound *IVb*; fluorescence curves of compounds *IVa,b* are identical

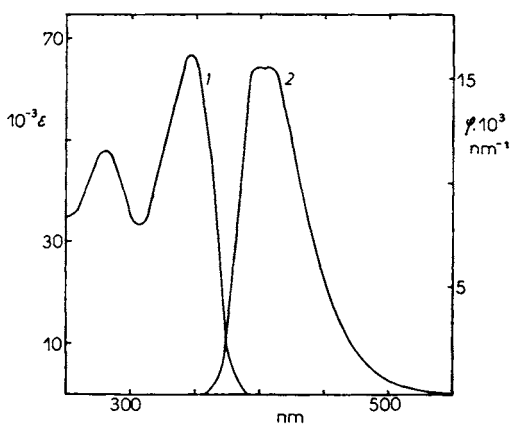


FIG. 2

Electronic spectra of 3,3''',5,5'''-tetra(4-methylphenyl)-4,4'''-dicyano-2,2'''-diazquaterphenyl (*VIIIa*), a solution in acetonitrile. 1 Absorption; 2 fluorescence

group in state S_1 is the distinct decrease of quantum yields in all compounds $IVa-IVc$ (0.15 to 0.24).

The extension of the molecular fragments by another phenyl group in compounds VIa,b permits, again in state S_1 , the coplanarization of the fluorophore E effectively. High quantum yields of fluorescence (0.82 and 0.80) are a consequence. The polarization of the electron transitions enabling the formation of the state S_1 leads again to an increase in polarity (formula IXb) and this is manifested by a higher solvent shift in 2-azaterphenyls VIa,b (41 and 42 nm) in comparison with 2-azaterphenyls $IIIa,b$ (28 nm), because the redistribution of the charge density takes place in a larger π -electron system. This more extensive electronic process is also accompanied by relatively larger geometric changes of the molecular structure and therefore the Stokes shift in compounds IVa,b is also substantially larger (101 and 105 nm). The 4,6-dicyano derivative VII is also remarkable, in the molecule of which two cross-conjugated fluorophores IXb are present. It therefore represents a special type, F, which is characterized by a double steric hindrance by both cyano groups as in fluorophore Xa . A slightly lower quantum yield of fluorescence, 0.67, can be explained by the mentioned steric effect, but the extremely high values of the Stokes and solvent shifts (165 and 98 nm) are surprising, indicating a high reorganization of the geometry of the molecular structure in the S_1 state in comparison with the S_0 state. In contrast to this diazaquaterphenyl derivatives $VIIIa-VIIIf$ evidently display in state S_1 a high degree of coplanarization of the fluorophore system G and the high quantum yields (0.69 to 0.83) connected with it. The Stokes shifts are, however, generally relatively low (59–62 nm) and the solvent shifts determined in substances $VIIIa,d$ are also lower than 10 nm. This shows that both the polarity and the solvation of the state S_1 are low. Evidently the same is true of the S_0

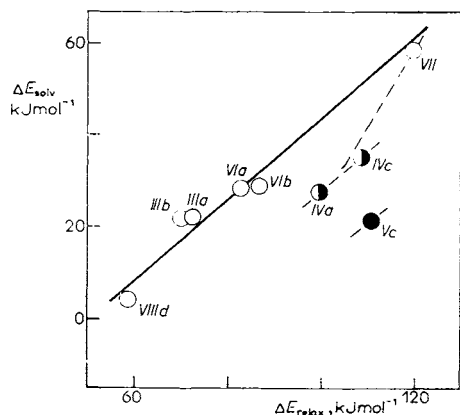


FIG. 3

Changes of the solvation energy ΔE_{solv} (cyclohexane-acetonitrile) versus relaxation energies ΔE_{relax} (acetonitrile) of S_1 states. Empty circles: 4-cyanofluorophores B, E, G, and F; half circles: 4,6-dicyanofluorophores C; full circle: 4-ethoxycarbonyl fluorophore D (see Table I)

state and it is a consequence of the introduction of 4- and 4''-cyano groups to both ends of the polyphenylene chain, in consequence of which the polarization of corresponding electron transitions in chromophore G can be distinguished more strongly from types B to F. It should be pointed out here that fluorophores B, E, and G are characterized by a distinct vibrational structure of the emission maxima measured in toluene. The measure of coplanarization of the molecules in S_1 states is thus distinct in these cases. In contrast to this, some derivatives with fluorophores of type A, C, and D do not display this vibrational structure, or they display indications of it in unsaturated hydrocarbons only.

To sum up it can be stated that the types B, E, F, and G are the most effective fluorophores in the solution phase. As for the geometrical changes of the molecular structure elicited by the transition of the molecules of the substances II–VIII investigated to states S_1 , the cases of 4,4''-dicyano derivatives VIIIa,d (type G) with minimal changes and 4,6-dicyano derivative VII (type F) with maximal changes represent extreme cases. We come thus to the conclusion that the polarization and the reorganization of the molecular structure during the transition from equilibrium geometries of S_0 states to the relaxed geometries of S_1 states are mutually conditioned processes among the cases investigated by us. Fig. 3 shows that between the differences of the solvation energies in S_1 states and the energies of the vibrational relaxation of these states (calculated from the solvent and Stokes shifts) a truly close linear correlation exists. Thus the above mentioned conclusion may be considered as substantiated.

REFERENCES

1. Krasovitskii B. M., Bolotin B. M.: *Organicheskie Lyuminofovy*. Khimiya, Leningrad 1976.
2. Kuthan J., Nesvadba P., Popl M., Fährnich J.: *This Journal* **44**, 2409 (1979).
3. Rusakowicz R., Testa A. C.: *J. Phys. Chem.* **72**, 2680 (1968).
4. Barrio M. C. G., Barrio J. R., Walker G., Novelli A., Leonard N. J.: *J. Amer. Chem. Soc.* **95**, 4891 (1973).
5. Marchalín Š., Kuthan J.: *This Journal* **50**, 1862 (1985).
6. Marchalín Š., Kuthan J.: *This Journal* **50**, 1870 (1985).
7. Marchalín Š., Kuthan J.: *This Journal* **50**, 1962 (1985).
8. Marchalín Š., Kuthan J.: *This Journal* **48**, 3123 (1983).
9. Kuthan J., Hakr J.: *This Journal* **32**, 1438 (1967).
10. Melhuish W. H.: *J. Phys. Chem.* **65**, 229 (1961).
11. Dawson W. R., Windsor M. W.: *J. Phys. Chem.* **72**, 3251 (1968).
12. Le Fèvre R. J. W., Sundaram A., Sundaram K. M. S.: *J. Chem. Soc.* **1963**, 3180.
13. Suzuki H.: *Bull. Chem. Soc. Jap.* **33**, 109 (1960).
14. Berlman I. B., Wirth H. O., Steingraber O. J.: *J. Phys. Chem.* **75**, 318 (1971).
15. Momicchioli F., Bruni M. C., Baraldi I.: *J. Phys. Chem.* **76**, 3983 (1972).
16. Gershuni S., Rabinowitz M., Agranat I., Berlman I. B.: *J. Phys. Chem.* **84**, 517 (1980).
17. Jaffé H. H., Orchin M.: *Theory and Applications of Ultraviolet Spectroscopy*, Chapter 15.3, p. 389. Wiley, New York 1962.

18. Berlman I. B.: *J. Phys. Chem.* **74**, 3085 (1970).
19. Fratev F.: *Z. Naturforsch. A* **30**, 1691 (1975).
20. Fratev F., Monev W., Polansky O. E., Stoyanov S., Tyutyulkov N.: *Z. Naturforsch. A* **32**, 178 (1977).
21. Berlman I. B. in the book: *Organic Scintillators and Liquid Scintillation Counting* (D. L. Horrocks, Chin-tzu Peng, Eds), p. 25. Academic Press, New York 1971.
22. Ilavský D., Kuthan J.: *This Journal* **42**, 662 (1977).

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