SOME 3-CYANO-4,6-DIARYL-2-PYRIDONES WITH LUMINISCENT PROPERTIES

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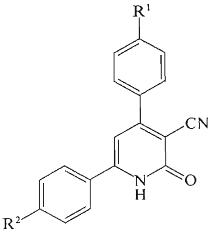
Fluorescence spectra of methanolic solutions of the 2-pyridone derivatives *I* to *XI* have been measured at laboratory temperature and interpreted. Influence of the substituents R^1 and R^2, the 3-cyano group, and that of methylation on quantum yield of the fluorescence has been followed. Preparation of the studied compounds *I* to *XI* has been described, and methylation of the compound *I* has been studied in detail.

In the previous report[1] it was shown that 3-cyano-4,6-diphenylpyridone (*I*) exhibits intensive blue fluorescence both in methanolic solution and in solid in contrast to the corresponding 3,4-dihydro derivative. Now we have been interested in the extent to which the mentioned optical property can be influenced by substitution at *para* positions of the aromatic nuclei of the compound *I* or by N-alkylation or elimination of the cyano group from the parent 2-pyridone skeleton. Therefore, we synthetized and studied spectroscopically a series of 3-cyano-4,6-diaryl-2-pyridones *I* to *VIII* extended by 4,6-diphenyl-2-pyridone (*IX*) and the methyl derivatives *X* and *XI*.

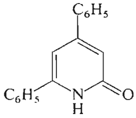
The pyridone derivatives *I* to *VIII* were obtained by condensation reactions of cyanoacetamide with either β-diketones[2-4] (the compounds *I*, *IV*, *V*, *VII*, *VIII*) or α,β-unsaturated ketones[1,5,6] with subsequent dehydrogenation of the primary 3,4-dihydro derivatives (the compounds *II*, *III*, *VI*).

In Experimental an improved preparation procedure of one of the starting compounds – bis-(4-phenylbenzoyl)methane – is described in detail. Condensation of this diketone with cyanoacetamide to the pyridone *VII* gives low yields (Table I), and the product had to be isolated chromatographically.

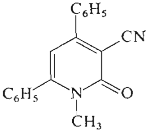
According to literature data, methylation of the pyridone *I* with methyl iodide gives the methyl derivative[7] *X* or the O-methyl isomer[1,8] *XI*. Having applied ^{1}H-NMR to the reaction products, we have found that methylation of the compound *I* is not selective, and solvent only influences the *X* to *XI* isomer ratio in the reaction mixture (Table II). By independent experiments it was also confirmed that the equilibrium $X \rightleftharpoons XI$, which could explain the formation of the alternative methyl isomer, is not established under the alkylation conditions.



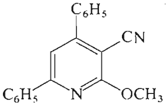
I, $R^1 = R^2 = H$
II, $R^1 = H$, $R^2 = CH_3$
III, $R^1 = CH_3$ $R^2 = H$
IV, $R^1 = R^2 = CH_3$
V, $R^1 = R^2 = t\text{-}C_4H_9$
VI, $R^1 = H$, $R^2 = C_6H_5$
VII, $R^1 = R^2 = C_6H_5$
VIII, $R^1 = R^2 = CH_3O$



IX



X



XI

RESULTS

Formulation of the Fluorescence Relative Quantum Yields

Presuming identical form of fluorescence curves in the studied compound series, the original expression[9] for the fluorescence quantum yield can be approximated by

$$q = N_f/N_a \approx I_f/I_a \,, \tag{1}$$

where *N*, *I*, *f* and *a* mean number of light quanta, intensity of the maximum at the spectral curve, fluorescence (emission) and absorption, respectively. If I_0 is the intensity of the radiation incident on the sample and if the Lambert–Beer law is obeyed, then it can be written

$$I_a = I_0(1 - \exp(-A)) = I_0(A_f/1! - A_f^2/2! + A_f^3/3! \ldots) \,, \tag{2}$$

where *A* stands for absorbance of the measured sample. Under the conditions used by us for measurements of fluorescence spectra of the compounds *I* to *XI*, where the concentration was 50 times lower than that in the measurements of their electronic absorption spectra, the quantity A_f attained the maximum value 0·04. For small A_f values the series in Eq. (*2*) can be approximated by the first member, *i.e.*

$$q \approx I_f I_0^{-1} A_f^{-1} = K I_f A_a^{-1} \,, \tag{3}$$

TABLE I

Preparation of New 3-Cyano-4,6-diaryl-2-pyridones

Compound[a]	Formula mol.wt.	Calculated/Found			M.p., °C	Yield, %	$\tilde{\nu}$, cm^{-1} νC≡N	(Nujol) νC=O	δ (ppm), (DMSO-d_6) standard TMS
		C	H	N					
IV	$C_{20}H_{16}N_2O$ 300·4	79·98 80·14	5·37 5·33	9·33 9·44	299—302	36	2 230 m	1 605 s 1 624 s	2·53 s (2 CH_3), 6·77 s (1 CH), 7·3—7·9 m (2 C_6H_4)
V	$C_{26}H_{28}N_2O$ 384·5	81·21 81·51	7·34 7·45	7·29 7·35	306—307	72	2 230 m	1 605 s 1 640 s	1·35 s (2 t-Bu), 6·8 s (1 (CH), 7·5—7·9 m (2 C_6H_4)
VI	$C_{24}H_{16}N_2O$ 348·4	82·47 82·51	4·63 4·90	8·04 7·70	290—292[b,c]	9·5	2 220 m	1 600 s 1 635 s	6·77 s (1 CH), 7·35—8·00 m (1 C_6H_5 + 1 $C_6H_5C_6H_4$)
VII	$C_{30}H_{20}N_2O$ 424·5	84·88 84·68	4·75 4·88	6·60 6·66	313—314	15	2 225 m	1 605 s 1 635 s	6·94 s (1 CH), 7·4—8·1 m (2 p-$C_6H_5C_6H_4$)
VIII	$C_{20}H_{16}N_2O_3$ 332·4	72·28 72·35	4·85 5·09	8·43 8·66	244—245·5	47	2 220 m	1 595 s 1 625 s	3·83 s (2 CH_3O), 6·88 s (1 CH), 6·95—7·95 m (2 C_6H_4)
X	$C_{19}H_{14}N_2O$ 286·3	79·70 79·88	4·93 5·02	9·78 9·54	175—176[d]	34	2 220 m	1 600 m 1 645 s	3·50 s (1 CH_3N), 6·34 s (1 CH), 7·4—7·9 m (2 C_6H_5)

[a] The compound *I* was prepared according to ref.[2]; *II*, *III*, *IX* according to[5]; *XI* according to[1]; [b] ref.[14] gives m.p. 291°C; [c] sublimation begins from about 250°C; [d] ref.[7] gives m.p. 175°C.

where K is constant of the apparatus involving also the presumed constant value I_0 and conversion of A_a in A_f. The A_a value is the absorbance read from UV absorption spectrum of the given substance. The values q calculated in this way give no information about absolute magnitude of the luminiscence quantum yields, but they make it possible to arrange the series of structurally similar compounds *I* to *XI* in increasing or decreasing order of the quantum yields. At the same time the q values enable estimates of effects of structural changes in molecules on fluorescence. Table III gives the found values I_f, A_a and q along with the relative parameters $q_r = q/61$ related to the standard compound *I* ($q = 61$).

TABLE II

Methylation of 3-Cyano-4,6-diphenyl-2-pyridone (*I*)

Methylation conditions	Procedure	Ratio of derivatives $O—CH_3/N—CH_3$
$KOH + CH_3I +$ acetone	ref.[8]	1 : 1·3
$CH_3ONa + CH_3I +$ methanol	ref.[7]	1 : 5·6
$NaOH + CH_3I +$ acetone	this report	1 : 1·3

TABLE III

Characteristics of Electronic Absorption and Fluorescence of the Compounds Studied

Compound	A_{361}[a]	λ_{max}[b] nm	I_f[c]	λ_f nm	q	q_r
I	0·80	363	48·8	435	61	1·00
II	0·76	366	58·0	437	76	1·25
III	0·66	362	34·0	437	52	0·85
IV	0·78	366	51·0	437	65	1·07
V	0·82	368	79·0	435	96	1·57
VI	0·81	370	108·0	440	133	2·18
VII	1·10	370	275·0	440	259	4·24
VIII	1·21	370	196·0	435	162	2·66
IX	0·37[d]	335	6·6[d]	415	18	0·29
X	0·50	354	3·9	430	8	0·13
XI	0·86[d]	325	246·0[d]	370	285	4·73

[a] $c = 4 \cdot 10^{-5}$M in CH_3OH, 1 cm cell; [b] wavelength of the longest-wave band in the absorption spectrum; [c] $c = 8 \cdot 10^{-7}$M in CH_3OH, λ_{exc} 361 nm; [d] measured at λ 330 nm.

Relations between Molecular Structure and Fluorescence

The chromophoric π-electron system of the compounds *I* to *VIII* only differs by the substituents R^1 and R^2. Changes of the followed experimental quantities connected with $S_1 \rightarrow S_0$ transitions of the $\pi^* \rightarrow \pi$ type can, therefore, be taken as a consequence of the substituent effect. King[10,11] studied disubstituted barbituric acids and showed that at a constant life time of the S_1 state within the studied compound series the fluorescence quantum yield should have decreased with increasing value of the substituent parameter σ^* in the Taft correlation equation. In fact, the mentioned author found close linear correlations of logarithms of relative quantum yields of fluorescence with the parameters σ^*. However, in the case of the compounds *I* to *VIII* no similar correlation was found between log q_r and various types of parameters (σ, σ_I, σ_R, see ref.[12]) or their sums when the effects of the both substituents R^1 and R^2 were considered. This fact is, first of all, ascribed to that the effect of the substituents R^1 and R^2 cannot be fully described by inductive mechanism as it was the case in the series of barbituric acids[10,11], and the theoretical presumptions[10,11] are not sufficiently fulfilled. If the compounds *VI* and *VII* (in which the substituents R^1 and R^2 increase fundamentally the extent of the conjugated π-system in the molecule) are excluded, then the quantity q_r really decreases with increasing value of the parameters σ (Table IV). Comparison of the q_r values of the compounds *I* and *IX* shows that elimination of cyano group from 3-position results in strong suppression of fluorescence. This effect is still more marked with the compound *X*. Most probably it is connected with deviation of the plane of aromatic ring of the 6-substituent from the plane of the molecule due to sterical interaction with N-methyl group.

TABLE IV

Comparison of Relative Quantum Yields of Fluorescence with the Substituent Constants

Compound[a]	log q_r + 1	$\sum\sigma$	$\sum\sigma_I$	$\sum\sigma_R$
VII	1·628	0·02	0·20	−0·02
VIII	1·425	−0·54	0·64	−1·26
VI	1·339	0·01	0·10	−0·10
V	1·196	−0·40	−0·16	−0·18
II	1·097	−0·17	−0·06	−0·07
IV	1·030	−0·34	−0·12	−0·14
I	1·000	0·00	0·00	0·00
III	0·930	−0·17	−0·06	−0·07

[a] The compounds *IX*, *X*, *XI* being of different structural type are not involved in the Table.

Consequently energy of the $S_0 \rightarrow S_1$ transition is increased, so that probability of the intercombination conversion $S_1 \rightarrow T_1$ is increased, and probability of deexcitation of the S_1 state by fluorescence is decreased. The high q_r value of the compound *VII* can be explained by analogous arguments, the 4-biphenylyl residue decreasing energy of the $S_0 \rightarrow S_1$ transition and, hence, also that of intercombination conversion leading to non-radiant deexcitation under conditions of the measurement.

EXPERIMENTAL

The temperature data are uncorrected. For the spectral measurements the following apparatus was used: Perkin-Elmer 325 (IR), Varian XL-100 (NMR), Unicam SP 800 (UV), Aminco-Bowman (fluorescence).

Purity of the synthetized compounds was checked by thin-layer chromatography on Silufol (Lachema, Brno; detection by UV light).

3-Cyano-4,6-bis(4-methylphenyl)-2-pyridone (IV). Bis(4-methylbenzoyl)methane (25·2 g) and cyanoacetamide (13·4 g) were boiled with 10 ml diethylamine in 200 ml ethanol 30 h. The crystals precipitated on cooling were collected by suction, washed with methanol and crystallized from xylene-dimethylformamide mixture. Yield 11 g (36%), m.p. 299—302°C.

Bis(4-tert-butylbenzoyl)methane. Mixture of 4-tert-butylacetophenone (96·6 g) and ethyl 4-tert-butylbenzoate (136 g) was added dropwise to suspension of sodium hydride (26·3 g) in 600 ml toluene with stirring. After 3 h boiling and standing overnight the reaction mixture was decomposed with 50% acetic acid. The organic layer was washed with water and with sodium hydrogencarbonate solution and evaporated until dry. The evaporation residue was crystallized from light petroleum to give 26·4 g 4-tert-butylbenzoic acid, the mother liquor was distilled in vacuum, and the fraction with b.p. 235—240°C/1 Torr was crystallized from ethanol to give 23 g (12%) crystals melting at 108—109°C. For $C_{23}H_{28}O_2$ (336·5) calculated: 82·10% C, 8·39% H; found: 82·22% C, 8·40% H.

3-Cyano-4,6-bis(4-tert-butylphenyl)-2-pyridone (V). Bis(4-tert-butylbenzoyl)methane (13·3 g) and cyanoacetamide (10 g) were boiled with 5 ml diethylamine in 100 ml ethanol 8 h. After standing overnight the precipitated crystals were collected by suction, washed with methanol, and crystallized twice from xylene-dimethylformamide mixture. Yield 11 g (72%), m.p. 306 to 307°C.

3-Cyano-4-phenyl-6-(4-biphenylyl)-2-pyridone (VI). The solution of sodium methoxide prepared from 1·48 g sodium and 50 ml absolute methanol was added to boiling mixture of benzylidene-*p*-phenylacetophenone[13] (8·5 g) and cyanoacetamide (2·52 g) in 100 ml absolute methanol. After 2 h standing 300 ml water was added, and the mixture was acidified with hydrochloric acid. The precipitated solid was collected by suction and dissolved in 200 ml acetic acid, whereupon solution of 1·5 g sodium nitrite in 20 ml water was added drop by drop with cooling. The precipitate separated on standing overnight was collected by suction and crystallized twice from n-butanol. Yield 1·0 g (9·5%), m.p. 290—292°C (sublimation up to about 250°C).

Bis(4-phenylbenzoyl)methane. Malonyl dichloride (23·9 g) was added drop by drop to mixture of 53 g aluminium chloride and 46 g biphenyl in 150 ml 1,2-dichloroethane with stirring and cooling at 0°C. After 2 h standing the mixture was decomposed by addition of ice, the separated yellow precipitate was extracted with warm chloroform, and the extract was evaporated. The evaporation residue was crystallized from acetic acid (charcoal). Yield 20 g (36%) crystals m.p. 218–220°C. For $C_{27}H_{20}O_2$ (376·4) calculated: 86·14% C, 5·36% H; found: 86·03% C, 5·76% H.

3-*Cyano*-4,6-*bis*(4-*biphenylyl*)-2-*pyridone* (VII). Bis(4-phenylbenzoyl)methane (1 g) and cyanacetamide (1 g) in 25 ml piperidine were heated at 90°C 48 h. Piperidine was distilled off and the residue was chromatographed on a silica gel column (⌀ 4 cm, $h = 40$ cm, benzene + 30% ethyl acetate). The uniform fraction was evaporated and recrystallized from mixture xylene–dimethylformamide. Yield 170 mg (15%) crystals, m.p. 313–314°C.

3-*Cyano*-4,6-*bis*(4-*methoxyphenyl*)-2-*pyridone* (VIII). Bis-(4-methoxyphenyl)methane (28·4 g) and cyanacetamide (25·2 g) were boiled with 10 ml diethylamine in 100 ml ethanol 80 h. The separated crystals were collected by suction, washed with methanol, and recrystallized twice from mixture xylene–dimethylformamide. Yield 15·5 g (47%), m.p. 244–246°C.

1-*Methyl*-3-*cyano*-4,6-*diphenyl*-2-*pyridone* (X). Dibenzoylmethane (11·2 g) and N-methylcyanacetamide (9·8 g) were boiled with 5 ml diethylamine in mixture of 100 ml ethanol and 50 ml benzene 30 h. The solvents were distilled off and the residue was chromatographed on a silica gel column (⌀ 4 cm, $h = 40$ cm, benzene–ethanol). Yield 5 g (34%) crystals, m.p. 175–176°C (ref.[7] gives m.p. 175°C).

Methylation of derivative I. *A*) The compound *I* (0·35 g) and methyl iodide (2 ml) were boiled with 0·1 g alkali hydroxide in 20 ml acetone 5 h. Thin-layer chromatography (Silufol, chloroform + 4% ethyl acetate, detection in UV light) proved the presence of the N-methyl derivative *X* (R_F 0·12) along with the O-methyl derivative *XI* (R_F 0·71). Their ratio (Table II) was determined from integral intensities of ^{1}H-NMR spectrum of evaporation residue of the reaction mixture. *B*) The compound *I* (0·35 g) and methyl iodide (4 ml) were boiled in 20 ml methanol containing 0·1 g dissolved sodium 13 h. Ratio of O- to N-methyl derivatives *X*, *XI* was determined as in above experiment (*A*).

Attempts of isomerization X $\rightleftharpoons$ XI. 1-Methyl-3-cyano-4,6-diphenyl-2-pyridone (*X*) (0·2 g) was boiled with 0·1 g potassium hydroxide in 20 ml acetone 6 h. Thin-layer chromatography (Silufol, chloroform + 4% ethyl acetate, detection in UV light) proved the absence of the O-methyl derivative in the reaction mixture. Analogous procedure was applied to the compound *XI*. The presence of the N-methyl derivative *X* in the reaction mixture could not be proved.

The spectroscopic measurements and elemental analyses were carried out in Central Laboratories of our Institute.

REFERENCES

1. Kuthan J., Nesvadba P., Donnerová Z., Trška P.: This Journal *42*, 2152 (1977).
2. Basu U.: J. Indian Chem. Soc. *7*, 481 (1930).
3. Basu U.: J. Indian Chem. Soc. *7*, 815 (1930).
4. Basu U.: J. Indian Chem. Soc. *8*, 119 (1931).
5. Barat Ch.: J. Indian Chem. Soc. *7*, 321 (1930).
6. Kohler E. P.: J. Amer. Chem. Soc. *44*, 2908 (1922).
7. Barat Ch.: J. Indian Chem. Soc. *7*, 851 (1930).
8. Bomika Z. A., Andaburskaya M. B., Pelcher J. E., Dubur G. J.: Khim. Geterotsikl. Soedin. *1976*, 1089.

9. Krasovickii B. M., Bolotin B. M.: *Organicheskiie Luminofory*. Khimiia, Leningrad 1976.
10. King L. A.: J. Chem. Soc., Perkin Trans. 2, 844 (1976).
11. King L. A.: J. Chem. Soc., Perkin Trans. 2, 1725 (1976).
12. *Advances in Linear Free Energy Relationships* (N. B. Chapman, J. Shorter, Eds), p. 28, 37. Plenum Press, London 1972.
13. Dilthey W.: J. Prakt. Chem. *101*, 177—206 (1921).
14. Jahine H., Zaher H. A., Sayed A. A., Sherif O.: J. Indian Chem. Soc. *1973*, 1122.

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