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Synthesis and investigation of solvent effects on the ultraviolet absorption spectra of 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones

DUŠAN Ž. MIJIN#, GORDANA S. UŠĆUMLIĆ# and NATAŠA V. VALENTIĆ#

Department of Organic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, P. O. Box 3503, YU–11001, Belgrade, Yugoslavia

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A number of 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones from cyanoacetamide and the corresponding alkyl ethyl acetoacetates were synthesized according to modified literature procedures. The alkyl ethyl acetoacetates were obtained by the reaction of C-alkylation of ethyl acetoacetate. An investigation of the reaction conditions for the synthesis of 4-methyl-3-cyano-6-hydroxy-2-pyridone from cyanoacetamide and ethyl acetoacetate in eight different solvents was also performed. The ultraviolet absorption spectra of synthesized pyridones were measured in nine different solvents in the range 200–400 nm. The effects of solvent polarity and hydrogen bonding on the absorption spectra are interpreted by means of linear solvation energy relationships using a general equation of the form $\nu = \nu_o + s\pi^* + a\alpha + b\beta$, where π^* is a measure of the solvent polarity, α is the scale of the solvent hydrogen bond donor acidities and β is the scale of the solvent hydrogen bond acceptor basicities.

Keywords: alkylation, ethyl acetoacetate, alkyl ethyl acetoacetates synthesis, 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones, spectroscopy, cyclization, ultraviolet absorption spectra, solvent effects, linear solvation energy relationships.

5-Substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones were synthesized for the first time at the end of 19th century.[1] Guareshi[2] cyclized alkyl acetoacetic amides and an cyanoacetic ester to get an ammonium salt which after the action of HCl gave 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones. In such a manner Guareshi first synthesized 4-methyl-3-cyano-6-hydroxy-2-pyridones and 5-ethyl-4-methyl-3-cyano-6-hydroxy-2-pyridone; and later 5-*n*-propyl-, 5-allyl-, 5-benzil-4-methyl-3-cyano-6-hydroxy-2-pyridones and some other 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones from the corresponding alkyl acetoacetic ester, ammonia and a cyanoacetic ester were also obtained.[2,3] Hope and Sheldon used a different route for the syntesis of these compounds where in the first step, ethyl acetoacetic ester and sodium cyanoacetate gave substituted glutaconates which were later cyclized using ammonia or KCN/ammonia.[4,5] Guareshi's

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procedure was used later by Ruzicka and Fornasir.[6] Much later, Bobbite and Scola obtained 4-methyl-3-cyano-6-hydroxy-2-pyridone from ethyl acetoacetate and cyanoacetamide in methanol in the presence of potassium hydroxide.[7] Previously we synthesized 4-methyl-3-cyano-6-hydroxy-2-pyridone using potassium carbonate and potassium hydroxide.[8]

In order to synthesize the desired 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones it is necessary to prepare alkyl ethyl acetoacetic esters. Alkyl ethyl acetoacetic esters were synthesized using two procedures known in the literature.[9–11] One classical method included sodium in absolute ethanol[9] and in the other, a PTC reaction,[10,11] with a PTC catalyst and base in a liquid-liquid system was used. In the second part of this work we report the synthesis of seven 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones using a modified Bobbite and Scola procedure as well as the investigation of the condensation of ethyl acetoacetate and cyanoacetamide in different solvents in the presence of potassium carbonate, potassium hydroxide and sodium hydroxide. IR, ^{1}H NMR and UV data are given for all the products.

EXPERIMENTAL

The alkyl acetoacetic esters were obtained using the following procedures:

Procedure A.

Sodium previously cut into clean small pieces was placed in a dry apparatus and absolute ethanol was added. After completion of the reaction, ethyl acetoaceatate was added. The appropriate alkyl halide was then added dropwise to the hot solution and the reaction mixture was heated to reflux for a period of time (Table I). The reaction mixture was cooled and filtered. The excess ethanol was removed by distillation and the product was obtained by further distillation using a short fractionating column.

Procedure B.

Ethyl acetoacetate, alkyl halide, water, toluene, a phase-transfer catalyst and potassium hydroxide were mixed and heated under reflux for a certain period of time (Table I). After cooling, water was added and the layers were separated. The aqueous layer was extracted with ether, the organic layers combined and dried over sodium sulfate. Distillation using a short fractionating column gave the desired product.

5-Substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones were obtained by the following procedure: In a typical experiment, 0.012 mol of alkyl ethyl acetoacetate, 0.019 mol of cyanoacetamide, 0.014 mol of base were placed in a thermostated flask and stirred on a magnetic stirrer in a appropriate amount of solvent for a period of time (Table II and Table V) at 60 ºC at 600 rpm. The reaction mixture was cooled and filtered. The obtained crystals were dissolved in hot water and after cooling to room temperature, the solution was acidified with dilute HCl. The formed solid was separated by filtration and washed with cold water and methanol.

The melting points were measured using an electrothermal melting point apparatus and are not corrected.

IR spectra were recorded on a Bomem FTIR Spectrophotometer, MB-Series in the form of KBr pellets for the pyridones and neat for the alkyl ethyl acetoacetates.

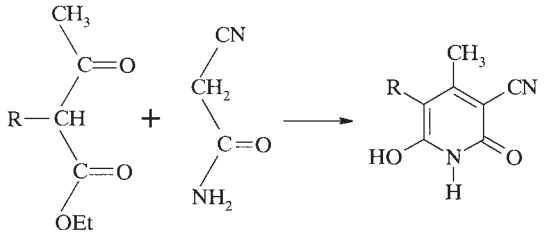
^{1}H-NMR spectra were determined as solutions in trifluoroacetic acid (CF_3COOD) for the pyridones and in chloroform ($CDCl_3$) for the alkyl ethyl acetoacetates using a Varian EM 390 instrument, with tetramethylsilane as an internal standard.

UV spectra were obtained on a Shimadzu UV-160A Spectrophotometar.

All other materials were commercial products.

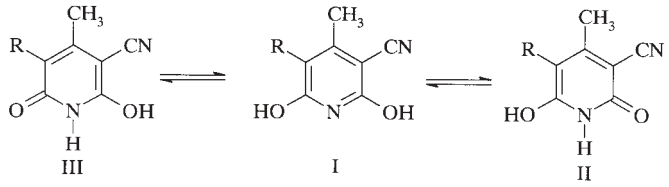
RESULTS AND DISCUSSION

Cyclization of cyanoacetamide with an alkyl ethyl acetoacetate belongs to a 3–2 type of condensation where the pyridine nucleus is formed.[1] This reaction can be presented as in Scheme 1.



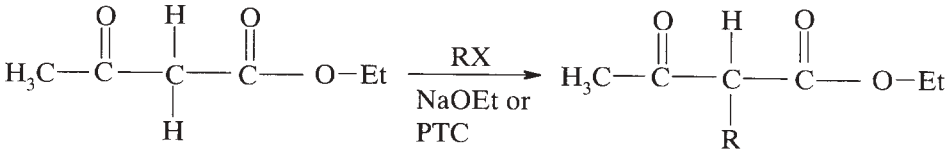
Scheme 1.

We showed earlier[8] that structure of the obtained product can be described on the basis of IR and ^{1}H-NMR data, by three tautomeric forms (Scheme 2). The most probable form(s), particularly in the solid state, are forms II and III, where the obtained product is in the form of pyridone, the forms which are stabilized by intermolecular hydrogen bonding.[12]



Scheme 2.

To perform the cyclization of cyanoacetamide with alkyl ethyl acetoacetates, the reaction of C-alkylation of ethyl acetoacetate was first performed (Scheme 3). The reaction conditions, as well as the boiling points and yields of the products are given in Table I. One can see from the yield that the best result in the C-alkylation of ethyl acetoacetate was obtained when the phase transfer catalyst was employed.



Scheme 3. C-alkylation of ethyl acetoacetate yielding alkyl ethyl acetoacetate (RX=MeI, EtBr, *n*-BuBr, *n*-PeBr, AllylBr).

5-Substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones, including 4-methyl-3-cyano-6-hydroxy-2-pyridone, were synthesized from cyanoacetamide and the corresponding alkyl ethyl acetoacetate in methanol in the presence of potassium hydroxide at 60 °C (Table II). The reactions were performed in different solvent volumes, as well as for different reaction times (one and eight hours). Longer reaction time did not give better yields of pyridones except for the allyl and *n*-butyl derivatives.

TABLE I. Synthesis of alkyl ethyl acetoacetates from ethyl acetoacetate and an alkyl halide

R	AAE	RX	Base	Solvent	Reaction time	B.p.	Yield
	mol	mol	mol	dm^3	hours	ºC	%
Me	0.2	MeI	Sodium	EtOH	5	182–4	18
		0.21	0.2	60			
Et	0.235	EtBr	Sodium	EtOH	5	193–6	11
		0.25	0.235	60			
n-Pr	0.235	*n*-PrBr	Sodium	EtOH	3.5	106–9	10.5
		0.25	0.235	64			
n-Bu	0.235	*n*-BuBr	Sodium	EtOH	6	222–4	15
		0.25	0.235	60			
n-Pe*	0.1	*n*-PeBr	KOH	toluene/H_2O	4	235–8	20
		0.1	0.1	30/6			
Allyl**	0.1	AllylBr	KOH	toluene/H_2O	4	205–8	43
		0.1	0.1	30/6			

*PTC using tetrabutylammonium bromide (0.001 mol) under reflux temperature; **PTC using tetrabutylammonium bromide (0.001 mol) and K_2CO_3 (0.1 mol) under reflux temperature.

TABLE II. Synthesis of 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones from alkyl ethyl acetoacetates and cyanoacetamide in methanol at 60 ºC (0.012 mol of α- alkyl ethyl acetoacetate, 0.0119 mol of cyanoacetamide, 0.014 mol of KOH, 600 rpm).

R	Reaction time hours	Methanol dm^3	M.p. ºC	Yield %
H	1	20	295–9	58
	8	20	293–7	46
Me	1	20	273–8	38
	8	40	265–70	36
Et	1	20	222–4	11
	8	30	223–5	7
n-Pr	1	20	211–3	25
	8	30	210–4	16
n-Bu	1	20	195–7	20
	8	20	195–9	33
n-Pe	1	20	165–7	21
Allyl	1	20	172–4	10
	8	30	159–63	18

The IR and ^{1}H-NMR data for the synthesized alkyl ethyl acetoacetates and 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones are given in Tables III and IV, respectively.

TABLE III. IR and ^{1}H-NMR data for the synthesized alkyl ethyl acetoacetates

R	IR (neat) ν/cm^{-1}	^{1}H-NMR ($CDCl_3$) δ/ppm
Me	2985.9; 2930.32; 1742.4; 1715.92; 1471.74; 1457.5; 1362.3; 1154.61; 1117.46	1.30 (6H, *dt*, C*H*$_3$–CH$_2$ and C*H*$_3$–CH), 2.27 (3H, *s*, CH$_3$–CO), 3.51 (1H, *q*, CH), 4.20 (2H, *q*, O–CH$_2$)
Et	2973.2; 2936.6; 2880.41; 2853.52; 1741.61; 1715.81; 1458.18; 1361.4; 1150.98; 1024.35	1.10 (3H, *t*, C*H*$_3$–CH$_2$–CH), 1.42 (3H, *t*, C*H*$_3$–CH$_2$–O), 2.03 (2H, *m*, CH–C*H*$_2$–CH$_3$), 2.40 (3H, *s*, CH$_3$–CO), 3.52 (1H, *t*, CH), 4.35 (2H, *q*, O–CH$_2$)
n-Pr	2963.57; 2936.41; 2876.06; 1742.32; 1716.39; 1465.57; 1420.23; 1360.64; 1239.54; 1189.32; 1151.52; 1040.03; 1024.62; 855.46	0.82 (3H, *t*, C*H*$_3$–(CH$_2$)$_2$), 1.20 (3H, *t*, C*H*$_3$–CH$_2$–O),1.70 (4H, *m*, (CH$_2$)$_2$), 2.18 (3H, *s*, CH$_3$–CO), 3.40 (1H, *t*, CH), 4.18 (2H, *q*, O–CH$_2$)
n-Bu	2959.64; 2932.61; 2874.03; 2863.03; 1740.15; 1715.7; 1466.33; 1360.25; 1244.12; 1221.88; 1183.11; 1151.68; 1113.87; 1025.42; 860.92	0.83 (3H, *t*, C*H*$_3$–(CH$_2$)$_3$), 1.20 (3H, *t*, C*H*$_3$–CH$_2$–O), 1.73 (6H, *m*, (CH$_2$)$_3$), 2.13 (3H, *s*, CH$_3$–CO), 3.40 (1H, *t*, CH), 4.15 (2H, *q*, O–CH$_2$)
n-Pe	2960.0; 2945.5; 2888.6; 1741.2; 1718.3; 1462.0; 1355.2; 1210.2; 1150.6; 870	0.83 (3H, *t*, C*H*$_3$–(CH$_2$)$_3$), 1.20 (3H, *t*, C*H*$_3$–CH$_2$–O), 1.75 (9H, *m*, (CH$_2$)$_4$), 2.14 (3H, *s*, CH$_3$–CO), 3.39 (1H, *t*, CH), 4.15 (2H, *q*, O–CH$_2$)
Allyl	3080.97; 2982.64; 2929.64; 2874.58; 1742.17; 1716.11; 1643.58; 1437.42; 1360.93; 1227.59; 1185.58; 1149.64; 1023.28; 921.05	1.25 (3H, *t*, C*H*$_3$–CH$_2$), 2.25, (3H, *s*, CH$_3$–CO), 2.57 (2H, *t*, CH–C*H*$_2$), 3.51 (1H, *t*, CH–CH$_2$), 4.20 (2H, *q*, O–CH$_2$), 5.10 (2H, *dd*, C*H*$_2$=CH), 5.70 (1H, *m*, CH$_2$=C*H*)

The effects of K_2CO_3, KOH and NaOH in different solvents on the cyclization reaction of cyanoacetamide with ethyl acetoacetate are shown in Table V. The reactions were perfomred in polar and nonpolar solvents both at 60 ºC and at reflux temperature. The melting points and yields of the products are also given in Table V. A reaction time of one hour was found to be sufficient for the synthesis. Much better results were obtained at lower temperatures where mixing was employed. It can be seen from the obtained results that the best results were obtained when hydroxides were employed in a nonploar solvent, such as isooctane. The best yield with K_2CO_3 was obtained in isoctane, which is in agreement with our previous work.[8] Generally, potassium hydroxide as a stronger base is a better catalyst for this reaction then potassium carbonate. The order of activity as far as the solvents are concerned is as follows: isooctane > cyclohexane > hexane > toluene > carbon tetrachloride > dichloromethane > methanol > water.

TABLE IV. IR and ^{1}H-NMR data for the synthesized 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones

R	IR (KBr) ν/cm^{-1}	^{1}H-NMR (CF_3COOD) δ/ppm
H	309.84; 2891.65; 2224.56; 1603.22; 1473.39; 1456.0; 1360.3; 1308.45; 1240.8; 1223.2; 1177.1; 907.63; 836.26; 742.31; 643.24	257 (3H, *s*, CH_3), 6.4 (1H, *s*, Ar–H)
Me	3445.89; 3315.98; 3056.14; 2915.15; 2224.16; 1636.94; 1606.59; 1487.76; 1434.81; 1373.93; 1224.25; 952.08; 858.78; 757.6	2.26 (3H, *s*, 5–CH_3, 2.67 (3H, *s*, 4–CH_3)
Et	3359.17; 3210.69; 3056.51; 2970.75; 2927.38; 2220.53; 1635.15; 1457.2; 1375.34; 1347.4; 13416.56; 1238.31; 1213.78; 1166.2; 1057.99; 986.99; 986.56; 866.48; 798.4; 776.4; 706.78	1.20 (3H, *t*, C*H*$_3$–CH_2), 2.68 (5H, *ms*, 4–CH_3 and CH_2)
n-Pr	3396.47; 3049.69; 2960.04; 2872.95; 2223.2; 1637.12; 1455.54; 1360.51; 1360.51; 1258.88; 1223.7; 1209.47; 1155.38; 897.98; 870.59; 766.86	1.08 (3H, *t*, C*H*$_3$–CH_2), 1.56 (2H, *m*, CH_3–C*H*$_2$), 2.68 (5H, *ms*, 4–CH_3 and CH_2–Ar)
n-Bu	3413.3; 3052.09; 2961.17; 2915.17; 2853.85; 2222.49; 1644.36; 1465.5; 1365.28; 1244.91; 1199.18; 1157.95; 918.77; 767.34; 715.88; 616.16	0.97 (3H, *t*, C*H*$_3$–CH_2), 1.50 (4H, *m*, CH_3–C*H*$_2$)$_2$), 2.64 (3H, *s*, 4–CH_3), 2.72 (2H, *m*, CH_2–Ar)
n-Pe*	3444.18; 3209.97; 2958.01; 2900.0; 2858.79; 2221.31; 1635.08; 1455.86; 1363.78; 1235.1; 1156.27; 902.4; 714.44	0.88 (3H, *t*, C*H*$_3$–CH_2), 1.27 (6H, *m*, CH_3–(C*H*$_2$)$_3$, 2.28 (3H, *s*, 4–CH_3), 2.50 (2H, *m*, CH_2–Ar)
Allyl	3395.92; 3059.29; 2901.61; 2223.84; 1636.93; 1456.56; 1431.55; 1362.51; 1620.9; 1219.51; 1186.55; 1156.22; 923.26; 909.14; 770.05; 716.19	2.66 (3H, *s*, CH_3), 3.50 (2H, *d*, =CH–C*H*$_2$), 5.20 (2H, *dd*, CH_2=CH), 5.90 (1H, *m*, CH)

*DMSO

The UV spectra of the same series of compounds was investigated in nine solvents. The effects of solvent polarity and hydrogen bonding capability on the absorption spectra are interpreted by means of the linear solvation energy relationships (LSER) concept proposed by Kamlet and Taft[13] using a general solvation equation of the form:

$$\nu = \nu_o + s\pi^* + a\alpha + b\beta \quad (1)$$

where, α, β and π^* are solvatochromic parameters and *a*, *b* and *s* are the solvatochromic coefficients.

In Eq. (1), π^* is an index of the solvent dipolarity/polarizability, which is a measure of the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. For the set of selected solvents, *i.e.,* non-HBD aliphatic solvents with a single dominant group dipole, the π^* value is proportional to the dipole moment of the solvent

molecule. The π* scale was selected to run from 0.00 for cyclohexane to 1.00 for dimethyl sulfoxide. The variable α is a measure of the solvent hydrogen-bond donor (HBD) acidity, and describes the ability of a solvent to donate a proton in a solvent-to-solute hydrogen bond. The α scale was selected to extend from zero for non-HBD solvents to about 1.00 for methanol. The variable β is a measure a of the solvent hydrogen-bond acceptor (HBA) basicity, and describes the ability of a solvent to accept a proton in a solute-to-solvent hydrogen bond. The β scale was selected to extend from zero for non-HBD solvents to about 1.00 for hexamethylphosphoric acid triamide.

TABLE V. Synthesis of 4-metyl-3-cyano-6-hydroxy-2-pyridone from ethyl acetoacetate and cyanoacetamide in different solvents (0.012 mol of alkyl ethyl acetoacetate, 0.0119 mol of cyanoacetamide, 0.014 mol of KOH, 20 cm^3 of solvent, 600 rpm)

Solvent	Reaction temperature ºC	Reaction time hours	M.p. ºC	Yield %
Methanol	60	1	295–9	58
		8	293–7	46
	60[a]	1	299–303	36
	reflux[b]	1	300–3	31
	reflux[c]	1	302–6	36
	reflux[d]	1	303–5	39
Water	60	1	301–6	36
		8	299–303	39
	reflux[b]	1	307–10	20
Toluene	60	1	300–5	63
		8	303–8	71
Hexane	60	1	296–300	70
		8	301–304	78
Cyclohexane	60	8	305–10	75
Isooctane	60	1	303–6	75
	60[a]	1	301–4	50
		8	305–10	83.5
	reflux[b]	1	298–302	33
Dichloromethane	60	8	300–4	60
Carbon tetrachloride	60	1	295–300	60.5
		8	294–8	70

[a]0.014 mol of K_2CO_3; [b]without stirring; [c]0.014 mol of NaOH without stirring; [d]0.014 mol of K_2CO_3 without stirring.

To explain the effect of the substituents on the electronic absorption spectra of the 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones, pyridone without substituents, which has three absorption bands, one at 350–380 nm, others at 260–280 nm and 208–210 nm, was taken as the reference. The results have shown that the lower energy

band is sensitive to the substituent electronic properties. No correlations were found for the higher energy band. The absorption frequencies of the lower energy band in nine solvents are given in Table VI. Examination of the data given in Table VI shows that there is an identical trend in the UV absorption frequencies of the investigated compounds in all solvents used. Increasing the chain length of the substituents generally results in batochromic shifts of the long wavelength absorption maximum as compared to that of the reference system.

TABLE VI. Ultraviolet absorption frequencies of the synthesized 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones in different solvents

Solvent	$\nu_{max} \times 10^{-3} \times cm^{-1}$						
	H	Me	Et	*n*-Pr	*n*-Bu	*n*-Pe	Allyl
Methanol	31.04	30.32	30.24	30.32	30.47	30.66	30.45
Ethanol	30.94	30.74	30.12	30.18	30.27	30.35	30.24
Propan-2-ol	30.71	30.64	30.91	30.66	30.67	30.68	30.81
Butan-1-ol	30.81	30.60	30.34	30.69	30.41	30.69	30.43
Ethylene glycol	30.86	30.17	30.21	30.79	30.23	30.34	30.19
t-Butanol	30.65	30.28	30.46	30.86	30.84	31.05	30.86
Acetonitrile	30.45	29.57	29.88	30.25	29.50	29.90	29.74
Dichloromethane	30.39	31.17	30.62	30.98	31.04	30.92	31.13
Dimethylformamide	29.83	29.38	30.10	29.62	29.48	29.66	29.50

For the purpose of exploring the correlations between the solvent effects and the electronic transition energies of the 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones, the absorption frequencies were correlated with the total solvatochromic Eq. (1). The correlation of the spectroscopic data in seven solvents (methanol, ethanol, propan-2-ol, butan-1-ol, *t*-butanol, ethylene glycol, and acetonitrile) were carried out by means of multiple linear regression analysis. The results of the correlations are presented in Tables VII and VIII.

TABLE VII. Results of the correlations with Eq. (1) for the synthesized 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones

Substituent	ν_0	*s*	*b*	*a*	R^a	s^b	n^c
H	31.31	–1.01	–1.01	1.12	0.9942	0.029	6
Me	29.15	–0.07	1.22	0.50	0.9997	0.021	5
Et	28.41	1.32	1.77	–0.38	0.9812	0.085	5
n-Pr	28.10	2.06	2.16	–0.37	0.9976	0.038	5
n-Bu	27.00	2.13	3.18	–0.43	0.9972	0.054	6
n-Pe	27.30	2.28	3.44	–0.95	0.9959	0.077	5
Allyl	27.08	2.35	3.43	–0.93	0.9982	0.039	6

[a]Correlation coefficient. [b]Standard error of the estimate. [c]Number of solvents.

TABLE VIII. Percentage contribution of calculated solvatochromic parameters

Substituent	π	β	α
H	32.16	32.16	35.03
Me	3.91	68.15	27.93
Et	38.04	51.00	10.95
n-Pr	44.88	47.05	8.06
n-Bu	37.11	55.40	7.49
n-Pe	34.18	51.57	14.24
Allyl	35.02	51.11	13.86

[a]Referred to results of correlations with Eq. (1).

The correlation coefficients obtained from Eq. (1) show that the data comply to a high level of reliability in all the selected solvents (Table VII). The stronger solute/solvent hydrogen bonding by the carbonyl group, as well as the increasing importance of the solvent polarity/polarizability in the stabilization of the electronic excited state lead to a hypsochromic shift with both increasing solvent hydrogen bond acceptor basicity and solvent polarity/polarizability and hence the positive sings for the coefficients of both β and π*. This suggests that most of the solvatochromism in 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones is due to the solvent polarity and basicity rather than to the solvent acidity. Increasing the chain length of the alkyl group generally leads to an increasing magnitude of the solvent polarity/polarizability and to the solvent hydrogen bond acceptor basicity compared to the reference system. The percentage contributions of the calculated solvatochromic parameters (Table VIII) show that the dominant solvent effect in all the alkyl substituted pyridones is the effect of the hydrogen bond acceptor basicity. This effect is dominant in 4,5-dimethyl-3-cyano-6-hydroxy-2-pyridone and decreased with increasing in chain length of the alkyl group. These results indicate that the steric effect between alkyl and hydroxy groups is important factor in the correlations between the structure as well as solvent effects and the electronic transition energies of the 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones. The satisfactory correlation of the ultraviolet absorption frequencies of investigated pyridones with Eq. (1) indicates that the correct model was selected. This means that this model gives a correct interpretation of the linear solvation energy relationships of the complex system of the 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones in different solvents. In this situation where both the solvents and the solutes are hydrogen-bond donors (and hence usually amphiprotic), it has proven to be quite difficult to untangle solvent dipolarity/polarizability, type-B hydrogen bonding*, and variable self-association effects from (usually multiple) type-A hydrogen bonding interactions*. For these reasons we have demonstrated that a solvatochromic equation with unambiguously distinct dependences on the three solvatochromic parameters π*, α and β can be used to evaluate the effects of both types of hydrogen bonding and of the solvent dipolarity/polarizability effect.[14]

* In type-B hydrogen bonding, the solute acts as a HBD (hydrogen-bond donor) acid and the solvent as a HBA (hydrogen-bond acceptor) base; in type-A hydrogen bonding, the roles are reversed.

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Abbreviations

PTC – phase transfer catalysis

TBA – tetrabutylammnonium chloride

И З В О Д

СИНТЕЗА И ИСПИТИВАЊЕ ЕФЕКТА РАСТВАРАЧА НА UV СПЕКТРЕ 5-СУПСТИТУИСАНИХ 4-МЕТИЛ-3-ЦИЈАНО-6-ХИДРОКСИ-2-ПИРИДОНА

ДУШАН Ж. МИЈИН, ГОРДАНА С. УШЋУМЛИЋ и НАТАША В. ВАЛЕНТИЋ

Технолошко-металуршки факултет, Универзитет у Београду, Карнегијева 4, 11001 Београд

У оквиру рада је извршена синтеза 5-супституисаних 4-метил-3-цијано-6-хидрокси-2-пиридона из цијаноацетамида и алкилетилацетацетата у присуству калијум-хидроксида у метанолу као растварачу. Алкилетилацетацетати су добијени реакцијом C-алкиловања етилацетацетата одговарајућим алкилхалогхенидима. Такође је извршено испитивање реакционих услова за синтезу 4-метил-3-цијано-6-хидрокси-2-пиридона из цијаноацетамида и етилацетацетата у присуству KOH, NaOH и K_2CO_3 у различитим растварачима. IR, ^{1}H-NMR и UV подаци су дати за синтетизоване пиридоне, а IR и ^{1}H-NMR подаци су дати за синтетизоване алкилетилацетацетате. Апсорпциони спектри 5-супституисаних 4-метил-3-цијано-6-хидрокси-2-пиридона су одређени у девет растварача различитих поларности у опсегу 200–400 nm. Утицај поларности растварача као и ефекат водоничне везе проучавани су методом линеарне корелације солватационих ефеката односно једначином облика $\nu = \nu_o + s\pi^* + a\alpha + b\beta$, у којој је ν апсорпциона фреквенца, π^* мера ефеката солватације везана за поларност растварача, α мера успостављања водоничне везе са протон-донорским растварачима, а β мера водоничне везе остварене са протон-акцепторским растварачима.

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