

OLIGOPHENYLENE 2,4,6-TRIARYLPYRIDINES AND ANALOGOUS DIAZA-*p*-TERPHENYLS, DIAZA-*p*-QUATERPHENYLS AND DIAZA-*p*-QUINQUEPHENYLS WITH LUMINISCENT ACTIVITY

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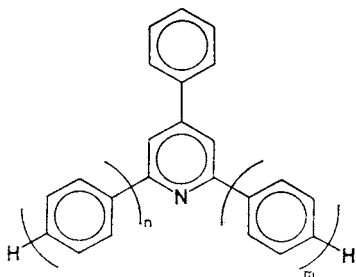
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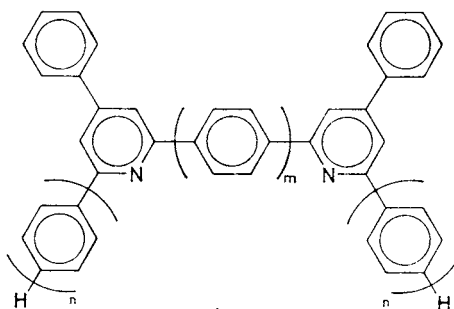
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Cyclocondensation of α,β -unsaturated aromatic ketones *V* and *VIII* with quaternary pyridinium salts *VI* in the presence of ammonium acetate gave 2,4,6-triarylpiperidines *I*, aryl-substituted diaza-*p*-terphenyls *IIa,b*, diaza-*p*-quaterphenyls *IIc,d* and diaza-*p*-quinquephenyls *IIe,f*. All the new polyphenylene compounds exhibit characteristic luminiscence in the visible spectral region.

It is known that some 2,4,6-triarylpiperidines¹ and oligophenylene-piperidine cyano derivatives² exhibit a remarkable fluorescence activity. In connection with our study of new organic luminophores we were interested in analogous polyphenylene-piperidines of the type *I* and *II* containing a greater number of aromatic nuclei.



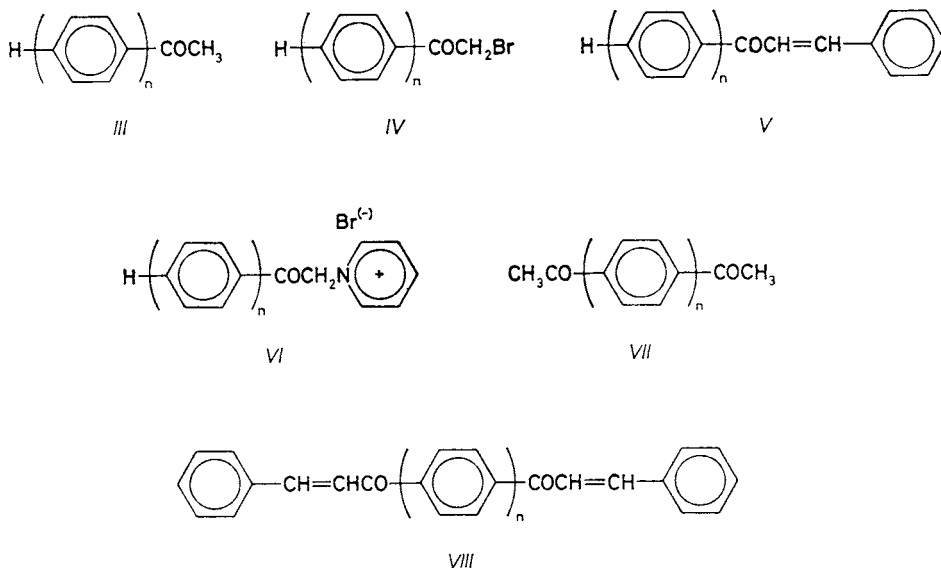
	m	n
<i>Ia</i>	1	1
<i>Ib</i>	1	2
<i>Ic</i>	1	3
<i>Id</i>	2	2
<i>Ie</i>	2	3
<i>If</i>	3	3



	m	n
<i>IIa</i>	1	1
<i>IIb</i>	1	2
<i>IIc</i>	2	1
<i>IId</i>	2	2
<i>IIe</i>	3	1
<i>IIf</i>	3	2

We prepared these compounds by the Kröhnke method^{3,4} consisting in reaction of cinnamoylarenes *V* and *VIII* with pyridinium salts *VI* in the presence of ammo-

niium acetate. The only hitherto described compounds of the type *I* and *II* are the derivatives *Ia* (ref.⁵), *Ib* (ref.⁶), and *Id* (ref.⁷). Our synthesis started from acetylarenes *III* and *VII* which were converted into the corresponding α,β -unsaturated ketones *V* and *VIII* by reaction with benzaldehyde⁸⁻¹⁰. These ketones reacted with pyridinium salts *VI* to afford arylpyridines *I* and *II*. The reaction was performed in the presence of ammonium acetate either in acetic acid (*Ia*, *b*, *d*) or in a mixture of dimethylformamide and acetic acid (1 : 1) (other compounds of the type *I* and *II*). This modification gave the desired products in 30–60% yields (Table I). The yield of the pyridine *If* increased only slightly when the reaction time was prolonged several times or when the mixture was sonicated (which generally positively influences the course of heterogeneous reactions). It appears that the low yields are caused not only by the extremely low solubility of the reaction components but also because the attempted introduction of two *p*-terphenyl moieties into the molecule of *I* or *II* proceeds too slowly and the reaction components undergo concurrent reactions.



In formulae *III*-*VIII*: $a, n = 1$ $b, n = 2$ $c, n = 3$

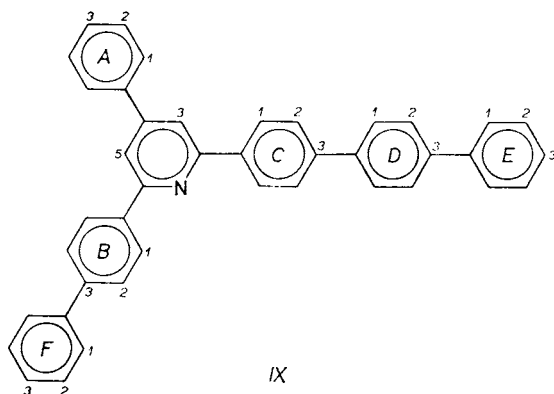
The derivative *Ie* was prepared by both the alternative ways, i.e. reaction of compounds *Vc* and *VIb* as well as reaction of compounds *Vb* and *VIc*. Since both procedures gave the same result under identical conditions (Table I), only one alternative was employed in the other cases. The reactions were monitored by thin-layer chromatography (TLC) and compounds *I* and *II* were well identified by their UV-fluorescence.

TABLE I
Analytical data for compounds *I* and *II*

Compound	Starting compounds Reaction times h	M.p. °C	Formula (M.w.)	Calculated/Found			IR spectrum (CHCl ₃), cm ⁻¹			
				% C	% H	% N	$\tilde{\nu}$ (CC)	$\tilde{\nu}$ (CN)	$\tilde{\nu}$ (CH)	$\tilde{\nu}$ (CH)
<i>Ia</i> ^a	<i>Va</i> + <i>VIa</i>						1 606 m	1 594 s	1 005 m	835 s
81	5						1 542 s	1 485 s		696 s
<i>Ib</i> ^a	<i>Va</i> + <i>VIb</i>						1 605 m	1 592 s	1 008 m	847 s
56	18						1 548 s	1 488 s		695 s
<i>Ic</i>	<i>Vc</i> + <i>VIa</i>	225—226	C ₃₅ H ₂₅ N (459.6)	91.46	5.49	3.05	1 605 s	1 592 s	1 001 m	833 s
65	15			91.76	5.56	2.78	1 545 s	1 483 s		697 s
<i>Id</i> ^a	<i>Vb</i> + <i>VIb</i>						1 610 s	1 597 s	1 008 m	848 s
42	7						1 545 s	1 488 s		696 s
<i>Ie</i>	<i>Vc</i> + <i>VIb</i> <i>Vb</i> + <i>VIc</i>	260—262	C ₄₁ H ₂₉ N (535.7)	91.92	5.47	2.61	1 608 s	1 595 s	1 000 m	830 s
60	24			91.39	5.81	2.65	1 540 s	1 487 s		695 s
<i>If</i>	<i>Vc</i> + <i>VIc</i>	above 310					1 605 s	1 600 s	1 005 m	843 s
6	24						1 530 s	1 483 s		698 s
8	60									

<i>Ila</i> 33	<i>VIIIa</i> + <i>VIa</i> 15	302—304	$C_{40}H_{28}N_2$ (536·7)	89·51 89·40	5·27 5·35	5·22 5·11	1 605 s 1 542 s	1 595 s 1 495 s	1 000 m	848 s 843 s 686 s
<i>Ilb</i> 56	<i>VIIIa</i> + <i>VIb</i> 15	317—320	$C_{52}H_{36}N_2$ (688·9)	90·65 91·01	5·28 5·36	4·07 3·86	1 606 s 1 543 s	1 696 s 1 492 s	1 002 m	840 s 690 s
<i>Ilc</i> 35	<i>VIIIb</i> + <i>VIa</i> 9	295—296	$C_{46}H_{32}N_2$ (612·8)	90·15 89·85	5·27 5·42	4·57 4·59	1 608 s 1 546 s	1 596 s 1 495 s	1 000 m	832 s 820 s 694 s
<i>Ild</i> 28	<i>VIIIb</i> + <i>VIb</i> 9	above 310	$C_{58}H_{40}N_2$ (765·0)	91·06 90·89	5·28 5·69	3·66 3·63	1 608 s 1 543 s	1 595 s 1 492 s	1 001 m	835 s 822 s 696 s
<i>Ile</i> 43	<i>VIIIc</i> + <i>VIa</i> 28	272—273	$C_{52}H_{36}N_2$ (688·9)	90·65 90·67	5·28 5·43	4·07 3·88	1 608 s 1 545 s	1 596 s 1 493 s	1 002 m	821 s 695 s
<i>Ilf</i> 60	<i>VIIIc</i> + <i>VIb</i> 30	above 310	$C_{64}H_{44}N_2$ (841·1)	91·39 90·91	5·28 5·38	3·33 3·48	1 608 s 1 542 s	1 595 s 1 490 s	1 002 m	847 s 820 s 695 s

^a Reaction was performed in acetic acid at 150°C (oil bath); other reactions were carried out in a 1 : 1 mixture of acetic acid and dimethylformamide at 180—200°C (oil bath).



The structure of compounds *I* and *II* is in accord with their spectral characteristics. The ^1H NMR spectra of pyridines *I* (Table II) exhibit multiplets of aromatic protons. The signals of protons in *ortho*-positions of the phenyl substituents and in positions 3 and 5 of the pyridine nucleus are shifted upfield relative to those of the *meta*- and *para*-protons. This shift depends on the distance from the pyridine nitrogen atom and on the size of substituents in positions 2, 4 and 6 of the pyridine nucleus. The numbering of positions is given in formula IX. The protons in position 3 and 5 appear as a single characteristic signal in the spectra of the symmetrical compounds *Ia* and *Id* whereas spectra of the unsymmetrical derivatives *Ib* and *Ic* contain two signals. The unsymmetrical derivative *Ie* has only one signal, apparently because the difference in substitution on the distant atoms *D3* and *F3* brings about no discernible anisotropic effects on the centers 3 or 5. In all compounds *I* the chemical shift of doublet due to protons in position *A1* is about 7.70 ppm, the coupling constant being 7.3–8.7 Hz. Chemical shifts of the protons in positions *B1* and *C1* are identical for the symmetrical compounds *Ia* and *Id* and similar for the other ones (*Ib*, *Ic*, *Ie*). Greater chemical shifts are observed with protons attached to benzene ring bearing a larger substituent. As seen from Table II, also other *ortho*-protons in compounds *I* can be clearly identified, similarly as the triplets of the terminal *para*-hydrogen atoms *D3*, *E3* and *F3* in compounds *Ib*–*Ie*. The ^1H NMR spectra of compounds *IIa*–*IIe* (Table III) exhibit a series of doublets of the *ortho*-protons and multiplets due to the *meta*- and *para*-protons. The assignment of the individual positions is given in formula X. The protons 3 and 5 of the pyridine nucleus are non-equivalent and their signals appear as doublets with coupling constants amounting to 1.4 Hz. The *A1*-protons in all compounds *II* have approximately the same shift, similar to that of analogous protons in compounds *I*. The chemical shift of *ortho*-protons in the individual positions *B1*, *B2*, *D1*, *D2*, and *E1* is influenced by their distance from both the pyridine nuclei. The ^1H NMR spectra of *I* and *II* indicate that the aromatic

TABLE II
Proton NMR spectra of pyridines *I* (in CDCl₃ at 24°C, tetramethylsilane as internal standard)

Position ^a	δ , ppm				
	<i>Ia</i>	<i>Ib</i>	<i>Ic</i>	<i>Id</i>	<i>Ie</i>
3	7.89 s	7.92 s	7.95 s	7.94 s	7.95 s
5	7.89 s	7.89 s	7.91 s	7.94 s	7.95 s
<i>A1</i>	7.75 d <i>J</i> = 8.2	7.68 d <i>J</i> = 7.3	7.67 d <i>J</i> = 8.5	7.69 d <i>J</i> = 8.2	7.71 d <i>J</i> = 8.7
<i>A2, A3</i>	7.43–7.55 m	7.43–7.55 m	7.44–7.58 m	7.46–7.60 m	7.45–7.58 m
<i>B1</i>	8.21 d <i>J</i> = 7.6	8.22 d <i>J</i> = 7.7	8.23 d <i>J</i> = 8.5	8.30 d <i>J</i> = 8.0	8.31 d <i>J</i> = 8.5
<i>B2</i>	7.43–7.55 m	7.43–7.55 m	7.44–7.58 m	7.75–7.78 m	7.65–7.69 m
<i>B3</i>	7.43–7.55 m	7.43–7.55 m	7.44–7.58 m	—	—
<i>C1</i>	8.21 d <i>J</i> = 7.6	8.28 d <i>J</i> = 7.3	8.32 d <i>J</i> = 8.5	8.30 d <i>J</i> = 8.0	8.32 d <i>J</i> = 8.4
<i>C2</i>	7.43–7.55 m	7.73–7.76 m	7.81 d <i>J</i> = 8.5	7.75–7.78 m	7.76–7.83 m
<i>C3</i>	7.43–7.55 m	—	—	—	—
<i>D1</i>	—	7.73–7.76 m	7.77 d <i>J</i> = 8.5	7.75–7.78 m	7.76–7.83 m
<i>D2</i>	—	7.43–7.55 m	7.77 d <i>J</i> = 8.5	7.46–7.60 m	7.76–7.83 m
<i>D3</i>	—	7.36 t <i>J</i> = 7.3	—	7.38 t <i>J</i> = 7.2	—
<i>E1</i>	—	—	7.71 d <i>J</i> = 8.5	—	7.76–7.83 m
<i>E2</i>	—	—	7.44–7.58 m	—	7.45–7.58 m
<i>E3</i>	—	—	7.36 t <i>J</i> = 7.4	—	7.25–7.29 m
<i>F1</i>	—	—	—	7.75–7.78 m	7.65–7.69 m
<i>F2</i>	—	—	—	7.46–7.60 m	7.45–7.58 m
<i>F3</i>	—	—	—	7.38 t <i>J</i> = 7.2	7.35–7.40 m

^a For numbering see formula IX.

nuclei are practically perpendicular to each other. A second possible interpretation, based on a very fast rotation of the aromatic rings about the connecting bonds, is less probable because of interaction of the *ortho*-hydrogen atoms.

The infrared spectra contain invariably absorption bands at 3 030, 1 605, 1 595, 1 540, 1 490, 1 000, 830 and 695 cm^{-1} (Table I). These wavenumbers can be assigned to stretching and deformation vibrations of the CC, CN and CH bonds of the pyridine and aromatic skeleton of compounds *I* and *II*.

TABLE III
Proton NMR spectra of compounds *II* (in CDCl_3 at 24°C , tetramethylsilane as internal standard)

Position ^a	δ , ppm				
	<i>IIa</i>	<i>IIb</i>	<i>IIc</i>	<i>IId</i>	<i>IIe</i>
3	7.92 d $J = 1.4$	7.98 d $J = 1.4$	7.91 d $J = 1.4$	7.96 d $J = 1.4$	7.91 d $J = 1.4$
5	7.98 d $J = 1.4$	8.01 d $J = 1.4$	7.95 d $J = 1.4$	7.97 d $J = 1.4$	7.95 d $J = 1.4$
A1	7.79 d $J = 7.6$	7.79 d $J = 8.4$	7.77 dd $J = 7.0$ $J = 1.4$	7.77 d $J = 6.6$	7.79 dd $J = 6.9$ $J = 1.5$
A2, A3	7.45–7.58 m	7.47–7.59 m	7.45–7.58 m	7.47–7.59 m	7.45–7.58 m
B1	8.38 s	8.41 s	8.3b d $J = 8.5$	8.35 d $J = 8.4$	8.32 d $J = 8.6$
B2	8.38 s	8.41 s	7.84 d $J = 8.5$	7.86 d $J = 8.4$	7.82 d $J = 8.6$
C1	—	—	—	—	7.80 s
D1	8.25 d $J = 7.1$	8.34 d $J = 8.4$	8.24 dd $J = 7.0$ $J = 1.4$	8.33 d $J = 8.4$	8.23 dd $J = 7.6$ $J = 1.5$
D2	7.45–7.58 m	7.81 d	7.45–7.58 m	7.79 d $J = 7.5$	7.45–7.58 m
D3	7.45–7.58 m	—	7.45–7.58 m	—	7.45–7.58 m
E1	—	7.71 d $J = 7.1$	—	7.70 d $J = 7.1$	—
E2	—	7.47–7.59 m	—	7.47–7.59 m	—
E3	—	7.37–7.42 m	—	7.37–7.41 m	—

^a For numbering see formula X.

those of the hydrocarbons, particularly by the unresolved vibrational structure of the absorption bands. Further, it is obvious that the absorption spectra represent envelope curves of many close electronic absorption bands and therefore they are not entirely characteristic of the individual types of the studied pyridine derivatives. The increasing number of aromatic nuclei in compounds *I* and *II* is manifested mostly by a slight bathochromic shift of the longest wavelength absorption maximum.

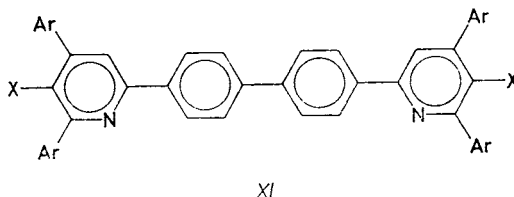


Table IV also shows that the fluorescence characteristics of *I* and *II* are much more variable than the corresponding absorption characteristics. Fluorescence maxima, measured in the solid phase, are bathochromically shifted (9–31 nm) relative to those obtained in toluene solutions. The increasing number of the *para*-bonded aromatic nuclei is accompanied not only by a bathochromic shift of the fluorescence maxima but also by increase of fluorescence quantum yield, replacement of the benzene ring by the pyridine one having no substantial effect. Comparison of fluorescence quantum yields for toluene solutions of *Iic* and *Iid*, containing the fragment XI ($X = H$) with those for the corresponding cyano derivatives² XI ($X = CN$) shows that the presence of the cyano group has no substantial effect (0.66 and 0.58 compared with 0.69 and 0.69). An analogous comparison of fluorescence maximum of *Ib–Ie*, *Iic* and *Iid* reveals a hypsochromic shift of 16–33 nm compared with the cyano derivatives. The relatively low values of the Stokes' shifts in the spectra of pyridines *I* and *II* (28–63 nm) indicate that transition into the excited state S_1 affects less the geometry of *I* and *II* when no CN group is present in the molecule.

EXPERIMENTAL

Melting points were determined on a Boetius block and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 325 spectrometer, 1H NMR spectra were measured on a Bruker AM 400 (400 MHz) instrument using tetramethylsilane as internal standard. Purity of the compounds was checked, and the reactions were followed, by TLC in benzene or tetrachloromethane on Silufol or Alufol foils (Lachema, Brno).

Electronic spectral measurements. Absorption spectra were taken on a Perkin-Elmer 330 spectrometer, fluorescence spectra on a Perkin-Elmer MPF-44B instrument. For the quantum yield determinations solutions of absorbance not higher than 0.01 were prepared. The spectra were corrected manually with regard to the instrument parameters. *p*-Terphenyl was selected as

standard; the given quantum yield for this compound in cyclohexane is reported¹⁴ to be $q_F = 0.93$ which calculated for a toluene solution gives $q_F = 0.88$. The excitation was effected in the maxima of the excitation spectra of the compound in question and nitrogen was bubbled into the solutions before and after the measurements.

The starting acetylarenes *IIIb*, *IIIc* and diacetylarenes *VIIb*, *VIIc* were prepared by Friedel-Crafts acetylation of biphenyl¹⁵ and *p*-terphenyl^{8,16}. Compound *VIIa* was obtained by acetoacetate synthesis from terephthaloyl dichloride^{17,18}. The acetyl derivatives *III* were brominated¹¹ to give compounds *IV* which on reaction with pyridine^{20,21} afforded pyridinium salts *VI*. Compound *IVc* was prepared preferably by Friedel-Crafts acylation of *p*-terphenyl²² with bromoacetyl bromide.

Pyridinium Salts *VIa*—*VIc*

A mixture of the corresponding bromoacetylarene *IVa*—*IVc* (5 mmol) and pyridine (5 ml) was refluxed for 3—4 h at bath temperature 145—150°C. After cooling, the precipitate was filtered, washed with ether and crystallized from ethanol or aqueous ethanol to afford compounds *VIa* to *VIc* in 91—98% yield. Compound *VIa* (91%), m.p. 198—200°C (reported²⁰ m.p. 198°C); compound *VIb* (94%), m.p. 233.5—234.5°C (reported²¹ m.p. 233°C); compound *VIc* (98%), for $C_{25}H_{20}BrNO$ (430.4) calculated: 69.77% C, 4.69% H, 18.570 Br, 3.26% N; found: 69.82% C, 4.90% H, 18.57% Br, 3.21% N. ¹H NMR (CD_3OD), δ : 4.70 s ((-CO-CH₂-N≡)), 7.40—9.00 m (arom. H). IR (KBr), $\tilde{\nu}_{max}$ (cm⁻¹): 3 030 w, 1 690 s, 1 600 s, 1 480 s, 770 s.

Styryl *p*-Terphenyl Ketone (*Vc*)

To a boiling solution of *IIIc* (1 g; 3.7 mmol) and benzaldehyde (3.9 g; 37 mmol) in tetralin (20 ml) was added dropwise 25% methanolic solution of KOH (3 ml) during 1 h. After reflux for 3 h the mixture was cooled and the precipitate filtered and washed with acetone and hot water. Yield 1.1 g (83%) of the product *Vc*. Crystallization from chloroform-methanol afforded yellow crystals melting at 243—245°C. For $C_{27}H_{20}O$ (360.5) calculated: 89.96% C, 5.60% H; found: 89.76% C, 5.83% H. ¹H NMR ($CDCl_3$), δ : 7.22—8.13 m (arom. H + 2 -CH=). IR (KBr), $\tilde{\nu}_{max}$ (cm⁻¹): 3 030 w, 1 660 s, 1 608 s, 1 592 s, 1 448 s, 985 m, 826 s, 758 s.

Compounds *Ia*—*If*

A mixture of ketone *Va*—*Vc* (1 mmol), pyridinium salt *VIa*—*VIc* (1.5 mmol), 1 : 1 mixture of acetic acid and dimethylformamide (20—50 ml) and ammonium acetate (2 g) was refluxed for the time specified in Table I. After the end of the reaction, the mixture was poured into water and the precipitate was filtered, washed with water and dried over phosphorus pentoxide in a desiccator. The dry material was dissolved in a small amount of chloroform and chromatographed on a silica gel column in tetrachloromethane-benzene (4 : 1). Fractions with the highest R_F value and marked UV-luminescence were collected. For yields and physicochemical data of the prepared compounds *I* see Tables I—IV.

Compounds *IIa*—*IIf*

A mixture of chalcone *VIIIa*—*VIIIc* (1 mmol), the corresponding pyridinium salt *VIa*—*VIc* (3 mmol), acetic acid (50 ml), dimethylformamide (50 ml) and ammonium acetate (4 g) was refluxed for times specified in Table I. The products were isolated as described for compounds *I*. For yields and physicochemical data see Tables I—IV.

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