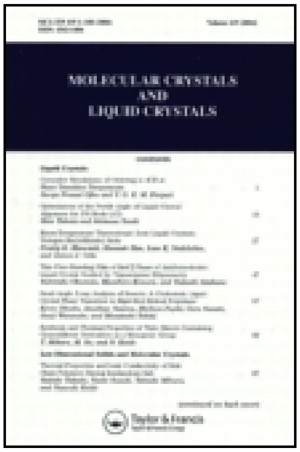

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New Yellow Dyes For Guest-Host Applications

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New Yellow Dyes For Guest-Host Applications

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A study is presented of the optical order parameters and spectroscopic properties of 3′-hydroxyquinophthalone and 3,9-disubstituted perylene dyes in nematic liquid crystalline mixtures. The results of this study are discussed in terms of the effects of the dye structure on the order parameters. From the systematic variation in structure, it is found that a thioester group and a short flexible chain such as an *n*-butyl group play a significant role in increasing the order parameters. In addition, preliminary data on the solubility and photostability of the dyes are reported.

Keywords: guest-host, dichroic dye, liquid crystal, quinophthalone, perylene, order parameter

I. INTRODUCTION

A yellow color is important not only as one of the three primary colors but as an ingredient for preparing a practically useful black or green color. The first yellow dyes investigated for guest-host systems were azo and azomethine dyes[1–6] which show very high order param-

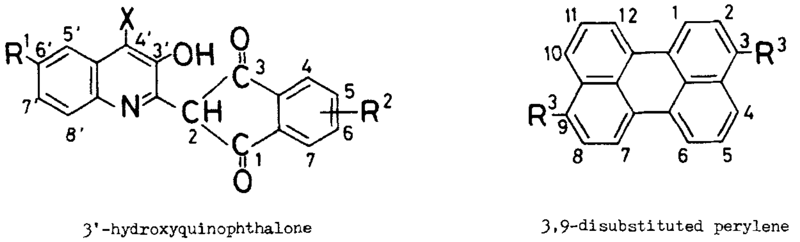


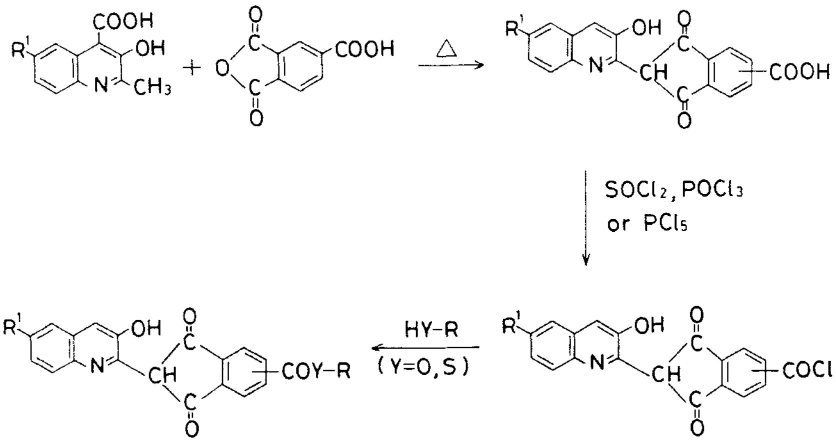
FIGURE 1 Simplified chemical structures of the 3'-hydroxyquinophthalone dyes and the 3,9-disubstituted perylene dyes.

eters in nematic liquid crystalline hosts. However, yellow dichroic dyes[7] other than azo and azomethine dyes have not yet been fully explored.

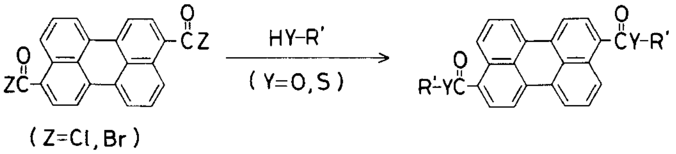
We wish to present new classes of yellow dichroic dyes for guest-host applications: quinophthalone and perylene dyes. We designed and synthesized a number of 3'-hydroxyquinophthalone and 3,9-disubstituted perylene derivatives, whose simplified structures are shown in Figure 1. The effect of various substituents on the order parameters and spectroscopic properties of the dyes has been examined in detail.

II. EXPERIMENTAL

The preparation of the dyes is illustrated in Scheme 1 and Scheme 2.



Scheme 1



Scheme 2

All dyes were purified by repeated column chromatography, recrystallization or sublimation. The melting points of the dyes were determined with a Perkin-Elmer DSC 7 differential scanning calorimeter. The nematic hosts used are listed in Table I.

The cells used during experimentation consist of two glass plates, with an area of 4 × 4 cm, each having a transparent layer of indium oxide. These oxide layers were coated with a rubbed polymer layer to obtain parallel alignment. The cell gap was about 10 μm.

The optical order parameter S of the dyes dissolved in the nematic liquid crystalline hosts was obtained using plane-polarized light by the formula:[2,8]

$$S = \frac{A_{//} - A_{\perp}}{2A_{\perp} + A_{//}}$$

where $A_{//}$ is the absorbance of the dye at its maximum absorption wavelength ($\lambda_{\max}$) when the polarization is parallel to the alignment direction and $A_{\perp}$ is the absorbance at $\lambda_{\max}$ when the polarization is perpendicular to the alignment direction. Optical absorption spectra were measured at 22 °C using a Hitachi 340 spectrophotometer.

The accelerated photodegradation tests of the dyes in the liquid crystalline medium were carried out with an Atlas Sunshine Weather O'meter, Type 65/XW-WR (Atlas Electric Co.). A carbon arc lamp was used as the light source for exposing samples, and the total light intensity at the cells was about 1×10^2 mW·cm^{-2}. During exposure, the cells were put on an aluminum plate. A UV filter was not employed. The accelerated tests were performed at temperatures of about 50 °C in a dry atmosphere. The photostability of the dyes was examined by monitoring the absorbance changes of the dyes in parallel mode during the tests. The cells containing only the host liquid crystal were also exposed for use as reference in the spectroscopic measurement.

TABLE I

Nematic hosts

Designation	Chemical species	T_{NI}/°C	$\Delta\varepsilon$
I.	A mixture of cyanophenylcyclohexanes and a cyanobiphenylcyclohexane (Merck ZLI-1132)	71$^{a)}$	10.3$^{a)}$
II.	A mixture of cyanobiphenyls and a cyano-terphenyl (BDH E-7)	60.5$^{a)}$	11.6
III.	A mixture of cyanoesters (Hoffmann-LaRoche RO-TN-101)	70	13.2
IV.	A mixture of phenylcyclohexylcarboxylates	68	-0.8
V.	A mixture of azoxybenzenes (Merck NP-5)	73$^{a)}$	-0.2$^{a)}$
VI.	A mixture of phenylcyclohexylcarboxylates (Chisso EN-18)	68.9	-5.1

a) catalog data

III. RESULTS AND DISCUSSION

3-1. Order parameter

The order parameters for 3′-hydroxyquinophthalones in ZLI-1132 are shown in Table II. The quinophthalone dyes reported here show a wide variation in order parameters, ranging from 0.53 to 0.70.

From a survey of the results shown in Table II, it can be seen that there are three factors which combine to raise the order parameters in the 3′-hydroxyquinophthalone compounds. Firstly, the introduction of the —COOR or —COSR group into the indandion ring may lead to an increase in the order parameter. Secondly, a benzene ring fusion onto the indandion ring gives rise to increasing the order parameter. This effect is demonstrated clearly by comparison of the results for Dyes 9 and 10. Thirdly, replacement of hydrogen in the 6′-position of the quinoline ring by an alkyl group such as —CH_3 and —$C_4H_9(n)$ results in higher S values. This effect is particularly pronounced when R^1 is an n-butyl group as in Dyes 10, 11, 12 and 13. It is noteworthy that the introduction of a short flexible chain such as an n-butyl group produces a marked increase in S.

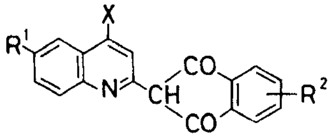
In the series of Dyes 3, 4, 5, 6 and Dyes 11, 12, 13, variations in R^2 have little effect on the order parameter. This is not surprising considering the presence of two isomers owing to intramolecular hydrogen bonding[9-11] as shown in Figure 2, one having a higher S value and the other having a lower S value. Since the S values of these isomers compensate each other, the resultant S value is apparently insensitive to the alternations in R^2. On the contrary, Dyes 1, 2, 9 and 10 have no isomers.

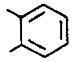
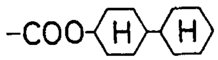
The S values for 3,9-disubstituted perylenes in ZLI-1132 are shown in Table III. The results indicate that a phenylene ring and a thioester group play a significant role in increasing the order parameter of the perylene derivatives. Dyes 16, 17, 18, 19 and 21 have order parameters ranging from 0.68 to 0.73 in ZLI-1132. The higher S values of these dyes can be attributed to elongation of the rigid portion of the dye molecules by the introduction of two phenylene rings. The effect of a thioester group is demonstrated by comparing S for Dye 20 with that for Dye 14. The replacement of an ester group by a thioester one causes an increase of 0.21 in S. However, the increase in S on going from Dye 16 to Dye 21 is not as great as in the case for Dyes 14 and 20.

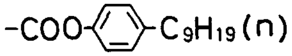
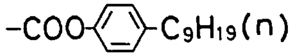
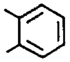
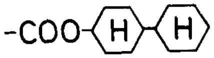
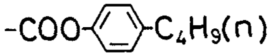
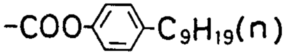
The results shown in Table III suggest that branching in the terminal alkyl group brings about a modest change in S. A comparison of Dyes 16 and 17 shows that the branching in the terminal butyl group lowers

TABLE II

Experimental data on 3′-hydroxyquinophthalone dyes



Dye No.	R^1	X	R^2	λ_{max}/nm (in ZLI-1132)	S (in ZLI-1132)	m.p./°C
1.	-H	-Br	-H	404 427 451	0.53	248.6
2.	-H	-H		415 439 464	0.55	330.8
3.	-H	-H	$-COOC_8H_{17}(n)$	402 428 449	0.60	156.9
4.	-H	-H	$-COSC_{12}H_{25}(n)$	402 430 450	0.60	130.7
5.	-H	-H		402 428 449	0.61	237.3

6.	-H	-H		402 429 449	0.61	179.2
7.	$-CH_3$	-H	$-COOC_8H_{17}(n)$	402 430 450	0.62	145.1
8.	$-CH_3$	-H		402 429 451	0.65	160.8
9.	$-C_4H_9(n)$	-H	-H	404 427 452	0.60	180.6
10.	$-C_4H_9(n)$	-H		417 441 467	0.70	232.0
11.	$-C_4H_9(n)$	-H		402 429 450	0.69	216.1
12.	$-C_4H_9(n)$	-H		402 431 451	0.68	123.1
13.	$-C_4H_9(n)$	-H		402 429 449	0.69	145.1

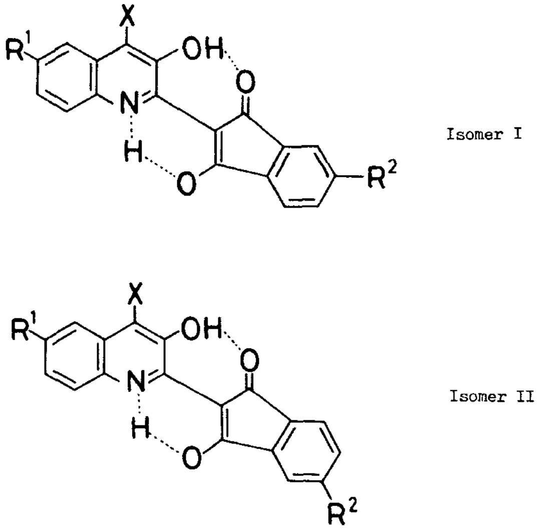


FIGURE 2 Two isomers of the 3′-hydroxyquinophthalone molecule.

S by 0.02. In contrast with this, when alkyl groups are directly linked to the ester groups (Dyes 14 and 15), a slight increase in *S* occurs in changing the terminal group from a normal alkyl to a branched one.

Table IV shows the order parameters for Dyes 6 and 16 in the different nematic hosts, along with the maximum absorption wavelengths (λ_{max}) for these dyes. *S* values for Dye 6 appear to be rather insensitive to nematic hosts, although a considerable decrease in *S* is observed in Hosts III and V. On the other hand, Dye 16 exhibits the highest *S* value in the nematic hosts having a negative dielectric anisotropy (Hosts IV and VI). This situation contrasts markedly with the behavior of anthraquinone dyes[12,13] where the converse effect is observed.

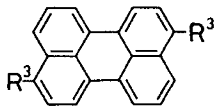
3-2. Absorption spectra

The maximum absorption wavelengths (λ_{max}) for the quinophthalones in ZLI-1132 are shown in Table II. The results indicate that variations in R^1 and R^2, except Dyes 2 and 10, have little effect on λ_{max}. In contrast with this, a fusion of the benzene ring with the indandion ring in Dyes 2 and 10 causes a noticeable bathochromic shift.

Typical absorption spectra for the quinophthalones in chloroform are shown in Figure 3. The spectra in ZLI-1132 are similar to those in chloroform: only a wavelength shift of a few nanometers is ob-

TABLE III

Experimental data on 3,9-disubstituted perylene dyes



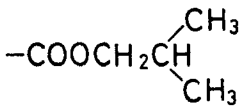
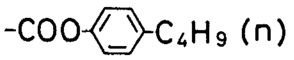
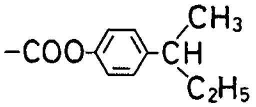
Dye No.	$-R^3$	λ_{max}/nm (in ZLI-1132)	S (in ZLI-1132)	m.p./°C
14.	$-COOC_8H_{17}$(n)	418 443 $\underline{471}$	0.40	128.2
15.	 $-COOCH_2\overset{CH_3}{\underset{CH_3}{CH}}$	417 443 $\underline{471}$	0.46	210.8
16.		422 449 $\underline{477}$	0.70	166.1
17.		424 449 $\underline{477}$	0.68	213.4

TABLE III (*continued*)

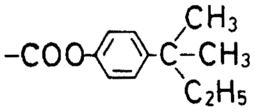
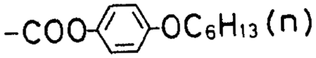
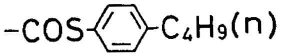
Dye No.	$-R^3$	λ_{max}/nm (in ZLI-1132)	S (in ZLI-1132)	m.p./°C
18.		422 450 477	0.68	245.0
19.		422 453 478	0.72	155.2
20.	$-COSC_8H_{17}(n)$	453 476	0.61	151.3
21.		458 480	0.73	157.0

TABLE IV

Absorption wavelengths and order parameters of dyes in different nematic hosts

Host	Dye 6		Dye 16	
	λ_{max}/nm	S	λ_{max}/nm	S
I.	449	0.61	477	0.70
II.	451	0.59	—	—
III.	450	0.53	479	0.71
IV.	450	0.58	477	0.73
V.	454	0.48	—	—
VI.	451	0.57	478	0.73

served. The visible absorption band for the 3′-hydroxyquinophthalone derivatives shows three peaks and the peak at the shortest wavelength of the three appears as a very weak shoulder of the main peak. It can be seen from Figure 3(c) that the benzene ring fusion onto the indandion ring induces the sharpening of the absorption band. It must be emphasized here that the visible band for the quinophthalones is considerably narrow. This remarkable feature results in the brilliant yellow color.

The maximum absorption wavelengths for the perylene dyes in ZLI-1132 are listed in Table III. It is obvious from this table that an appreciable bathochromic shift is produced by replacement of —COO— by —COS— and interposing a phenylene ring. Typical absorption spectra for the perylene dyes in chloroform are shown in Figure 4. When the perylene nucleus has —COO— at its 3- and 9-positions, the visible absorption curve shows three peaks. As shown in Figure 4 (b), however, a large change in the spectral curve takes place with the replacement of —COO— by —COS—.

3.3. Solubility and photostability

Some of the dyes reported here have been found to be considerably soluble in ZLI-1132. For example, Dyes 3, 4, 5, 6, 8, 9, 12, 13, 16,

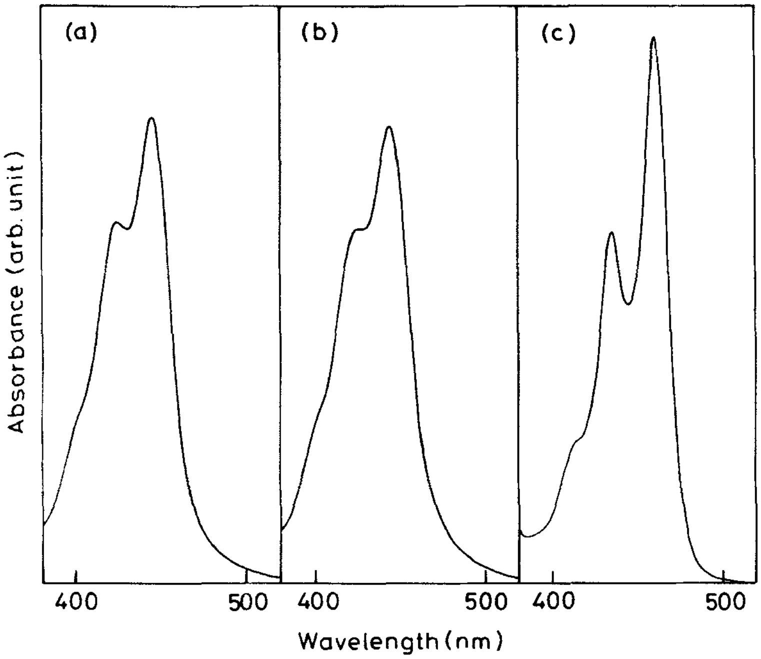


FIGURE 3 Typical absorption spectra for the 3'-hydroxyquinophthalone dyes in chloroform: (a) Dye 3; (b) Dye 6; (c) Dye 2.

20 and 21 exhibit a solubility over 1 wt% at room temperature. In particular, the values for Dyes 12, 13, 16 and 20 exceed 3 wt%.

Some selected results from the accelerated photodegradation tests are illustrated in Figure 5. For comparison, a well known anthraquinone dye[14] (BDH, D-44) has been subjected to the same test. Each dye tested, as illustrated by the data of Figure 5, shows excellent photostability in ZLI-1132. It is worth noting that the fading rates of the quinophthalone in ZLI-1132 are as slow as those of the representative anthraquinone dye.

IV. CONCLUSION

The effects of molecular structure on the order parameters and spectroscopic properties have been examined for a number of 3'-hydroxyquinophthalone and 3,9-disubstituted perylene dyes. From systematic variation in structure, it has been found that a thioester group and a short flexible chain such as an *n*-butyl group play an important

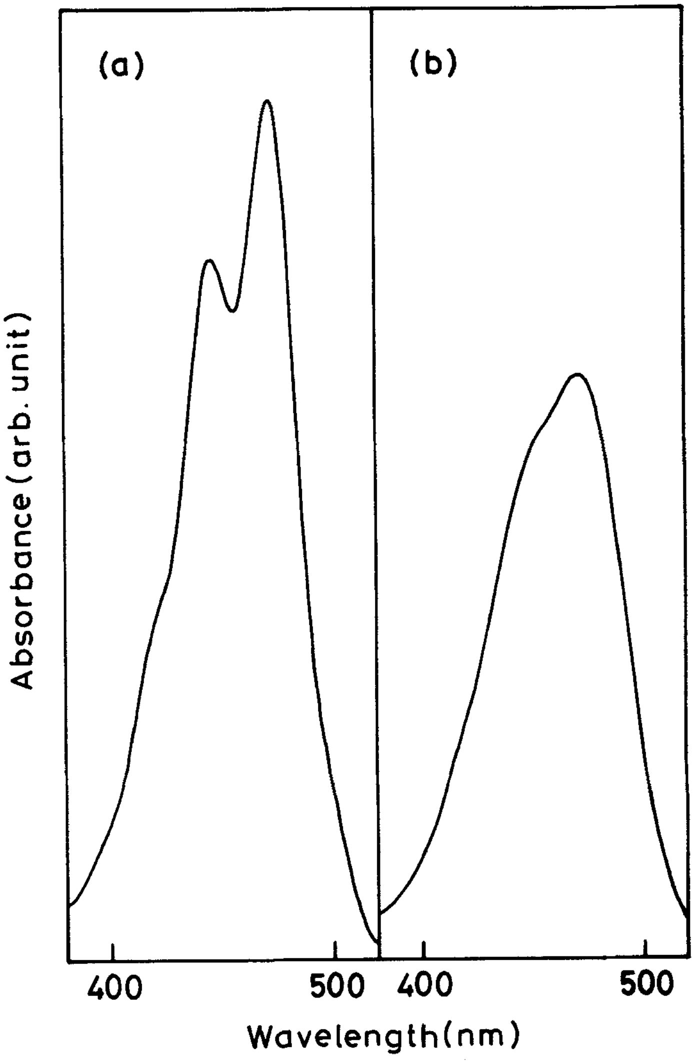


FIGURE 4 Typical absorption spectra for the 3,9-disubstituted perylene dyes in chloroform: (a) Dye 16; (b) Dye 21.

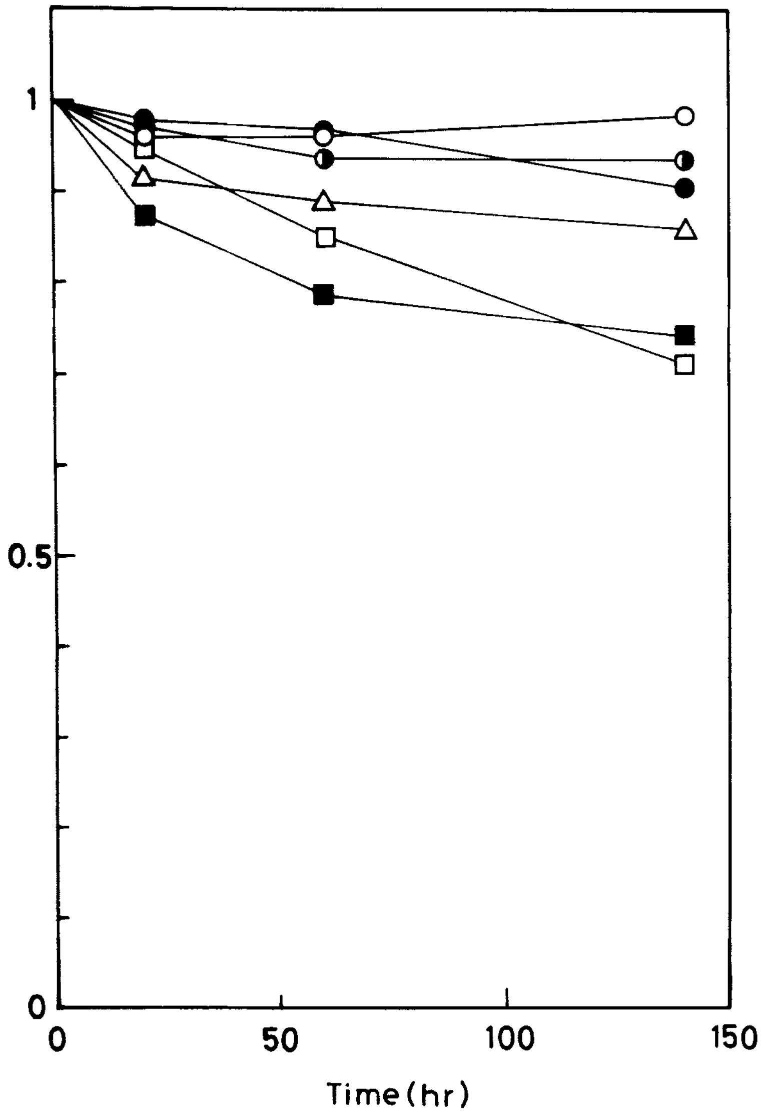


FIGURE 5 Time dependence of the absorbance for the quinophthalone and perylene dyes during the accelerated photodegradation tests: ○, Dye 2 (464 nm); ●, Dye 3 (449 nm); ◑, Dye 6 (449 nm); ■, Dye 14 (471 nm); □, Dye 16 (477 nm); △, BDH D-44 (548 nm).

role in increasing the order parameters. Furthermore, the 3'-hydroxyquinophthalone derivatives have shown excellent photostability comparable to those of the representative anthraquinone dye.

Acknowledgments

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