CHARACTERIZATION OF NEW EXCIMER PUMPED UV LASER DYES
2. *p*-QUATERPHENYLS

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New excimer-pumped laser dyes based on *p*-quaterphenyl are described and the associated performance parameters are presented. A discussion of the variations in the performance parameters found is made in terms of dye chemical structures. Most of the dyes studied are significantly better than the chosen reference dye BBQ. The best dye in the series (*dye 3*) is stabilized both by ring-alkylation and by ring-bridging. The net effect is the production of a new dye with a lifetime ten times greater than that of the reference dye BBQ.

KEY WORDS: *p*-quaterphenyl, laser dye, excimer pumped, ultraviolet.

INTRODUCTION

The oligophenylenes have been recognized[1] as good candidates for new laser dyes in the near ultraviolet region for some time. In the case of 308 nm excimer pumping, many *p*-quaterphenyl dyes are attractive since their first singlet-singlet absorptions are typically in this wavelength region, thus providing for efficient pumping. However, most of the *p*-quaterphenyl derivatives are not suitable for pumping by the third harmonic of Nd:YAG (355 nm) since their wavelengths of maximum absorption are bathochromically shifted relative to 355 nm. In this regard it is to be

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especially noted that the ring-bridged derivatives, such as those studied here, have absorption maxima which are red-shifted relative to the parent dye p-quaterphenyl. Thus, many of these ring-bridged dyes are able to be pumped with 355 nm Nd:YAG radiation providing for efficient conversion in the blue spectral region for this important pumping source.[2]

Selected p-quaterphenyl derivatives, pumped by excimer laser radiation, have been examined by Rinke, Gusten and Ache.[3,4] Kauffman and co-workers[5,6] have reported results for a series of p-quaterphenyls under flash-lamp pumping conditions. In the first paper in this series,[7] we presented our work on several new derivatives of p-terphenyl. A preliminary account of our work on excimer laser pumped p-quaterphenyls has been given.[8] In this paper we present a more detailed account of our results for a series of new excimer pumped p-quaterphenyl dyes.

EXPERIMENTAL DETAILS

The experimental apparatus and methods used in this study have been described in detail in the previous paper.[7] Although these dyes have been examined over a period of months, the dye lifetime and conversion efficiency data come from measurements done under identical operating conditions. For the sake of internal standardization on a day-to-day basis, the dye BBQ,[9] dye 14 in Table 1, in p-dioxane solvent was used as a benchmark. Before each study the dye laser was tuned up with BBQ to give the performance values given in Table 1. In this manner, results from day-to-day, especially for lifetimes, could be related quantitatively. In this study 100 ml volumes were used in the small Lambda Physik circulators with no cover gas circulation. The optimum concentrations listed in Table 1 are for the oscillator-preamplifier stage of the dye laser.

The dyes described in this study have been synthesized by methods previously described.[5-8] BBQ was used as purchased from Exciton, Inc. The solvent p-dioxane was purchased from Fisher Scientific Co. as an analytical reagent and used only when freshly opened.
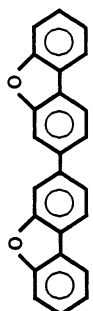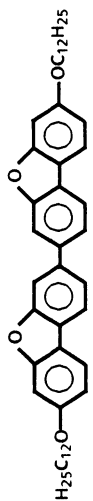

RESULTS AND DISCUSSION

The dyes studied are identified and numbered in Table 1 where pertinent performance characteristics are also summarized. For the sake of discussion, we have separated the dyes into two classes: singly and doubly ring-bridged p-quaterphenyls. Using this difference in ring-bridging as a means of classification has the practical consequence of distinguishing the tuning curves of the dyes. Figures 1 and 2 demonstrate this point for several of the dyes studied. Within each bridging class, the dyes are listed in the order of increasing laser wavelength maximum. The performance characteristics of the internal standard dye BBQ and two related dyes are given last in the table.

Table 1 Photophysical characteristics of laser dyes

Dye No.	Dye Structure	CONCENTRATION OPTIMUM (mol/ℓ)	LASER MAXIMUM (nm)	TUNING RANGE (nm) FWHM	TUNING RANGE (nm) Full	$E_{1/2}$ (kJ/ℓ)	CONVERSION EFFICIENCY (%)
			SINGLY RING-BRIDGED				
1		5.2×10^{-4}	(360)* 376	368 - 383	357 - 384	130	12.0
2		5.0×10^{-4}	(360) 376	358 - 383	357 - 385	170	12.8
3		4.0×10^{-4}	(365) 382	374 - 388	361 - 389	430	12.6
4		5.0×10^{-4}	(371) 387	377 - 395	370 - 396	28	14.6
5		5.0×10^{-4}	(375) 391	373 - 400	371 - 402	88	15.7
6		7.6×10^{-4}	(378) 393	384 - 402	375 - 404	70	12.7

Table 1—*continued*

Dye No.	Dye Structure	Concentration Optimum (mol/ℓ)	Laser Maximum (nm)	Tuning Range (nm)		$E_{1/2}$ (kJ/ℓ)	Conversion Efficiency (%)
				FWHM	Full		
	DOUBLY RING-BRIDGED						
7		4.2×10^{-4}	374	364 - 380	362 - 383	100	12.0
8		7.2×10^{-4}	391	382 - 399	380 - 402	48	13.8
9		6.0×10^{-4}	382	376 - 389	371 - 390	200	14.9
10		6.2×10^{-4}	396	387 - 404	385 - 405	32	16.5
11		5.0×10^{-4}	398	388 - 406	386 - 407	57	16.5
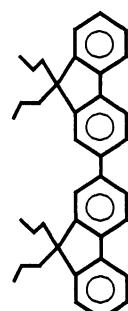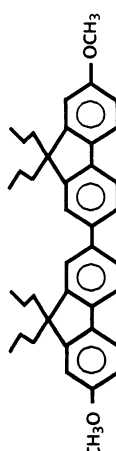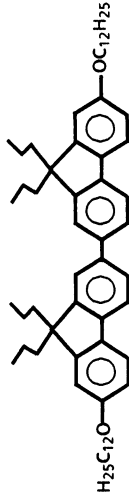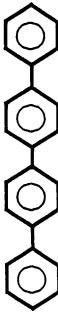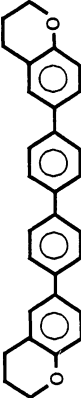
Table 1—*continued*

Dye No.	Dye Structure	CONCENTRATION OPTIMUM (mol/ℓ)	LASER MAXIMUM (nm)	TUNING RANGE (nm) FWHM	TUNING RANGE (nm) Full	$E_{1/2}$ (kJ/ℓ)	CONVERSION EFFICIENCY (%)
				REFERENCE DYES			
12		3.4×10^{-4}	(352) 368	361 - 376	348 - 382	-- **	14.0
13		4.5×10^{-4}	(372) 388	369 - 398	365 - 402	64	14.0
14 (BBQ)		3.2×10^{-4}	(368) 386	376 - 393	364 - 395	32	15.2

* Wavelengths in parentheses denote secondary peaks in tuning curves.
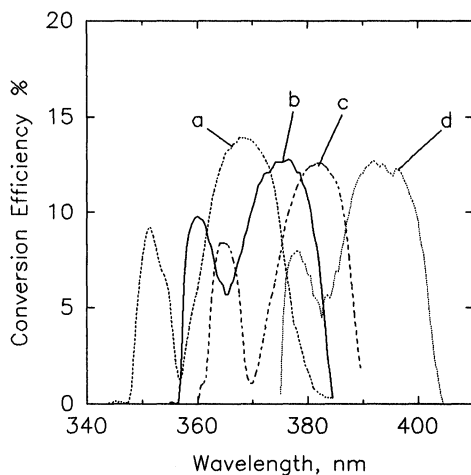** Not determined in this study. See reference 7

Figure 1 The tuning curves (conversion efficiency versus wavelength) of selected singly ring-bridged quaterphenyls and, for comparison, *p*-quaterphenyl, in *p*-dioxane solvent. The dye concentrations are all at the optimum values listed in *Table 1*. The curves are: curve a, dye 13; curve b, dye 2; curve c, dye 3; curve d, dye 6.

General Properties of Dyes

Overall, the conversion efficiencies listed in *Table 1* vary only from 12 to 16% making any one dye acceptable from that standpoint. Compared with BBQ (*dye 14*), most of the lifetimes are longer and, thus, these new excimer pumped dyes represent a relative improvement in stability. Indeed, *dye 3* represents more than an order of magnitude enhancement in stability relative to BBQ.
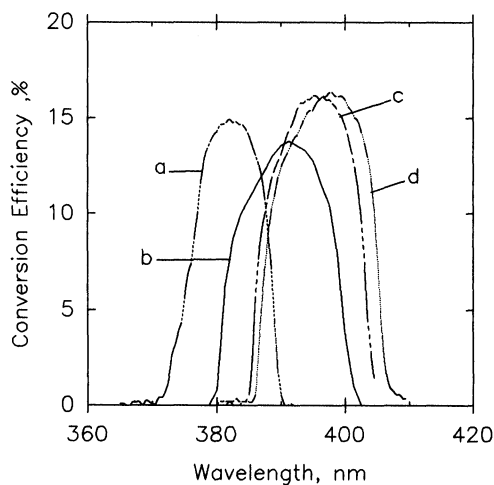

Figure 2 The tuning curves (conversion efficiency versus wavelength) of selected doubly ring-bridged quaterphenyls in *p*-dioxane solvent. The dye concentrations are all at the values listed in *Table 1*. The curves are: curve a, dye 9; curve b, dye 8; curve c, dye 10; curve d, dye 11.

Singly-bridged Quaterphenyls

The singly-bridged dyes all have similarly shaped, doubly featured, tuning curves as indicated in Figure 1. In turn, these tuning curves are closely related to that of *p*-quaterphenyl itself which is also shown for the sake of comparison. In each tuning curve the shorter wavelength feature corresponds to the first vibronic component of the fluorescence; the second to the second component.

Inspection of the characteristics of *dyes 1* and *2* in *Table 1* in comparison with *p*-quaterphenyl, *dye 12*, shows that single ring-bridging has the effect of red-shifting the tuning curve by roughly 8 nm. The conversion efficiencies of *dyes 1* and *2* are also slightly reduced compared to *dye 12*. These results are consistent with those of Rinke, Gusten and Ache[4] who studied similar, but not identical, ring-bridged *p*-quaterphenyls. Substitution of methoxy groups on the ethyl side chains (*dye 1* versus *dye 2*) gives a moderate improvement in lifetime, and only slightly affects the remaining dye parameters, as expected.

Using *dyes 1* and *2* as comparison structures, it can be seen that the following conclusions hold for the remaining singly-bridged dyes:

1. The substitution of alkoxy groups at the terminal ring ends of the parent structure (*dyes 4, 5, 6*) greatly reduces the dye lifetime. In the case of the methoxy substituted dye (*dye 4*), the lifetime is reduced to the level of BBQ (*dye 14*). In this context it appears that rigidization of the aryloxy groups as found in *dyes 5* and *6*, serves to partially arrest photochemical degradation. This effect is analogous to the observed increase in lifetime found in 7-amino-coumarins when the amino group is rigidized,[10] reducing non-radiative loss of excited state energy. The substitution of methoxy groups (*dye 4*) at the terminal ring positions also results in a redshift in the tuning curve of 11 nm. Rigidization (see *dyes 5* and *6*) further redshifts the tuning curve about 5 nm.

2. Substitution of *t*-butyl at the terminal ring positions redshifts the tuning curve (compare *dyes 2* and *3*) by 6 nm. This substitution also dramatically improves the dye lifetime by a factor of 2.5. We found a very similar result for the 4,4″-*t*-alkyl-substituted *p*-terphenyls.[7] Thus, it appears that ring substitution by tertiary alkyl groups produces the most long-lived oligophenylene laser dyes.

3. While each tuning curve represents two vibronic components of the fluorescence, the usefulness of a specific dye varies due to the intensity variation in the tuning curve *between* the two vibronic components. For example, the wavelength region between the two components in *p*-quaterphenyl (see Figure 1), around 357 nm, has a conversion efficiency of about 10% of the maximum value. This large "hole" in the tuning curve attenuates the usefulness of the dye in this particular region. With the exception of *dye 3*, none of the singly-bridged derivatives is as extreme in this respect as *p*-quaterphenyl. Nonetheless, the "hole" in the tuning curve remains an inconvenience as one tunes through the gain profile of the dye. Almost any substitution on the basic *p*-quaterphenyl we have studied leads to an enhancement of the usefulness of the dye (see curves in Figure 1) since the minimum gain value is generally increased with chemical substitution. In a separate paper,[11] we

have also discussed how one can construct laser dye mixtures to overcome this inconvenience.
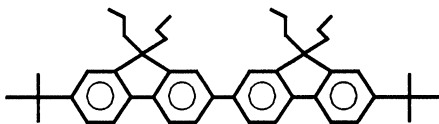
Doubly-bridged Quaterphenyls

Double ring-bridging (see *dyes 7* and *9*), in general, changes the shape of the tuning curves to one which has one strong broad feature as indicated in *Table 1* and Figure 2. It does not matter which chemical entity, methylene or isoelectronic oxygen (see *dyes 7* and *9* in *Table 1*), is used in the double bridging, for a single broad tuning curve results. In this regard our results are consistent with the results of Rinke, Gusten and Ache.[3]

   With further chemical substitution on the terminal aromatic rings, it is found that aryl-oxy derivatization (*dyes 8, 10*, and *11*) results in red-shifting the tuning curve the most. Adding a complicated hydrocarbon function (*dye 11* versus *10*) in place of methyl on the oxygen only slightly red-shifts the tuning curve. However, such a substitution has the desirable consequence of nearly doubling the lifetime. Comparison of the parent doubly-bridged dyes (*dyes 7* and *9*) yields several interesting facts. First, the oxy-bridged dye is blue-shifted compared to the substituted methylene dye. Second, the stability (half-life) of the substituted methylene derivative, *dye 9*, is greater by a factor of 2 than the corresponding oxy-bridged compound, *dye 7*. This relative stability ratio does not at first appear to be consistent with the results of Rinke, Gusten and Ache,[3] who found the opposite ratio for the unsubstituted methylene-bridged dye. As has previously been discussed,[5] substituting all hydrogens with alkyl groups makes an important contribution to dye stability. A similar discussion may be applied to these *p*-quaterphenyl dyes. Thus, it is probable that the unsubstituted methylene bridge is the chemical site of weakness not observed when the bridge is protected by alkylation. Third, the lifetimes of the doubly-bridged compounds are all as good as or better than that of BBQ. As can be seen by comparing *dyes 13* and *14* (BBQ), the addition of a rigidized ether group enhances the stability of the alkoxy derivative by roughly a factor of 2, as it did in the singly ring-bridged *dyes 5* and *6* versus *4*.

CONCLUSIONS

In conclusion, we have studied a series of excimer pumped *p*-quaterphenyl dyes which are significantly better than the chosen reference dye BBQ. As we have noted previously for the *p*-terphenyls,[7] the ring-alkylated dyes stand out as the more stable derivatives. In turn, ring-bridging serves to enhance the stability of the *p*-quaterphenyls further. The addition of oxygen to the aromatic rings in the *p*-quaterphenyls, as in the case of the *p*-terphenyls,[7] reduces the performance of the dyes significantly. However, the addition of oxygen to exocyclic alkyl groups can be beneficial to dye stability. The best dye in this series, *dye 3*, offers more than an order of magnitude improvement in stability at the expense of only a slight decrease in conversion efficiency compared to the reference dye BBQ.

It would appear, comparing *dye 9* with *1*, and *dye 3* with *2*, that an outstanding new material could be made by combining double ring-bridging with *t*-alkylation, as in the new dye below.[12]

Acknowledgements

References

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2. Seven of these new dyes in *p*-dioxane solution have been evaluated by John Montgomery of Lumonics Inc. using 355 nm Nd:YAG pumping. His results are briefly summarized here by permission (see *Table 1* for dye structures): *Dye 4* (389 nm, 378–395 nm, 20%); *Dye 5* (393 nm, 382–400 nm, 19%); *Dye 7* (376 nm, 369–381 nm, 15%); *Dye 8* (392 nm, 383–400 nm, 19.5%); *Dye 9* (384 nm, 377–388 nm, 18%); *Dye 10* (396.5 nm, 388–409 nm, 20%); *Dye 11* (398 nm, 391–404 nm, 21%); where the first through third numbers in parentheses denote the lasing maximum, the full tuning range and the conversion efficiency, respectively.
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12. As we showed that *t*-amyl and *t*-butyl groups were similarly effective in increasing the lifetime of *p*-terphenyl laser dyes (Ref. 7), we found it synthetically expedient to prepare 7,7'-di-*t*-amyl-9,9,9',9'-tetraethyl-2,2'-bifluorene. The experimental conditions in these recent measurements have been refined since our measurements on the quaterphenyls listed in this paper were done. Under these refined conditions we find that the reference dye BBQ has a half-life of 67 kJ/liter and that the new dye has a half-life of at least 500 kJ/liter. Thus, it is clear that the new dye is an excellent dye as predicted.