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Photophysical Properties of Squaraine Derivatives: Evidence for Charge Separation

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The polarity dependent fluorescence quantum yields and lifetimes at room temperature have been measured for two squaraine dyes, SQ-DMA and its crown ether derivative SQ-CR. The unstructured fluorescence bands and the polarity independent k_f values indicate fluorescence from one single species. The nonradiative decay rates increase strongly with solvent polarity, indicating a polarity-induced intramolecular fluorescence quenching process. The latter could be due to the formation of a nonemissive twisted intramolecular charge transfer (TICT) state. Low-temperature measurements and the comparison of SQ-DMA and SQ-CR support this view.

Introduction

Colored squaric acid derivatives (squaraine dyes) have gained some importance due to their numerous applications.[1] They are used for photosensitization in imaging processes[2−4] and in solar energy conversion.[5,6] Several studies have been made regarding their photophysical properties.[7−22] Some of these studies reported multiple fluorescence with three bands, the ratio of which changed with increasing solvent polarity and with the substitution pattern of the squaraine dye.[11,12] One of these bands was assigned to a twisted intramolecular charge transfer (TICT) state;[7−12] for reviews on TICT states see refs 23−25. Other researchers, however, did not report multiple bands,[13−22] so that the situation remains unclear. Although aggregation phenomena play an important role in the present literature (refs 15, 26 and references therein), the nonradiative decay behavior of the uncomplexed dye systems is still not well understood.

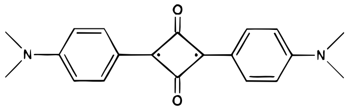
We therefore decided to determine the photophysical properties independently and to enlarge the scope of the experiments incorporating a systematical study of the fluorescence and nonradiative decay rate constants k_f and k_{nr} as a function of solvent polarity and temperature.

We also included a squaraine derivative possessing an aza-crown-ether function capable of complexing metal ions which have recently been studied in a different context.[15,16] The interest came from the realization that dyes with multiple fluorescence are the candidates of choice for developing ion-sensitive fluorescence probes.[27] Moreover, as the squaraine dyes studied here absorb in the long-wavelength region of the visible spectrum, they possess potential interest as laser-diode-excitable fluorescence probes.

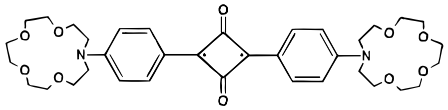
Experimental Section

Bis[4-(dimethylamino)phenyl]squaraine (SQ-DMA) and its aza-crown-ether derivative (SQ-CR) were synthesized according to the very versatile and straightforward method reported by H.-E. Sprenger and W. Ziegenbein.[28,29] It involves the condensation of 1 equiv of squaric acid and 2 equiv of *N*,*N*-dimethylaniline in a mixture of 1-butanol and benzene. After the water has been distilled off azeotropically, blue crystals precipitate at room temperature. Recrystallization from a mixture (4/1) of methylene chloride and *n*-hexane gave 36% of SQ-DMA: mp, found 275 °C (lit. 276 °C[28]). The same procedure with phenylaza-15-crown-5 instead of *N*,*N*-dimethylaniline leads to blue crystals of SQ-CR: mp, found 272 °C (lit. 215 °C[15]), yield 40%. ^{1}H NMR ($CDCl_3$, 250 Mhz) δ: 3.54−3.96, m, 40H; 6.78, d, $J = 9.1$ Hz, 4H; 8.4, d, $J = 9.1$ Hz, 4H. ^{13}C NMR ($CDCl_3$, 250 Mhz) δ: 53.42, $-CH_2-N$; 68.22, 70.02, 70.45, 71.27, CH_2-O; 112.74, 120.12, 133.32, 153,69, C_{arom}; 185.26, 188.10 $C_{cyclobutane}$.

The solvents used were of spectrograde quality (mostly Merck, Uvasol) and were nonfluorescent at the sensitivity levels used.



SQ-DMA



SQ-CR

Absorption spectra were measured on a Cary 17 spectrometer, and quantum-corrected fluorescence spectra (concentrations < 10^{-4} M) on a Perkin-Elmer 650-60 fluorimeter. A solution of Basic Blue 3 in ethylene glycol has been used as quantum counter, which allows the correction in the spectral range up to 700 nm.[30] For the determination of fluorescence quantum yields, a solution of Rhodamine 101 in ethanol ($\phi_f = 1.0$) has been taken as standard. Fluorescence spectra were independent of concentration and excitation wavelength. For the determination of temperature dependent quantum yields the temperature effects on the refractive index as well as the density of solvent have been taken into account.

Fluorescence decay traces were measured for aerated solutions with single-photon-counting equipment described elsewhere[31] using synchrotron radiation from BESSY (single bunch mode) as excitation source. The decays $F(t)$ were fitted using the least-

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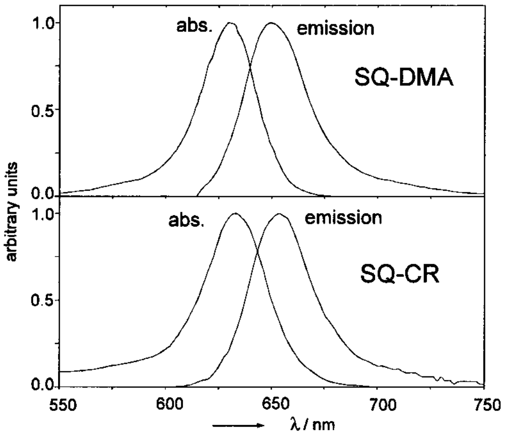

Figure 1. Absorption and fluorescence spectra of SQ-DMA and SQ-CR in CH_2Cl_2 at room temperature.

TABLE 1: Comparison of Room-Temperature Photophysical Data for SQ-DMA with Literature Values

solvent	λ_{max}^{abs}/nm	λ_{max}^{em}/nm	ϕ_f	τ_f/ns	ref
CH_2Cl_2	627.6	646,660,702	0.65		11
	628	648,657,700	0.65	(4.0/0.7)[a]	12
		single band	0.62−0.69		17
	628	654	0.45	1.5[b]	19
	628	650	0.42	1.3[c]	this work
$CHCl_3$	624	646,656,695	0.80		12
	626	642	0.70	2.3[c]	this work

[a] Referred to literature. [b] Trans. Absorption. [c] Single photon counting.

squares iterative reconvolution technique and a multiexponential model function. In the less polar solvents, a single exponent was sufficient, whereas in the highly polar solvents, some long-decay components of low weight (<10% quantum yield) could be detected, which were, however, not reproducible. In view of the stability problems reported below, only the main decay component which was unaffected by these problems was used in these cases.

TABLE 2: Thermal and Photostability Data for SQ-DMA and SQ-CR

		% of initial absorbance	
compound	solvent	thermal (after 1 week)	photochemical (after 30 min)[a]
SQ-DMA	CH_2Cl_2	100	
	ethanol	48	92
	acetonitrile	24	
SQ-CR	CH_2Cl_2	74	93
	ethanol	53	94[b]
	acetonitrile	0	74

[a] Irradiation at absorption maximum (fluorimeter PE 650−60) with slitwidths of 5/5 nm; normal duration for fluorescence spectra about 1.5 min. [b] After 12 min irradiation.

TABLE 3: Spectral and Photophysical Data at Room Temperature for SQ-DMA and SQ-CR in Solvents of Different Polarity

solvent	$\Delta f'$	λ_{max}^{abs}/ nm	λ_{max}^{em}/ nm	$\Delta\nu_{1/2}$/ cm^{-1}	$\Delta\nu_{St}$/ cm^{-1}	ϕ_f	τ_f/ ns
			SQ-DMA				
toluene	0.013	627	641	724	348	0.85	2.25
dioxane	0.020	625	640	726	375	0.83	2.22
$CHCl_3$	0.148	626	642	722	398	0.70	2.27
THF	0.210	627	642	722	373	0.68	1.63
CH_2Cl_2	0.218	628	650	753	540	0.42	1.23
BuCN	0.275	629	650	758	514	0.17	0.59
EtOH	0.289	632	654	798	532	0.09	0.16
ACN	0.305	628	652	842	586	0.08	0.16
MeOH	0.309	630	656	837	629	0.04	<0.1
			SQ-CR				
toluene	0.013	632	646	593	343	0.54	2.34
dioxane	0.020	630	648	663	440	0.71	2.53
$CHCl_3$	0.148	632	652	703	485	0.61	2.43
Et_2O	0.167	623	638	684	377	0.79	2.29
THF	0.210	634	648	708	340	0.70	2.24
CH_2Cl_2	0.218	634	655	793	506	0.37	1.72
BuCN	0.275	636	656	744	479	0.39	1.30
EtOH	0.289	637	660	822	547	0.21	0.66
ACN	0.305	633	656	788	554	0.15	0.52
MeOH	0.309	638	663	860	591	0.09	<0.1
H_2O	0.319	640	666	934	610	0.09	

Results

Solvent Polarity Effects. Absorption and fluorescence spectra of the two compounds are depicted in Figure 1. The spectral structuring of the fluorescence as reported in refs 7−12 is not observed in methylene chloride nor in any of the other solvents investigated. There was no concentration effect within the range 10^{-8} -10^{-6} mol/L. Table 1 contains a comparison of the spectra and photophysical properties with the available literature data on SQ-DMA. There are discrepancies not only in the spectra but also in the fluorescence quantum yields and lifetimes. In judging the reliability of the data it is advisable to compare the results from different laboratories. Only in the laboratory of K. Y. Law have multiple fluorescence bands been observed.

The thermal and photostability properties of the two dyes were also tested (Table 2), and it was generally found that slow decomposition of the solutions occurred in the dark, more strongly for SQ-CR, and in polar solvents. Some photodecomposition was also observable but on levels which did not affect the recording of the fluorescence spectra. All the measurements reported here were made under conditions where decomposition effects could be excluded.

Table 3 summarizes the spectral and photophysical properties in differently polar solvents. A slight red shift of absorption and emission and broadening of the spectra are observed, and the Stokes shift increases with solvent polarity. It remains, however, small on an absolute scale compared to the typical Stokes shift of around 13 000 cm^{-1} reported for TICT systems in acetonitrile.[24] Much more stringent are the solvent polarity effects on fluorescence quantum yields and lifetimes. As a general trend for the compounds studied, lifetimes and quantum yields decrease with increasing solvent polarity. The corresponding rate constants (calculated according to eqs 1 and 2) show that this is entirely the effect of a solvent-polarity-induced nonradiative decay which starts to be important in the more polar solvents (Table 3), whereas k_f stays constant within experimental uncertainty throughout the solvents investigated. This is summarized in Figure 2, which also shows that k_{nr} is far smaller in SQ-CR than in SQ-DMA. While the difference of k_{nr} values is rather small in nonpolar solvents (a factor of 1.2 in CH_2Cl_2), it grows with augmentation of solvent polarity (a factor ≈ 4 in ACN). The rate constants k_{nr} increase for both compounds and in polar solvents with different properties (nitriles, alcohols; see Table 3) such that specific solvent effects can be excluded as their source. We can thus conclude that (i) there is no evidence for a change of the emitting state along the polarity scale investigated (constant k_f); the k_f value for SQ-CR seems to be somewhat reduced; (ii) in sufficiently polar solvents, a polarity-induced intramolecular fluorescence quenching process sets in which is stronger for SQ-DMA than for SQ-CR.

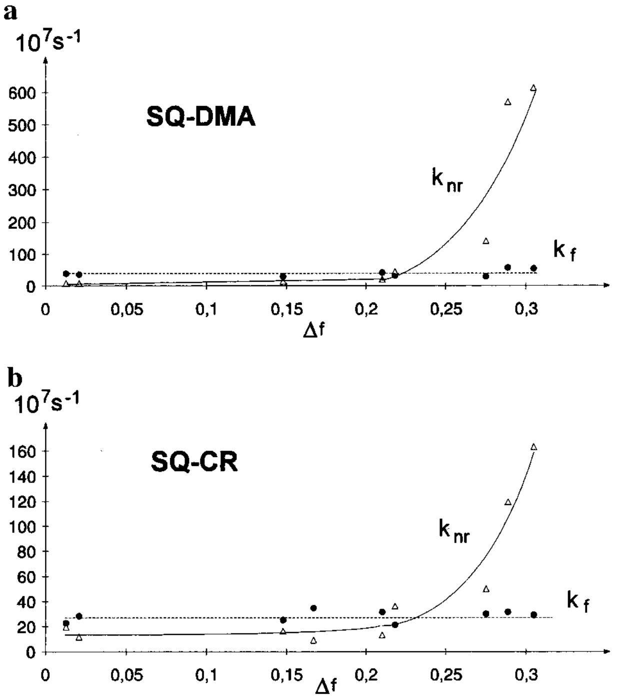

Figure 2. Radiative (k_f) and nonradiative (k_{nr}^{tot}) decay rate constants at room temperature for SQ-DMA (a) and SQ-CR (b) as a function of solvent polarity.

TABLE 4: Photophysical Rate Constants for SQ-DMA and SQ-CR at Room Temperature in Ethanol

compound	$k_f/10^7$ s^{-1}	$k_{nr}/10^7$ s^{-1}
SQ-DMA	36.1[a]	568.8
SQ-CR	25.5[a]	119.7

[a] Average value independent of solvent polarity (see Figure 2a,b).

Comparative data for the solvent ethanol are summarized in Table 4.

$$k_f = \phi_f/\tau_f \tag{1}$$

$$k_{nr}^{tot} = k_f(\phi_f^{-1} - 1) \tag{2}$$

Low-Temperature Effects. Figure 3 shows fluorescence and fluorescence excitation spectra at different temperatures. The fluorescence spectra exhibit a narrowing upon cooling and a red shift of the maximum from 650 nm at 298 K to 664 nm at 173 K, which is stronger than the polar-solvent-induced shift at room temperature (Table 3). There seems to be a red fluorescence tail above 700 nm, but in view of the declining sensitivity of the photomultiplier in this wavelength region, we do not attach too much significance to it. The excitation spectra (Figure 3a) also shift to the red to a similar extent; the Stokes shift remains thus fairly small and temperature independent and does not support large charge redistribution in the fluorescent excited state.

The nonradiative rate constants, however, depend not only on polarity but also on temperature. This is borne out by the fluorescence quantum yields (Table 5), which increase nearly up to unity, and by the increasing lifetimes collected in Table 6. This table also contains the strongly temperature dependent total nonradiative rate constants calculated using eq 2 by combining fluorescence quantum yields and lifetimes. The fluorescence rate constant (from eq 1) remains approximately constant down to low temperatures.

Figures 4 and 5 summarize the data for k_{nr}: In Figure 4, total nonradiative rate constants are calculated using the solvent independent mean k_f value (Table 4) and eq 2. These rate constants contain both a temperature independent part (mainly intersystem crossing and internal conversion) and a temperature dependent part (eq 3). The latter part can be isolated using eq 4, and the values are summarized in Figure 5.

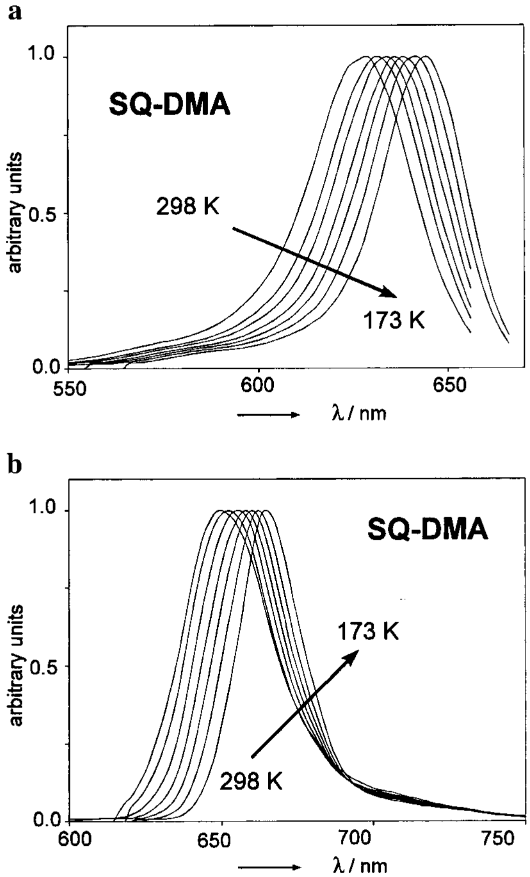

Figure 3. Fluorescence (b) and fluorescence excitation spectra (a) of SQ-DMA in CH_2Cl_2 as function of temperature.

TABLE 5: Low-Temperature Fluorescence Quantum Yields of SQ-DMA and SQ-CR

	SQ-DMA		SQ-CR	
T/K	CH_2Cl_2	EtOH	CH_2Cl_2	EtOH
298	0.42	0.08	0.37	0.21
273	0.60	0.18	0.48	0.36
253	0.69	0.28	0.57	0.57
233	0.86	0.40	0.64	0.74
213	0.86	0.64	0.65	0.73
193	0.89	0.80	0.66	0.75
181			0.66	0.81
173	0.93	0.88		
162				0.89

$$k_{nt}^{tot}(T) = k_{nr}^{o} + k_{nr}(T) \tag{3}$$

$$k_{nr}(T) = \tau^{-1}(T) - \tau_0^{-1} \tag{4}$$

Two points should be emphasized: (i) From the temperature dependent behavior, it can readily be seen that even in methylene chloride solvent intramolecular fluorescence quenching takes place at room temperature; (ii) there is no significant difference between k_{nr}^{tot} (Figure 4) and $k_{nr}(T)$ (Figure 5). This means that the temperature independent part of k_{nr} is very minor, in accordance with the high fluorescence quantum yields reached at low temperature. The Arrhenius slopes calculated from the $k_{nr}(T)$ data in ethanol are 15.9 kJ/mol for SQ-DMA and 8.6 kJ/mol for SQ-CR.

TABLE 6: Low-Temperature Fluorescence Lifetimes (in ns) and Rate Constants of SQ-DMA and SQ-CR[a]

	CH_2Cl_2		EtOH	
T/K	τ_f/ns	$k_{nr}/10^7\ s^{-1}$	τ_f/ns	$k_{nr}/10^7\ s^{-1}$
		SQ-DMA		
298	1.23	47.2	0.16	575
273	1.53	26.1	0.46	178
253	1.83	16.9	0.72	97
233	2.08	6.7	1.18	50.8
213	2.34	6.0	1.65	21.8
193	2.45	4.5	2.08	9.6
173	2.54	2.8	2.4	5.0
		SQ-CR		
298	1.72	36.6	0.66	120
273	2.11	24.6	1.06	60.4
253	2.31	18.6	1.46	29.5
233	2.47	14.6	1.84	14.1
213	2.57	13.6	2.19	12.3
193	2.60	13.1	2.24	11.2
181	2.61	13.0	2.27	8.4
162			2.31	4.8

[a] Monitored at two different emission wavelengths near the maximum and ca. 30 nm red-shifted and fitted globally.

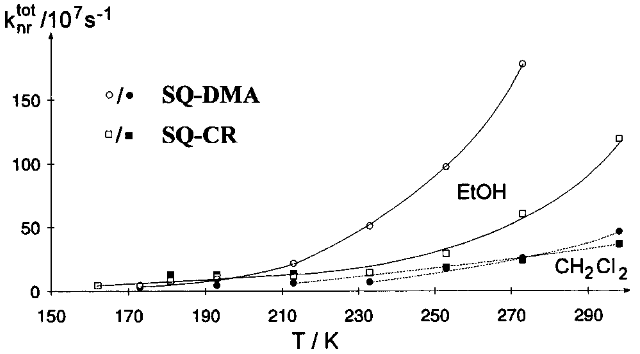

Figure 4. Total nonradiative decay rate constants as a function of temperature for SQ-DMA (circles) and SQ-CR (squares) in two solvents of different polarity, ethanol (—, ○, □) and CH_2Cl_2 (···, ●, ■), derived from fluorescence quantum yields (eq 3).

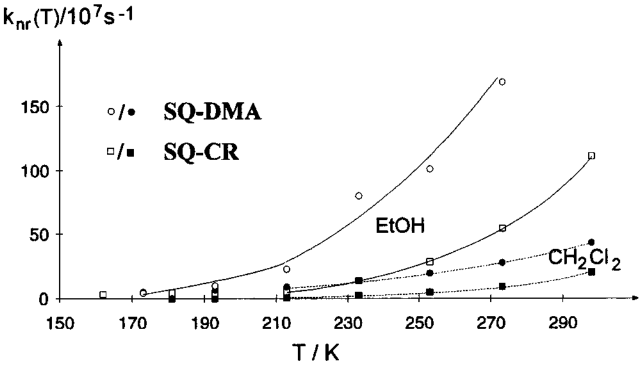

Figure 5. Temperature dependent part $k_{nr}(T)$ of the total nonradiative decay rate constants as a function of temperature for SQ-DMA (circles) and SQ-CR (squares) in two solvents of different polarity, ethanol (—, ○, □) and CH_2Cl_2 (···, ●, ■), derived from fluorescence lifetime measurements (eq 4).

Discussion

The finding of an unstructured fluorescence for the squaraines investigated raises the question as to the possible reason for the discrepancies with respect to the structured ("multiple") spectra observed by Law.[2,3,7−12] These multiple spectra were interpreted by the formation of an emissive TICT state and by solute−solvent complexes or exciplexes.[7−12] We show here that the fluoresence characteristics across the entire fluorescence band are unchanged, but that a polar state, possibly a TICT state, acts as a nonemissive funnel to the ground state. Regarding the question of structured spectra in refs 2, 3, and 7−12, all these spectra, irrespective of solvent, compound, and temperature, possess minima or inflections at 650 and 690 nm, which are not observed here. A possible cause for these inflections is the use of instrument correction curves, which do not fully correct for the wavelength characteristics of the detection system (mainly monochromator and photomultiplier). We avoided this possibility as far as possible by using the long wavelength dye basic blue as quantum counter in the correction procedure of Kopf and Heinze.[30]

The unstructured fluorescence band, the single-exponential lifetimes in less polar solvents including methylene chloride, and the constant k_f values across the entire polarity range (Table 3) are in favor of an interpretation by one single emitting species. It cannot be excluded, however, that a very weakly fluorescing species in polar solvents, a product of the intramolecular fluorescence quenching process, remained undetected due to the difficulties with compound stabilities (see Experimental Section and Table 2).

The question arises as to the nature of the intramolecular fluorescence quenching process. It is clearly correlated with solvent polarity, and a first attempt of an interpretation can be made by assuming the presence of a highly polar state which is lowered in polar solvents and causes the intramolecular fluorescence quenching if it is assumed that it is weakly fluorescing or nonfluorescing. In this respect, all the experimental facts are comparable to TICT formation in compounds such as (dimethylamino)benzonitrile (DMABN),[23,24] Michlers ketone (MK),[32] or dimethylanilinosulfone DMAPS[33] with the exception of the absence of the TICT emission band.

Whether the postulated near-complete electron transfer occurs could be independently checked in a few cases by transient absorption spectroscopy (compare, for example, refs 34−36). To experimentally verify whether an intramolecular twisting motion occurs along with charge transfer, however, normally the investigation of rigidized or conformationally restricted model compounds is necessary. This has been extensively done for DMABN.[23,24] A model compound study is also available for MK which shows the absence of the second fluorescence band for the bridged model compound.[32] Similarly as in MK, and DMAPS, charge separation in SQ-DMA and SQ-CR by the TICT mechanism would involve symmetry breaking with, most probably, one of the dialkylanilino groups orthogonal to the rest of the molecule being capable of acting as efficient electron donor.[32−34]

In the absence of rigidized model compounds, the temperature dependent studies and the comparison of SQ-DMA with SQ-CR may give some indication as to the involvement of a twisting in the intramolecular fluorescence quenching process. The apparent activation energy for SQ-DMA in ethanol (E_{obs} = 15.9 kJ/mol), calculated from an Arrhenius plot of the temperature dependent part of the nonradiative decay rate constants, is smaller than the activation energy for the solvent mobility of ethanol (E_η = (16.6 kJ/mol), determined from an Arrhenius-type plot of η^{-1} in the temperature range under investigation.[37] This indicates a barrierless or near-barrierless excited-state potential for the quenching process.[32,38] The temperature dependence of $k_{nr}(T)$ shown in Figure 5 would then be due to the viscous influence alone, thus indicating that a large-amplitude motion is connected with this process. The fact that SQ-CR, which possesses bulkier substituents, shows a much smaller nonradiative rate constant than SQ-DMA is consistent with the assumption that this large-amplitude motion can be identified with an intramolecular twisting motion because this is expected to be slowed for increasing rotor size.

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