hydronium ion catalysis. Providing photochemical proton transfer reactions do not have α values much lower than those found here, it should be possible to investigate this phenomenon more widely than has been the case. Another great advantage is that because α values are likely to be smaller in photoreactions, it should be possible to utilize a wider range of catalyst pK_{HA} values than in corresponding thermal reactions. Hence it might well be easier generally to detect and measure Brønsted curvatures photochemically.

In view of the great current interest in proton transfers involving excited states,[13,45,52] such investigations may lead to valuable new insights into the detailed mechanisms of such processes.

Electrochemical and Spectroscopic Analyses of the Thermodynamics of the Reversible Dimerization of Cyanine Radical Dications

J. R. Lenhard* and R. L. Parton

Contribution from the Research Laboratories—Photographic Products Group, Eastman Kodak Company, Rochester, New York 14650. *Received February 27, 1987*

Abstract: Radical dications initially formed during the one-electron oxidation of alkyl-substituted, cationic dicarbocyanine dyes were found to undergo reversible dimerization in acetonitrile at room temperature. The site of radical–radical coupling was determined by NMR spectroscopy to be at an approachable even-methine carbon of the polymethine chain. The $C\cdots C$ bond dissociation energy in the dimer was determined for a series of variously substituted dicarbocyanines from the temperature dependence of UV–vis spectra and was found to range from 12.2 to 16.8 kcal/mol. The corresponding free entropy change involved with the dimer dissociation process ranges from 21 to 32 eu. Upon consideration of the dicarbocyanine structures, the experimental results can be interpreted in terms of steric destabilization of the covalently bonded dimer.

Cyanine dyes have been widely used as spectral sensitizers for silver halide and other inorganic semiconductor materials.[1,2] In silver halide based photographic systems these dyes provide for color separation, in addition to extending the response of silver halide beyond its intrinsic ultraviolet and blue-light photosensitivity. The generic cyanine dye structure involves two heterocyclic nuclei that are linked by a conjugated chain containing an odd number of methine carbon atoms. Dicarbocyanines, which contain five methine carbons, are typically used to impart spectral sensitivity in the red region. Substituent modifications involving either the heterocyclic nuclei or the polymethine chain are the synthetic approaches commonly used to fine-tune dye properties to achieve a desired spectral wavelength response or to gain additional improvements in sensitization efficiency.

Predictions of the efficiency of spectral sensitization of silver halide by cyanine dyes are often based on the electrochemical properties of the particular dye.[3-5] In a recent report describing the measurement of the reversible redox potentials of cationic cyanines it was shown that the stability of the radical dication formed during one-electron oxidation is markedly dependent on the type and extent of substitution in the polymethine chain of the dye.[6] Cyanine radical dication stability was demonstrated to be greatly improved by alkyl substitution at the methine carbons to electronically stabilize the radical and/or sterically inhibit radical–radical coupling reactions. More detailed studies of dye radical stability have since resulted in the discovery of a remarkable collection of chain-substituted dicarbocyanine radical dications that undergo reversible C–C bond formation at room temperature.

This paper reports the results of thermodynamic and kinetic characterization of the reversible dimerization of thiadicarbocyanine and quinodicarbocyanine radical dications in acetonitrile solution. Thermodynamic parameters ΔG, ΔH, and ΔS, describing the dimerization equilibria for a series of variously substituted dyes, are evaluated from temperature-dependent absorption spectra. Complementary information concerning the relative rates of formation and dissociation of the dimers is provided by cyclic voltammetry. Together with product-analysis data, these results indicate that the dicarbocyanine radical/dimer equilibrium is largely controlled by the degree of steric strain in the dimer.

Experimental Section

A. Reagents and Solvents. Dyes were synthesized by previously established procedures,[7,8] and analyzed by thin-layer chromatography, UV-vis spectrophotometry, and ionographic analysis. All dyes were obtained as the *p*-toluenesulfonate (pts) or perchlorate (ClO_4^-) salts for electrochemical studies; however, chemical oxidations were carried out on bromide and iodide salts as well. Ferric chloride hexahydrate ($FeCl_3$, Kodak Laboratory Chemicals) and potassium hexafluorophosphate (Alfa) were used as received. Tetrabutylammonium tetrafluoroborate ($TBABF_4$, Kodak Laboratory Chemicals) was recrystallized three times from ethanol/water mixtures and dried in vacuo. Acetonitrile (CH_3CN, MCB spectrograde) for electrochemistry or radical thermodynamic studies was dried over 4A molecular sieves (Kodak Laboratory Chemicals, baked at 400 °C). Solvents for synthetic use were Kodak reagent grade.

B. Apparatus. Electrochemical measurements were performed with a Princeton Applied Research Corp. (PAR) 173 potentiostat in conjunction with a PAR 175 universal programmer, PAR 179 digital coulometer, and 124A lock-in amplifier. A Hewlett-Packard Model 239A low-distortion oscillator was used in ac measurements. Formal oxidation and reduction potentials were obtained via phase-selective, second-harmonic ac voltammetry or by cyclic voltammetry as described previously.[6] Voltammetric data were obtained at 22 °C at a Pt disk electrode (0.1 cm^2) or a Pt microelectrode (10-μm diameter). Current–voltage curves were recorded on a Hewlett-Packard Model 7045A X–Y recorder or on a Tektronix 5115 storage oscilloscope. All potentials were measured vs. the NaCl saturated calomel electrode and converted to the Ag/AgCl reference by adding 40 mV. Controlled-potential coulometry was performed with a PAR 337A cell system equipped with a Pt gauze working

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[1] West, W.; Gilman, P. B. In *The Theory of the Photographic Process*; James, T. H., Ed.; Macmillan: New York, 1977; p 277.

[2] Sturmer, D. P. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Interscience: New York, 1979; p 393.

[3] Gilman, P. B. *Pure Appl. Chem.* **1977**, *47*, 357.

[4] Large, R. L. In *Photographic Sensitivity*; Cox, R., Ed.; Academic Press: New York, 1973; p 241.

[5] Piechowski, A. P. *J. Electroanal. Chem.* **1983**, *45*, 67.

[6] Lenhard, J. *J. Imag. Sci.* **1986**, *30*, 27.

[7] Hamer, F. M. In *The Chemistry of Heterocyclic Compounds*; Weissberger, A., Ed.; Interscience: New York, 1964; Vol. 18.

[8] Slominskii, Y. L.; Romanov, N. N.; Stetsenko, Z. N.; Tomachev, A. I. *Zh. Org. Khim.* **1979**, *15*, 865.

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electrode (electrolysis time for >98% completion is ca. 2 min). Electrooxidized dye solutions were transferred to appropriate cells for spectrophotometric or ESR measurements. Solutions for voltammetric examination contained ca. 5 × 10^{-4} M dye and 0.1 M of the supporting electrolyte and were deaerated with nitrogen prior to examination. UV–vis spectra were recorded on a Hewlett-Packard 8450 or a Cary 219 spectrophotometer. NMR spectra were obtained with a Bruker WP-80 or an IBM WP270SY spectrometer. Proton chemical shifts are reported in parts per million on the δ scale from internal TMS. ESR spectra were recorded on an IBM-Bruker ER-200 instrument. Melting points are uncorrected and were measured with a Thomas-Hoover capillary melting point apparatus.

C. **Equilibrium Measurements.** Radical/dimer mixtures were prepared by dissolution of the authentic solid dimer or by electrochemical oxidation of a dye solution at an appropriate applied voltage. In each case, the radical/dimer mixture was transferred to a 0.5- or 1.0-cm quartz spectrophotometric cell and quickly cooled in an ice/salt bath to −10 °C. The chilled cell was transferred to the spectrophotometer (flushed with N_2), the UV–vis spectrum was recorded, and then the cell was gradually warmed to obtain data at higher temperatures. The temperature of the spectrophotometer cell block was varied (or maintained) with a Forma-Temp. refrigerated, circulating bath. Sample temperatures (±3 °C) were measured in a parallel cell with a Digitec Model 5810 digital thermometer. For less stable radicals, a flow system was used so that the solution could be rapidly cooled outside the spectrophotometer. Data taken during the cooling cycle were more or less identical with those taken during the warming cycle but were less conveniently obtained.

General Procedure for Chemical Oxidation of Dyes and Isolation of Dimers. The dicarbocyanine dye salt (1 mmol) was combined with 150–200 mL of methanol. In some cases the dye did not completely dissolve initially. Excess ferric chloride (1.8–2.5 mmol) in 50–100 mL of water was added, and the blue mixture was stirred for 15–20 min until yellow. The mixture was filtered and a large excess of potassium hexafluorophosphate (10–15 mmol) in 150–250 mL of water was added to precipitate the product. The noncrystalline precipitate was collected and dried. When necessary the dimeric product was purified by dissolution in a minimum amount of acetone or acetonitrile, and the solution was filtered into 150–200 mL of rapidly stirred ethyl acetate. The product precipitated and was collected and dried.

Dimer of Dye 6. Yield 79%; mp >145 °C (dec); ^{1}H NMR (CD_3CN) δ 3.60 (m, 8 H), 3.98 (t, 2 H), 4.75 (m, 8 H), 6.95 (d, 4 H), 7.0 (m, 8 H), 7.95 (d, 4 H), 8.20 (d, 4 H).

Anal. Calcd for $C_{46}H_{38}N_4S_4P_4F_{24}$: C, 40.8; H, 2.8; N, 4.1. Found: C, 40.8; H, 3.0; N, 4.1.

Dimer of Dye 5. Yield 43%; mp >195 °C (dec); ^{1}H NMR (CD_3CN) δ 2.25 (m, 8 H), 2.88 (m, 8 H), 4.42 (m, 8 H), 4.43 (t, 2 H), 7.00 (d, 4 H), 7.75 (m, 8 H), 7.92 (dd, 4 H), 8.15 (dd, 4 H).

Anal. Calcd for $C_{50}H_{46}N_4S_4P_4F_{24}\cdot 4H_2O$: C, 40.6; H, 3.7; N, 3.8. Found: C, 40.6; H, 3.3; N, 3.7.

Dimer of Dye 7. Yield 43%; mp >145 °C (dec); ^{1}H NMR is complex, indicating the presence of several isomers.

Anal. Calcd for $C_{48}H_{50}N_4S_4P_4F_{24}\cdot 2H_2O$: C, 40.4; H, 3.8; N, 3.9. Found: C, 40.2; H, 3.7; N, 3.9.

Dimer of Dye 8. Yield 64%, mp >190 °C (dec); ^{1}H NMR (CD_3CN) δ 3.42 (t, 8 H), 4.20 (t, 2 H), 5.02 (t, 8 H), 7.18 (d, 4 H), 7.95 (t, 4 H), 8.20 (m, 16 H), 8.92 (d, 4 H).

Anal. Calcd for $C_{54}H_{46}N_4P_4F_{24}\cdot H_2O$: C, 48.0; H, 3.6; N, 4.2. Found: C, 48.1; H, 3.6; N, 4.2.

Dimer of Dye 9. Yield 54%; mp 140–145 °C (dec); field desorption mass spectrum, *m/e* 538 ($M(PF_6)_2^{2+}$); ^{1}H NMR is complex, indicating the presence of several isomers.

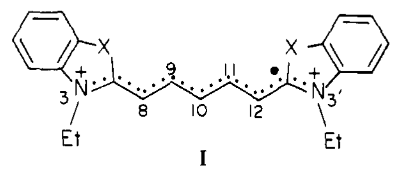
Anal. Calcd for $C_{56}H_{58}N_4P_4F_{24}\cdot 2H_2O$: C, 47.9; H, 4.4; N, 4.0. Found: C, 47.5; H, 4.2; N, 3.9.

Dimer of Dye 13. Yield 74%; mp >120 °C (dec).

Anal. Calcd for $C_{72}H_{66}N_4S_4\cdot 4PF_6$: C, 51.0; H, 3.9; N, 3.3. Found: C, 50.8; H, 4.2; N, 3.7.

Results and Discussion

The one-electron oxidation of a cationic dicarbocyanine dye initially generates the corresponding radical dication I. The odd electron is delocalized between the two equivalent nitrogen atoms and is presumed to reside principally at the even-numbered carbon atoms 8, 10, and 12 of the pentamethine chain. This alternation of spin density in the dicarbocyanine radical ion is extrapolated from the ESR results of Oehling and Baer obtained for cyanine (monomethine) and carbocyanine (trimethine) dyes.[9] Their results indicate the odd electron to predominate at the even-numbered methine carbons. These assigned positions of high radical density are consistent with the relative distribution of π-electron densities in the highest occupied molecular orbital of the parent dye in its ground state.



I

X= S , –CH=CH–

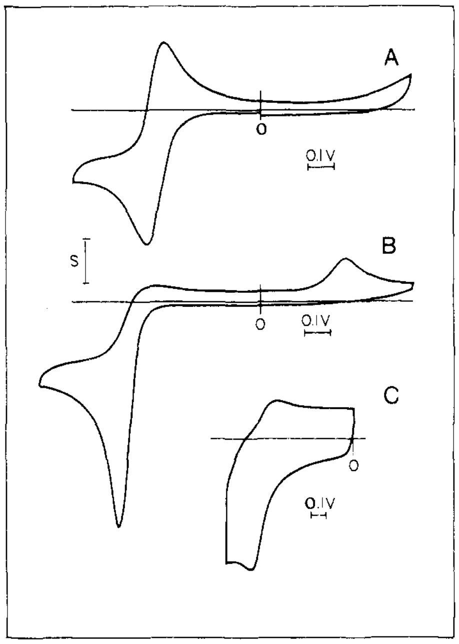


Figure 1. Cyclic voltammograms for dicarbocyanine dyes in $CH_3CN/0.1$ M $TBABF_4$: (A) 0.33 mM dye **1**, $v = 0.1$ V/s, $S = 50\ \mu A/cm^2$; (B) 0.50 mM dye **7**, $v = 0.1$ V/s, $S = 50\ \mu A/cm^2$; (C) 0.50 mM dye **7**, $v = 200$ V/s.

The reversibility of the cyclic voltammograms obtained for dicarbocyanine dyes in acetonitrile solution is dependent on the nature of substitution incorporated within the polymethine chain. Figure 1 compares cyclic voltammetry results obtained under conditions of slow potential scan for the oxidation of two related thiadicarbocyanine dyes. Structures for these and other variously substituted dicarbocyanines derived from benzothiazole and 2-quinoline nuclei are presented in Table I. As exemplified by the data obtained for dye **1** (curve A, Figure 1), dyes containing sufficient alkyl substitution within the pentamethine chain to electronically stabilize the radical dication and/or sterically inhibit dimerization exhibit reversible cyclic voltammetry. Dyes **1–4** of Table I, which contain alkyl substituents at methine carbons 8, 10, and 12 or have three alkylene bridges, yield reversible (chemically and electrochemically) voltammograms for potential scan rates ranging from 20 mV/s to 20 V/s.[10]

In contrast, dyes **5–9**, which have one or more unsubstituted or sterically accessible even-methine carbon atoms, exhibit chemically irreversible, one-electron voltammograms in acetonitrile as illustrated by Figure 1, curve B. This behavior is consistent with rapid dimerization (radical–radical coupling) of the corresponding radical dications. A cathodic wave for the reduction of the stable dimeric product is typically observed in the potential range −0.4 V to −0.7 V. Irreversible cyclic voltammograms were also obtained for dyes **5–9** in experiments using potential scan rates ranging from 20 mV/s to 2 V/s. At higher scan rates, the radical–radical coupling reaction can be partially outrun for some dyes, and cathodic current for the reduction of the dication can

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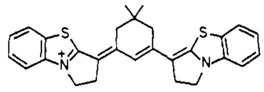
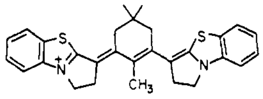
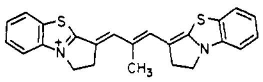
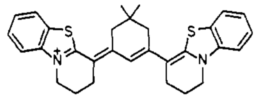
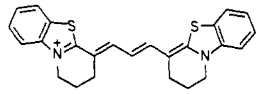
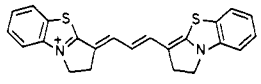
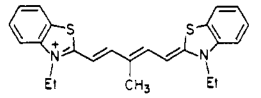
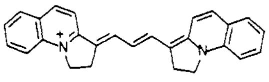
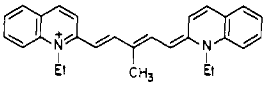
(9) Oehling, H.; Baer, F. *Org. Magn. Reson.* **1977**, *9*, 465.

(10) The difference between the anodic and cathodic peak potentials is 59 mV, except at potential sweep rates higher than 1 V/s, where uncompensated resistance broadens the voltammetric waves.

Table I. Thermodynamic Parameters for Dicarbocyanine Radical/Dimer Equilibria in Acetonitrile

dye no.	structure	$K_d \times 10^7$, M (10 °C)	ΔH, kcal/mol	ΔS, cal/(mol deg)	ΔG(20 °C), kcal/mol
1		350	12.2	22.5	5.6
2		450	12.4	23.8	7.0
3		130			
4		111 (−5 °C)			6.1
5		10.5	16.8	32.0	7.4
6		7.0	16.4	29.8	7.7
7		10.4 (20 °C)			8.0
8		0.3	15.9	21.4	9.6
9		0.1			10.1

be observed (curve C). The second-order rate constant for the dimerization of cyanine radical dications in acetonitrile (~22 °C) has previously[6] been estimated from electrochemical potential data to be about 10^6 M^{-1} s^{-1}. Cyclic voltammetric data for the dyes of Table I and their oxidation products are listed in Table II.

Controlled-potential coulometry experiments performed with dyes **1**–**4** gave results that are consistent with formation of a persistent radical dication. Figure 2 shows, for example, absorption spectra of a 5.8 μM solution of the triply bridged thiadicarbocyanine dye **1** obtained before and after exhaustive one-electron oxidation at +0.7 V vs. Ag/AgCl. The radical dication of dye **1** exhibits an absorption maximum at 498 nm in acetonitrile and a molar extinction coefficient ϵ of 1.25×10^5 M^{-1} cm^{-1}. An additional but relatively weak absorption band is also observed (but not shown here) at 872 nm ($\epsilon \sim 1 \times 10^3$). Immediate reduction of this solution at +0.2 V regenerates ~95% of the parent dye (λ_{max} = 667 nm, $\epsilon_{max} = 2.4 \times 10^5$ M^{-1} cm^{-1}). A 10^{-4} M solution of electrogenerated radical dication of dye **1** gave a stable but unresolved ESR signal (g = 2.003). The radical dication of dye **1** has a half-life (at 22 °C) of about 3 h in purified acetonitrile. Dyes **2**–**4** were found to behave similarly during coulometric analysis; however, differences in the long-term stability of the various radical dications are apparent. Solutions of radical dication can also be prepared by chemical oxidation using $FeCl_3$ or $AgNO_3$.

Absorption spectra obtained from an electrooxidized solution of dye **6** are also shown in Figure 2. Dye **6** is similar in structure to dye **1** in its substitution at methine positions 8 and 12 but differs in the lack of the central neopentylene bridge. Relative to the corresponding data for dye **1** (i.e., curve B), there is increased absorption at 330 nm and evidence of only trace amounts of radical dication at 500 nm for the solution of oxidized dye **6**. Although irreversible on the cyclic voltammetric time scale, the dimerization of dye **6** radical dication is reversible in coulometric analysis. Electroreduction of the solution of Figure 2, curve D, at +0.1 V, a potential capable of reducing the trace radical ion present but not sufficient to directly reduce the dimer, results in nearly *complete regeneration* of curve C. The regeneration of dye **6** is confirmed by voltammetric examination of the electrolysis solutions.

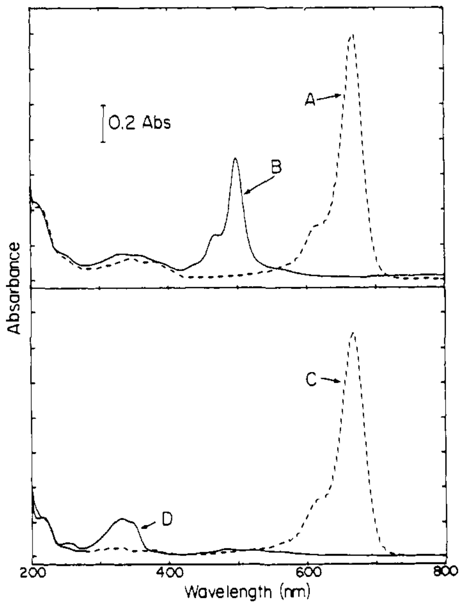


Figure 2. Absorption spectra obtained at 22 °C for dicarbocyanine dyes in $CH_3CN/TBABF_4$: 5.8 μM dye **1** before (A) and after (B) exhaustive electrolysis at 0.7 V; 5.1 μM dye **6** before (C) and after (D) electrolysis at 0.7 V.

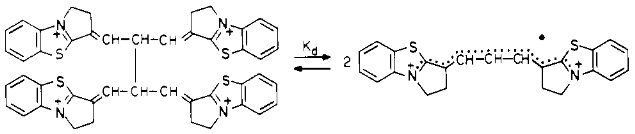
Chemical oxidation of dye **6** was performed at room temperature by treating a methanol solution of the dye with aqueous ferric

Table II. Electrochemical and Spectral Data for Dicarbocyanine Dyes, Radical Dications, and Dimers in Acetonitrile[a]

compd	E_{ox}, V	E_{red}, V	cyclic voltammetry[b]	λ_{max}, nm	$\epsilon_{max} \times 10^{-5}$, M^{-1} cm^{-1}
dye **1**	0.425	−1.090	rev	668	2.40
radical **1**				498	1.25
dimer **1**			irr	344	0.80[c]
dye **2**			rev	666	1.92
radical **2**				499	0.96
dimer **2**			irr	334	0.80[c]
dye **3**	0.34	−1.08	rev	674	2.00
radical **3**				489	1.00[c]
dimer **3**			irr	342	0.8[c]
dye **4**	0.493	−1.00	rev	672	1.65
radical **4**				512	0.83
dimer **4**			irr	350	0.80[c]
dye **5**	0.520	−0.985	irr	663	2.05
radical **5**				494	1.02[c]
dimer **5**		−0.36	irr	336	0.86
dye **6**	0.43	−1.0	irr	666	2.50
radical **6**				480	1.20[c]
dimer **6**		−0.52	irr	335	0.88
dye **7**	0.613	−0.929	irr	647	2.42
radical **7**				490	1.20[c]
dimer **7**		−0.37	irr	342	0.85[c]
dye **8**	0.290		irr	751	1.85
radical **8**				492	0.92[c]
dimer **8**		−0.54	irr	361	0.88
dye **9**	0.478	−0.927	irr	705	2.11
radical **9**				488	1.05[c]
dimer **9**		−0.42	irr	369	0.93

[a] Redox potentials for dyes and dimers were measured by second-harmonic ac voltammetry and by cyclic voltammetry (v = 0.1 V/s), respectively, and are reported vs. Ag/AgCl. [b] Cyclic voltammogram recorded for each at 0.1 V/s designated as reversible (rev) or irreversible (irr). [c] Estimated value.

Scheme I



chloride. The oxidation product was isolated in high yield by counterion exchange precipitation and found to be a covalently bonded, tetracationic dimer resulting from radical–radical coupling. The site of dimerization was determined by NMR spectroscopy to be the central carbon (10 position) of the pentamethine chain. Particularly indicative of coupling at the 10,10′ positions for the dimers of dyes **5**, **6**, and **8** is the simplicity of the NMR spectra due to symmetry. In each case the central methine protons are equivalent and appear as a triplet in the region δ 4.0–4.4. They are coupled to the adjacent vinyl protons, which appear as a doublet in the region δ 6.9–7.2.

The electrochemical reduction potential and UV absorption spectrum for the purified dimer in acetonitrile are identical with that generated during controlled-potential electrolysis of the parent dye.

In acetonitrile the tetracationic dimer of dye **6** (λ_{max} = 330 nm) reversibly dissociates and rapidly establishes an equilibrium with the radical dication (λ_{max} = 480 nm). UV–vis spectra and ESR data were both found to be a function of concentration and temperature. UV–vis absorption spectra recorded for a 10^{-5} M solution of dye **6** dimer at various temperatures are displayed in Figure 3.

The radical/dimer equilibrium may be expressed as a dissociation process as in Scheme I, where the dissociation constant, K_d = [radical]^2/[dimer], can be calculated from spectral data. At 20 °C, $K_d = 1.89 \times 10^{-6}$ M, from which ΔG, the free energy of dissociation, is calculated to be 7.68 kcal/mol. A plot of the dissociation constants extracted from the data of Figure 3 vs. $1/T$ is linear over the range 0–60 °C (correlation coefficient = 0.9986). The slope of this plot corresponds to a carbon–carbon bond enthalpy of 16.4 kcal/mol. The entropy change due to dissociation of the dimer according to Scheme I, obtained from the intercept, is 29.8 cal K^{-1} mol^{-1}.

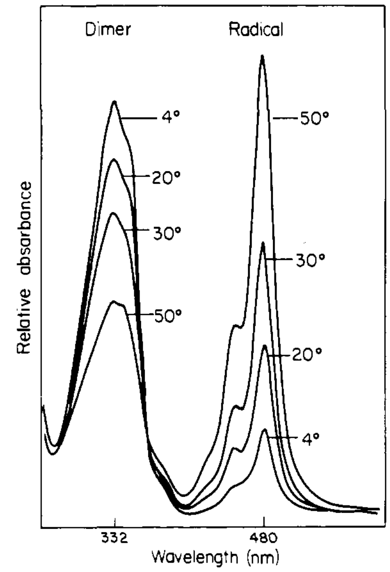


Figure 3. Absorption spectra of an equilibrium mixture of dimer and radical dication for dicarbocyanine **6** as a function of temperature.

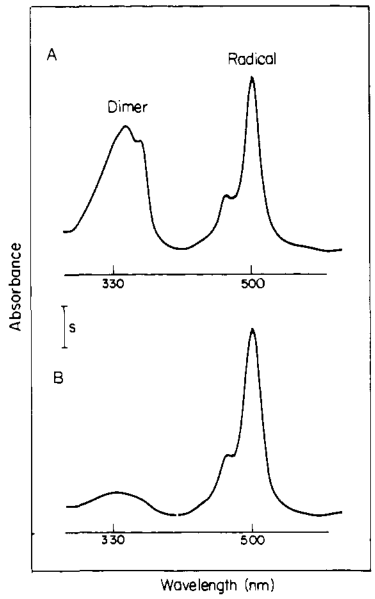


Figure 4. Absorption spectra for a 41 μM solution of electrogenerated dye **1** radical dication in $CH_3CN/TBABF_4$: (A) T = 3 °C, S = 0.1 Abs; (B) T = 38 °C, S = 0.2 Abs.

Interestingly, the absorption spectra for electrochemically prepared dye **1** radical dication solutions were also found to be temperature dependent. Although the dimeric product is not readily isolated, clear evidence for reversible dimerization of this highly substituted thiadicarbocyanine radical is seen in low-temperature spectra (Figure 4). By analogy to dye **6**, the absorption band at 330 nm of Figure 4 can be assigned to the methine-bridged dimer of dye **1**. Relative to the case of dye **6**, however, the position of the dimerization equilibrium strongly favors the radical dication form at room temperature, apparently because of increased steric strain in the dimer. The carbon–carbon bond energy in dimeric **1**, as calculated from a plot of −ln K_d vs. $1/T$, is correspondingly smaller (by 4.2 kcal/mol) than that determined for dye **6** dimer.[11]

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[11] The radical dications also exhibit some absorption in the wavelength range 310–350 nm. The dimer absorption data used for the equilibrium calculations of Table I include a correction for spectral absorption due to the radical.

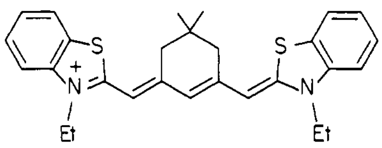
Radical dications derived from the remaining dyes of Table I also undergo reversible dimerizations as in Scheme I. NMR analysis indicates dimerization proceeds at the central methine position for dyes **5**, **6**, and **8**; however, a mixture of the 8–8′, 8–10′, and 10–10′ isomers for dyes **7** and **9** is suggested by the complexity of the NMR spectra obtained for these dimers. NMR data could not be obtained for the dimers of dyes **1–4**. Dimer dissociation constants obtained from equilibrium concentrations at 10 °C are listed in Table I together with available thermodynamic data. Radical/dimer solutions for dyes **5–9** were prepared by dissolution of the solid dimer in neat CH_3CN. Dyes **1–4** were not isolable in the dimeric state; thus appropriate solutions were prepared by electrolysis in CH_3CN containing 0.1 M $TBABF_4$. Since the presence of the electrolyte shifts the equilibrium in favor of the dimer form, the data for dyes **1–4** in Table I should be considered as an upper limit for comparison purposes.[12] For some dyes, competing modes of (irreversible) radical dication consumption become important near and above room temperature, causing ΔH to vary over the experimental temperature range. Values for reaction enthalpy and entropy are omitted in these cases. Data for all dyes were experimentally obtained during warming of the freshly prepared radical/dimer sample in order to minimize the involvement of these irreversible side reactions. Spectral and electrochemical data for the dyes, radical dications, and their respective dimeric products are listed in Table II.[13]

The dyes of Table I are listed roughly in order of decreasing value of the dimer dissociation constant, K_d. Reaction free energies, ΔG, obtained at 20 °C, range from 5.6 to 10.1 kcal/mol. The respective dimer C–C bond enthalpies are seen to vary from 12.2 to 16.8 kcal/mol, whereas values for the entropy of dimer dissociation are grouped near 22 and 32 eu.

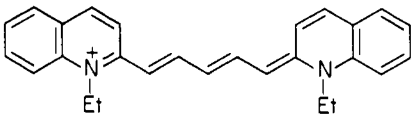
The thermodynamics of dimerization should depend on the relative magnitudes of the energy gain arising from the C–C bond formation and of the π-electron delocalization energy loss that results from a reduction of the conjugated system.[14] The data of Table I clearly demonstrate that steric factors play a major role in determining C–C bonds energies in these methine-linked dicarbocyanine derivatives. In general, structurally crowded cyanine radicals (dyes **1–4**) are resistant to dimerization, have the weaker C–C dimer bond energies, and exhibit dimer dissociation equilibria that favor the radical dication over the dimer form in 10^{-5} M (total dimer + radical concentration) solutions at room temperature. Conversely, for less substituted radicals, such as those containing a simple (and unobstructing) 10-methyl substituent, the dimeric state is seen to predominate. The data of Table I also indicate distinct differences in the dimer equilibria between thia- and quinodicarbocyanine radical dications.[15] Electrochemical data qualitatively show that the rates of dimerization of the thiadicarbocyanines are similar to those for the analogous quinodicarbocyanine radicals; however, the observed rates of dimer dissociation for the latter class are much smaller. The comparatively small values of the quinodicarbocyanine equilibrium constants K_d are largely a reflection of this slow rate of dimer dissociation.

Although there have been a number of reported examples of sterically hindered molecules that undergo facile and reversible C–C bond cleavage, the majority of investigations have involved the coupling of neutral free-radical species, the triphenylmethane and hexakis(alkylthio)ethanes being most notable.[16-20] The values for the reaction free energy, enthalpy, and entropy of dimer/radical dissociation presented here are similar to the corresponding values determined for the triphenylmethanes, but are remarkably small in comparison to the ethane C–C bond energy of 80 kcal/mol. Despite the recent activity in this general area, examples of electrochemically active compounds that undergo reversible dimerization remain rare. Rate and equilibrium constants have been reported for the dimerization of neutral pyridinyl,[21] pyranyl,[22,23] and phenoxyl radicals,[24] thioether cation radicals,[25] and 9-cyanoanthracene anion radical.[26] This paper provides thermodynamic information that is fundamentally important toward understanding the details of dimerization for organic redox systems.

Evaluation of the electrochemical properties of a large number of cyanine dyes, including dyes of various methine chain lengths, indicates that steric-hindrance factors alone do not provide for dissociation of covalently linked dicarbocyanines. Extensive delocalization of the odd electron and electronic stabilization of the radical dication by alkyl substitution at the even-numbered methine carbons seem necessary for achieving reversibility in the radical coupling reaction. For radical dications derived from unsubstituted dicarbocyanines or from dyes that contain alkyl substituents or hydrocarbon ring systems exclusively at the *odd-numbered positions* of the pentamethine chain, the dimerization reaction was found to be totally irreversible.[27] Dyes **10** and **11** are examples of dicarbocyanines whose radical dications undergo an irreversible radical–radical coupling reaction. Further details concerning the oxidation chemistry of unsubstituted dicarbocyanines will be presented in a separate report.[28]



Dye 10



Dye 11

Through appropriate modification of the parent-dye molecular structure the dimerization of dicarbocyanine radicals can be

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[12] The addition of $TBABF_4$ to dilute radical/dimer mixtures for dyes **5–9** reduces the concentration of radical and increases the concentration of dimer. This shift in equilibrium is due presumably to a Debye–Hückel salt effect and not to ion pairing.

[13] Radical instability also prevents experimental determination of optical extinction coefficients for some. With few exceptions, the extinction of carbocyanine and dicarbocyanine radical dications is half that of their parent dyes. Accordingly, the radical dication extinctions could be estimated from data for the dye parent. The uncertainty in the equilibrium calculations is determined by the accuracy in dimer or radical extinction estimates.

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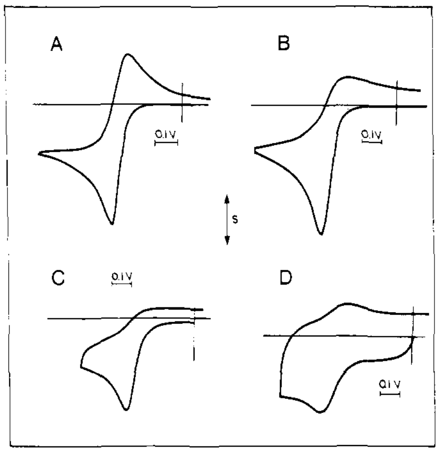
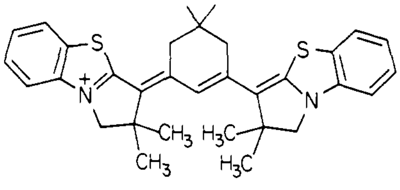


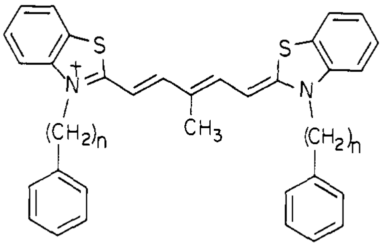
Figure 5. Effect of potential scan rate (v) on the cyclic voltammetric response for 0.6 mM dye **13** in CH_3CN/0.1 M $TBABF_4$. (A) v = 0.02 V/s, S = 40 μA/cm^2; (B) v = 0.2 V/s, S = 0.12 mA/cm^2; (C) v = 20 V/s, S = 1 mA/cm^2; (D) v = 500 V/s, S = 40 nA.

prevented. Alkyl substitution patterns that lead to excessive congestion about the central methine carbon are particularly effective. In the case of dye **12**, for example, the presence of the C–C neopentylene and N–C isobutylene bridges sterically precludes the critical approach necessary for carbon–carbon bond formation between radical ions. Solutions of dye **12** that were subjected to exhaustive one-electron oxidation exhibit UV–vis absorption spectra showing the presence of radical dication (λ_{max} = 496 nm) but no detectable UV-absorbing dimer. That neither the absorption spectrum nor an associated ESR spectrum was found to be temperature dependent is consistent with the radical ion being unable to dimerize. ESR spectra obtained for 10^{-4} M solutions of dye **12** radical in acetonitrile were broad and featureless as was found for dye **1** radical dication.



Dye 12

In addition to the steric interactions noted above for substitutions involving the pentamethine chain, dramatic effects have been obtained by incorporating bulky substituents in the N–alkyl segments of unbridged dicarbocyanine radicals. For N,N'-diphenylalkyl analogues of 10-methyl-substituted dyes **7** and **9**, the dimer dissociation reaction exhibits a peculiar dependence on the length of the N-alkyl chain. The effects on dye electrochemical properties are illustrated by the data of Figure 5, which shows cyclic voltammetry for N,N'-diphenethyl-10-methylthiadicarbocyanine (dye **13**) recorded at several different potential sweep rates.



Dye 13, n = 2
Dye 14, n = 1
Dye 15, n = 3

If the potential scan rate is kept lower than 0.02 V/s (curve A), a reversible cyclic voltammogram is obtained and the ratio of the anodic to cathodic peak currents is near unity. In this experimental time frame the rate of dimer dissociation can keep pace with the rate of radical reduction occurring at the electrode surface. As the potential scan becomes faster, these rates diverge and the peak current ratio decreases until at 20 V/s (curve C) a voltammetric waveform consistent with total (chemical) irreversibility is obtained. At the fastest scan rates employed, a reduction peak for the transient radical dication was observed and the ratio of anodic to cathodic peak currents again increases, indicating that the radical–radical coupling reaction has been partially outrun. Our experiments did not allow for sweep rates sufficiently fast to entirely outrun dimer formation to obtain a completely reversible voltammetric wave. The data of Figure 5 are fully consistent with the digital simulation results of Evans et al. for a reversible dimerization reaction.[24b]

Interestingly, the N-benzyl and N-(phenylpropyl) analogues of dye **13** (dyes **14** and **15**, respectively) yield cyclic voltammograms at scan rates of 500 and 20 V/s that are very similar to those of curves C and D of Figure 5. However, reversibility was not reestablished at slow potential scan rates as was seen for dye **13**. Irreversible cyclic voltammograms (like curve C, Figure 5) were obtained for both dyes at all potential scan rates lower than 20 V/s. In effect, the electrochemical behavior of dyes **14** and **15** is nearly identical with that of the N,N'-diethyl analogue, dye **9**.

The similarity of the fast-scan cyclic voltammetric results obtained for dyes **13–15** indicates, albeit qualitatively, that the rates of dimerization of the respective radical dications are nominally the same. On the other hand, the rates of dimer dissociation, as diagnosed by the slow-scan rate data, differ substantially. If these differences were the result of steric congestion at the methine carbons by the pendant N-(phenylalkyl) groups, then the respective dimerization constants and the observed trend in the electrochemical properties would be expected to progress regularly with the length of the N-alkyl chain. Molecular models show that in none of the respective dimers does the phenyl fragment cause steric strain nor is it apparent that the phenyl group interferes with radical–radical coupling. Space-filling models do reveal, however, that the phenyl groups in dye **13** are optimally located for overlap with the methine π-system. This interaction is precluded in dye **14** by the short N-alkyl chain, whereas for the phenylpropyl analogue, dye **15**, the extended length of the chain allows for many other possible configurations making such an interaction (entropically) less favorable. The unusual electrochemical properties of dye **13** are thus attributed not to steric hindrance but rather to a through-space stabilization of the radical dication by the N-phenethyl group.

Summary and Conclusion

Cationic dicarbocyanine dyes undergo monoelectronic oxidation at relatively low potentials to give the corresponding radical dications. In acetonitrile solution, these radical species are susceptible to dimerization at the even carbon atoms of the pentamethine chain. For dyes bearing one or more alkyl substituents at the even-methine positions, the dimerization reaction is found to be reversible. By virtue of the clean electrochemical response noted for the parent dicarbocyanine dyes and the exceptional optical characteristics of the radical, i.e., high extinction and favorable λ_{max}, quantitative information regarding dicarbocyanine radicals has been acquired by both electrochemical and spectroscopic methods. Both the individual rates of dimer formation and dissociation are found to be dependent upon the nature of the parent heterocycle as well as on the type and extent of substitution incorporated into the methine chain. Dimerization equilibrium constants are linearly related to inverse temperature, which allows calculation of the free enthalpy and entropy of reaction. The observed differences in the carbon–carbon bond strengths among various dicarbocyanine derivatives is related to the amount of steric strain in the respective dimer.

These alkyl-substituted dicarbocyanines represent a unique addition to the elite list of electrochemically active compounds that undergo reversible dimerization. It remains to be seen how general a phenomenon this is among homologous cyanine dyes.

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