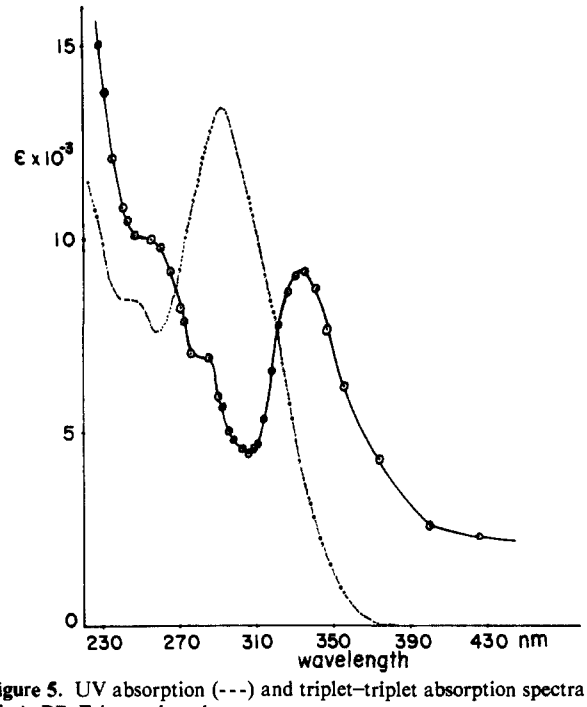

Figure 5. UV absorption (---) and triplet–triplet absorption spectra (⊙) of *cis*-BPyE in methanol.

but they could not observe $^nT \leftarrow {}^1T$ absorption in fluid solution at room temperature. However, we observed strong $^nT \leftarrow {}^1T$ absorption for *trans*- and *cis*-BPyE in the fluid solution at room temperature just like in the nitro-substituted stilbenes.[39,40] in which nitro groups enhance the rate of the intersystem crossing. Nitroarmatics very often show only phosphorescence and no fluorescence. In the presence of nitro substituents, the intersystem crossing is enhanced to such a degree that triplet states are populated. Intersystem crossing enhancement is entirely associated with the participation of (n,π^*) states of nitro groups in the decay processes. The charge-transfer character of the excited states of nitro-substituted stilbenes does not seem to influence intersystem crossing, as indicated by *p*-cyano-*p'*-methoxystilbene which lacks a nitro group and shows much weaker triplet–triplet absorption at low temperatures.[40]

The transient species of stilbene generated by the flash photolysis in glassy matrices at 77 K have previously been identified as triplet states.[38,41] The transient spectra (difference absorption spectra) of *trans*-BPyE in nonpolar and polar solvents show a similar shape and absorption maximum (Figure 3) as shown in the nitro-substituted stilbenes.[39] The solvent shift of the transient absorption (triplet–triplet absorption) in nitro-substituted silbenes is unusually large and is accompanied by a change in the shape of the absorption spectra. In order to explain the solvent shift, Fischer and co-workers[42] assumed that the lowest triplet state for the nitro-substituted stilbenes changes from $^3(n,\pi^*)$ to $^3(\pi,\pi^*)$ in character as the solvent polarity increases. In BPyE flash photolysis, the triplet–triplet absorption maxima are blue-shifted as the polarity of the medium increases (Figure 4 and Table VI). The triplet–triplet absorption spectra also show fine structure and the shape of the spectra changes (Figure 4) as the medium is changed from *n*-hexane to methanol. These effects may be due to the increase of the energy gap between $^3(n,\pi^*)$ and lowest $^3(\pi,\pi^*)$ as the polarity of the medium increases in contrast to nitro-substituted stilbenes.

From these results, it is concluded that the transient of BPyE is a triplet state and direct trans ⇌ cis photoisomerization of BPyE proceeds through the triplet excited state in contrast to stilbene.

Conclusions

Photochemical trans ⇌ cis isomerization of BPyE which has both the (n,π^*) state and (π,π^*) state on direct excitation is strongly affected by the polarity of solvents. Intersystem crossing is enhanced because the $^1(\pi,\pi^*)$ state and the lowest $^1(n,\pi^*)$ state are extensively mixed as the polarity of solvents increases. Azulene quenching on the photoisomerization and nanosecond laser spectroscopy results also indicate an efficient intersystem crossing on direct excitation of BPyE in contrast to stilbene and their aza analogues. It is therefore concluded that the photoisomerization of BPyE on direct excitation occurs from the triplet excited state in contrast to stilbene.

Acknowledgment. This investigation was supported by the Korea Science and Engineering Foundation. We are grateful to Prof. Jack Saltiel of Florida State University for many helpful discussions.

Registry No. *trans*-BPyE, 62141-47-3.

(39) Bent, D. V.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1974**, *78*, 446.
(40) Goerner, H.; Schulte-Frohlinde, D. *Ber. Bunsenges Phys. Chem.* **1978**, *82*, 1102.
(41) Heinrich, G.; Blume, H.; Schulte-Frohlinde, D. *Tetrahedron Lett.* **1967**, *47*, 4693.
(42) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 3907.
(43) Nakashima, N.; Yoshihara, K. *J. Chem. Phys.* **1982**, *77*, 6040.

Stereoselectivity in the Photolysis of Diastereomeric Diazene Surfactants in Aggregated Media[1]

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Abstract: *meso*- and (±)-bis(cyanododecanoyl)diazene free diacids and their dimethyl esters have been photolyzed in chlorobenzene solution, in water above and below their cmc's, and in bilayer vesicles with dipalmitoylphosphatidylcholines. In water above the cmc and in chlorobenzene there is sharply differentiated stereoselectivity in the product ratios of the free diacid diastereomers, the (±) always giving the greater retention. The (±) diastereomer also shows the greater driving force toward aggregation in micelles and in monolayers where its surface properties are dramatically different from those of the meso isomer. A simple explanation is proposed to relate the aggregation properties to the stereochemistry. The possible broad significance of these results to biochemistry is suggested.

Many important biological processes are stereoselective and take place at the interfaces of aggregated assemblies such as membranes, lipid bilayers, or organelles rather than in isotropic media. Considering that form and function are usually correlated

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at both the molecular and biological levels, it is reasonable that chiral interfaces should be important to biochemistry. However, there have been remarkably few studies aimed deliberately at elucidating the effects of aggregation on the physical and stereochemical properties of chiral molecules. Recent reports from this laboratory have reviewed the sparse literature on chiral surfactants when spread as monolayers at the air–liquid interface.[2-6] A few studies of chiral surfactants as enzyme models in micelles and reversed micelles have also been reviewed.[7-11] However, we know of no case where the stereochemical outcome of a simple reaction has been examined in a variety of aggregated and isotropic media.

This article presents the first example known to us of such a study using the meso (I) and (±) (II) diastereomers of a two-chain diazene surfactant analogue of the familiar free radical initiator AIBN. The results are significant for their relevance to (a) our recent report[1] of stereoselective thermal and photochemical decomposition in phospholipid vesicles of these diastereomers and (b) the notion that interfacial physical properties of diastereomeric surfactants may be differentiated sharply in monolayers and micelles—a reasonable expectation, but one with virtually no precedent.

Radical pairs generated by decomposition of chiral initiators normally lose their relative stereochemistry in homogeneous solution. However, when constrained within the environment of vesicles made by mixing and sonicating I or II with dipalmitoylphosphatidylcholine (DPPC), diastereomeric excesses (de) as high as 70% were found for the radical coupling products compared to de's of only 2–7% for the decomposition of the dimethyl esters of I and II in chlorobenzene solution.[1] In order to explore the effects of aggregation on radical pair diastereoselectivity, we have extended these studies to two other kinds of organized assemblies—micelles in aqueous buffer at pH 10 and monolayers at the air–water interface.

Experimental Section

Materials. Water was purified by reverse osmosis (Milli-R04, Millipore) followed by deionization (Milli-Q, Millipore), after which it was doubly distilled from alkaline permanganate and sulfuric acid. Hexane (Fisher, Spectrograde) was distilled from molecular sieves and chromatographed through silica gel (Davidson, 100–200 mesh) and basic alumina (Woelm, activity grade 1). Absolute ethanol (Aaper Alcohol and Chemical Co.) was distilled from magnesium ethoxide. Sulfuric acid (MCB, ACS reagent) was distilled before use. Fisher pH 7 and pH 10 buffers were used for photolysis experiments and cmc determinations as supplied. Chlorobenzene was purified by washing with water, saturated $NaHCO_3$ (aqueous) and H_2SO_4 (concentrated). It was then dried with Na_2SO_4 and distilled from barium oxide. Diazenes I and II were prepared as previously described and were purified (>99%) by C-18 reversed-phase HPLC. Large-scale separations (200–300 mg) were achieved with a Dynamax Macro C-18 Column (Rainin) at 9 mL/min; 70:30:0.2 CH_3CN:H_2O:HOAc. The *meso*-diazene elutes first on reverse-phase HPLC.

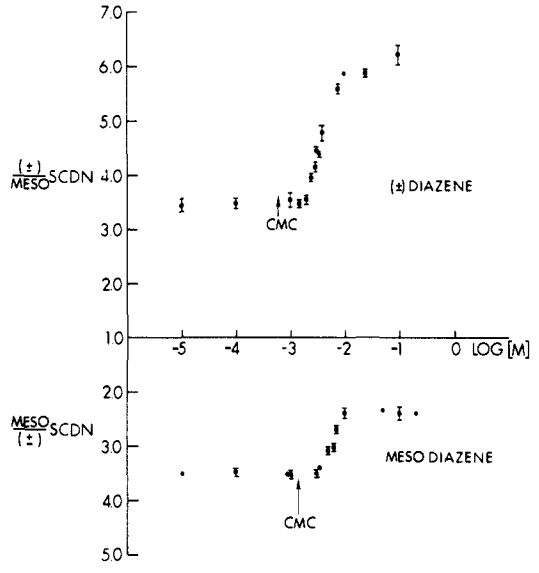
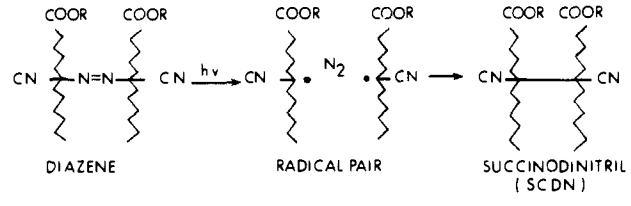


Figure 1. Product ratio or *meso*- and (±)-succinodinitriles formed from photolysis of I or II at 22 °C.

Scheme I



Monolayer and cmc Measurements. Pressure–area isotherms were acquired on an automated, Langmuir-type film balance described elsewhere.[2] The resulting data were recorded by both an analog strip chart recorder and a microcomputer-based data acquisition system. The surfactant films were solvent cast from 9:1 hexanes/ethanol (v/v) solution (ca. 0.2 mg/mL). For each film, two compression–expansion cycles were collected with a compression rate of 15.5 $Å^2$ $molecule^{-1}$ min^{-1}. Air and subphase temperatures were regulated at 22.0 ± 0.5 °C. Isotherms were collected on both an air-equilibrated, pure water subphase (ca. pH 5.5) and a dilute sulfuric acid subphase adjusted to pH 3.0. Surface potentials were recorded by using a Sargent-Welch pH 6000 electrometer equipped with a glass pH electrode and a ^{244}Cm ionizing electrode contained in a shielded enclosure.

Critical micelle concentrations were determined by the surface tension method using a DuNouy ring tensiometer (Cenco). Surfactant solutions were prepared by serial dilution using commercial pH 10 buffer (Fisher) without further purification. The surface was aged for 1 h at 22 ± 0.1 °C prior to each measurement.

Photodecomposition and Product Analysis. In a typical experiment, a known volume of a stock solution of I and II in $CHCl_3$ was added to a water-jacketed Pyrex reaction vessel. Chloroform was removed in vacuo, and a known volume of solvent was added along with a small magnetic stirbar. All aqueous solutions were checked under a microscope for homogeneity. The reaction vessel was kept at a constant temperature during photolysis by a circulating bath operating at 22 °C. Photolyses were generally carried out for 6–10-h periods with an OSRAM X80 900W/ORF lamp.

Workup of the product mixture was as follows: lauric acid in methanol (150 μL of a 3 mg/mL solution) was added to the reaction mixture, and for aqueous solvents the solution was made acidic with 1 M NH_4Cl and extracted several times with ether. The ether fraction was dried, and solvent was removed in vacuo. The residue was analyzed by suspending the material in 100 μL of 800:200:2 CH_3OH:H_2O:HOAc and injecting it onto an Ultrasphere-(ODS) 5-μm column (Altex). HPLC solvent was 800:200:2 CH_3OH:H_2O:HOAc. At 0.7 mL/min typical elution times are *meso*-SCDN = 40 min and (±)-SCDN = 51 min. Under these conditions, lauric acid, the internal standard, elutes in 74 min.

Results

Product Stereochemistry. Table I summarizes the product ratios of the diastereomeric succinodinitriles (SCDN) produced by photolysis of the diastereomeric bis(cyanododecanoyl)diazenes

(1) A preliminary communication of the results of decomposition of diazenes I and II in phospholipid vesicles has been published: Brittain, W. J.; Porter, N. A.; Krebs, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7652.
(2) Arnett, E. M.; Chao, J.; Kinzig, B. J.; Stewart, M. V.; Thompson, O.; Verbiar, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 389.
(3) Arnett, E. M.; Gold, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 636.
(4) Stewart, M. V.; Arnett, E. M. *Top. Stereochem.* **1982**, *13*, 195.
(5) Arnett, E. M.; Thompson, O. *J. Am. Chem. Soc.* **1981**, *103*, 968.
(6) Arnett, E. M.; Chao, J.; Kinzig, B.; Stewart, M.; Thompson, O. *J. Am. Chem. Soc.* **1978**, *100*, 5575.
(7) Fendler, J. H. "Membrane Mimetic Chemistry"; Wiley: New York, 1982.
(8) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975.
(9) O'Connor, C. J.; Lomax, T. D.; Ramage, R. E. *Adv. Colloid Interface Sci.* **1984**, *20*, 21.
(10) Magid, L. J. In "Reversed Micelles"; Luisi, P. L., Straub, B. E., Eds.; Plenum: New York, 1984; pp 181.
(11) Moss, R. A.; Chiang, Y.-C. P.; Hui, Y. *J. Am. Chem. Soc.* **1984**, *106*, 7506.
(12) Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867.

Table I. Diastereoselectivity of Diazene Photodecomposition[a]

solvent	concn, M	diazene	product ratio	de[b]	% yield[c]
pH 10 buffer	2.0×10^{-1}	meso diacid	meso/(±) = 2.40 ± 0.03	41	30
pH 10 buffer	1.0×10^{-1}	meso diacid	meso/(±) = 2.40 ± 0.13	41	30
pH 10 buffer	5.0×10^{-2}	meso diacid	meso/(±) = 2.32 ± 0.01	39	31
pH 10 buffer	1.0×10^{-2}	meso diacid	meso/(±) = 2.40 ± 0.08	41	32
pH 10 buffer	7.0×10^{-3}	meso diacid	meso/(±) = 2.69 ± 0.06	46	32
pH 10 buffer	6.0×10^{-3}	meso diacid	meso/(±) = 3.03 ± 0.04	50	33
pH 10 buffer	5.0×10^{-3}	meso diacid	meso/(±) = 3.08 ± 0.06	51	34
pH 10 buffer	3.5×10^{-3}	meso diacid	meso/(±) = 3.41 ± 0.01	55	29
pH 10 buffer	3.0×10^{-3}	meso diacid	meso/(±) = 3.50 ± 0.04	56	17
pH 10 buffer	1.0×10^{-3}	meso diacid	meso/(±) = 3.53 ± 0.03	56	
pH 10 buffer	9.0×10^{-4}	meso diacid	meso/(±) = 3.52 ± 0.02	56	
pH 10 buffer	1.0×10^{-4}	meso diacid	meso/(±) = 3.49 ± 0.03	56	
pH 10 buffer	1.0×10^{-1}	(±) diacid	(±)/meso = 6.20 ± 0.15	72	36
pH 10 buffer	2.5×10^{-2}	(±) diacid	(±)/meso = 5.82 ± 0.04	71	37
pH 10 buffer	1.0×10^{-2}	(±) diacid	(±)/meso = 5.85 ± 0.03	71	37
pH 10 buffer	4.0×10^{-3}	(±) diacid	(±)/meso = 4.81 ± 0.10	65	34
pH 10 buffer	3.5×10^{-3}	(±) diacid	(±)/meso = 4.45 ± 0.03	63	40
pH 10 buffer	3.4×10^{-3}	(±) diacid	(±)/meso = 4.44 ± 0.06	63	45
pH 10 buffer	3.0×10^{-3}	(±) diacid	(±)/meso = 4.14 ± 0.08	61	42
pH 10 buffer	2.5×10^{-3}	(±) diacid	(±)/meso = 4.00 ± 0.13	60	38
pH 10 buffer	2.0×10^{-3}	(±) diacid	(±)/meso = 3.52 ± 0.05	56	34
pH 10 buffer	1.5×10^{-3}	(±) diacid	(±)/meso = 3.45 ± 0.01	55	41
pH 10 buffer	1.0×10^{-3}	(±) diacid	(±)/meso = 3.55 ± 0.03	56	
pH 10 buffer	1.0×10^{-4}	(±) diacid	(±)/meso = 3.48 ± 0.07	55	
pH 10 buffer	1.0×10^{-5}	(±) diacid	(±)/meso = 3.45 ± 0.10	55	
DPPC emulsions[d]	5%[e]	meso diacid	meso/(±) = 2.32 ± 0.02	40	
DPPC emulsions[d]	5%[e]	(±) diacid	(±)/meso = 6.23 ± 0.65	72	
chlorobenzene	10^{-3}	meso-dimethyl ester	meso/(±) = 1.05 ± 0.10	3	
chlorobenzene	10^{-3}	(±)-dimethyl ester	(±)/meso = 1.16 ± 0.02	7	
chlorobenzene	10^{-3}	meso diacid	meso/(±) = 1.72 ± 0.03	26	26
chlorobenzene	10^{-3}	(±) diacid	(±)/meso = 5.78 ± 0.05	71	29

[a] 22 °C, unfiltered Hg–Xe lamp through Pyrex photolysis until all diazene was consumed. Products of photolysis are stable to the conditions of decomposition. All runs were run at least in duplicate. [b] Diastereomeric excess. [c] % yield of (±)- and *meso*-SCDN, HPLC analysis with lauric acid internal standard. The other major products formed are the diastereomeric peroxides where –N=N– of the diazene is replaced by –O–O–. [d] 10 mg of DPPC (dipalmitoylphosphatidylcholine) in 1 mL; pH 7 phosphate buffer. [e] % diazene to phospholipid. Experiments with lower concentrations of DPPC and diazene gave essentially the same results (i.e., below the cmc for both *meso*- and (±)-diazenes.

shown in various media. Even at high dilution in water, significant (ca. 3.5) diastereoselectivities are seen in the photolysis products from I and II. No diastereomeric interconversion of diazene was observed during photolysis.

We attribute this stereoselectivity from (presumably) monomeric diazenes to association of the intermediate radical pair with the solvent via the carboxylate head groups. This association reduces the mobility of the radicals and decreases the rate of processes which randomize radical-pair stereochemistry relative to the rate of radical coupling.

Figure 1 portrays the remarkable fact that *photolysis of micellar (±)-diazene gives increasingly higher retention of its original stereochemistry* (to give (±) products) as the concentration and the extent of micellization increases (vide infra). *In contrast, the meso compound loses the degree of retention* from about 3.5 in solutions below the cmc to about 2.5 in the more concentrated solutions above it. Roughly sigmoidal curves in both cases suggest saturation of the stereoselective processes in response to increasing concentration.

The significant observation from photolysis in water is the stereoselectivity of the process at all concentrations and the dramatic difference between the way the diastereomeric product ratio from photolysis of *meso*- and (±)-diazenes responds to increasing concentration above the cmc.

The results for photodecomposition of I and II contrast sharply to the loss of stereochemistry observed for decomposition of the dimethyl esters of I and II in chlorobenzene. This randomization of radicals is typical of pairs generated in organic solvents and reflects the ease of reorientation of one prochiral radical center to the other in nonviscous isotropic media.[13] The photochemistry of the free diacids of I and II in chlorobenzene solvent differs from that of the dimethyl esters, with the stereochemical outcome being

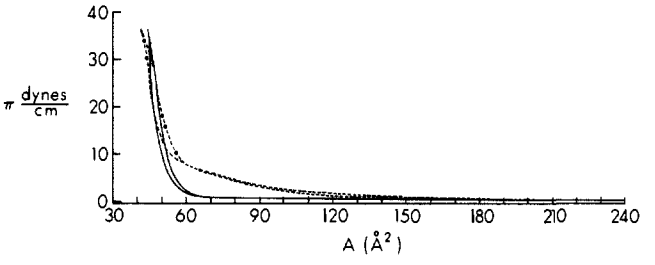


Figure 2. Pressure–area isotherm for (±)- and *meso*-diazenes on pure water subphase at 22.0 °C compressed at 15.5 Å^2 molecules^{-1} min^{-1}. Solid line for (±), dashed line for meso.

similar to the result obtained in aqueous media. Thus in chlorobenzene both (±) and meso diacids photolyze with significant stereoselectivity, the (±) diastereomer giving succinodinitrile products in higher diastereomeric excess than the *meso*-diazene precursor.

cmc Measurements. The lower cmc of (±)-diazene (6.0×10^{-4} M) compared to the meso diastereomer (1.3×10^{-3} M) is statistically significant based on three replica measurements with six or more points per determination and implies that intermolecular aggregation of II is considerably more facile than I (the free energy change for the monomer → micelle transition is more exergonic).

Monolayer Results. In the hope of comparing these results to those from photolysis in monolayers at the air–water interface, solutions of I and II were spread on water and photolyzed at 22 °C. Although this process was repeated 60–100 times and the photolyzed film recovered by aspiration, we were unable to retrieve enough material to provide suitable samples for HPLC analysis to allow definitive comparison with the micellar or vesicular results.

However, examination of the physical surface properties of the diastereomeric monolayers provides novel information about the intermolecular stereochemistry of packing in monolayers which

(13) Gaines, G. L. "Insoluble Monolayers at the Liquid-Gas Interface"; Interscience: New York, 1966.

Table II. Static Surface Potentials for Diazenes on Dilute Acid Subphase at 22.0 °C

area/molecule, Å^2 molecule^{-1}	surface potential, mV	
	(±)	meso
60	245.8 ± 9.4	199.1 ± 8.5
100	147.8 ± 8.6	121.7 ± 4.7
140	109.2 ± 5.7	76.8 ± 4.5
200	68.5 ± 2.5	51.5 ± 3.9

appears to be relevant to the stereochemical results of photolysis in vesicles and micelles.

Figure 2 compares the variation of surface pressure, π, in response to compression followed by expansion of monolayer films of I and II. Compression and expansion rates were 15.5 Å^2 molecule^{-1} min^{-1}, produced by movement of a Teflon barrier driven by a constant speed motor as described elsewhere.[2] No less than six replica π/A curves were run both on pure water and on 0.001 N aqueous H_2SO_4. No important differences were noticeable as a result of changing substrate pH. Although some hysteresis is detectable in the difference between the compression and expansion regimes in Figure 2, there was little difference between the appearance of π/A isotherms generated from repeated compression–expansion cycles of the films and those from the first such cycle other than an apparent loss of surfactant from the monolayer most likely due to film collapse.

The stabilities of the films were also tested by compressing them to various surface pressures, stopping the Teflon barrier, and watching for loss of pressure over a period of 1 min. By this test all films were stable at pressures up to 10 dynes/cm, but above that the (±) film showed a slightly greater instability than the meso up to a collapse pressure close to 30 dynes/cm.

Surface potential measures the charge separation created by the vector component of the surfactant's molecular dipole that is perpendicular to the air–water interface. Thus, the surface potential yields information about the interfacial orientation of the surfactant molecules. When variation of surface potential as a function of surface area was followed under compression, a dramatic difference between the films was seen. The (±) films showed abruptly varying potentials under the probe as the film was compressed, indicating "patchiness" as might be expected if separated islands of rigid film were passing under the probe.

When surface potentials were measured under static conditions, the results (Table II) indicate that those of the (±) molecules in the film are considerably higher at all surface areas than those of the meso diastereomers. Detailed interpretation of surface potentials is a dubious activity, especially for ionizable monolayers.[13] We shall go no further than to note that this property shows large differences between the films of the diastereomers, and the difference implies that the (±) film has a greater degree of orientation of the head groups relative to the surface than does its meso diastereomer. The final static surface potentials at 60 Å^2/molecule for both of these two-chain diazenes are in the normal range for single-chain fatty acids close to their limiting surface areas of 20–24 Å^2/molecule, where their hydrocarbon chains are packed perpendicular to the water surface, and suggests the same arrangement for the diazenes at the limiting area.

Several attempts to obtain quantitative comparisons of the film's viscosity by forcing them through a slit in the barrier[13] failed with our present equipment. However, a dramatic qualitative difference was found by floating a small Teflon disk on films which had been spread on the surfaces of clean samples of water in Petri dishes. The area per molecule was adjusted by the quantity of a dilute solution of the surfactant in 9:1 hexane:ethanol delivered to a dish of known area. A translational force was applied to the disk with a gentle jet of nitrogen blowing at a steady rate and at the same position with respect to the surface of the disk. Film pressures at each molecular area may be approximated from Figure 2.

This simple, but important, test of intermolecular forces in the films at various surface pressures and areas confirms yet again the stronger forces of aggregation in the (±) film. At 100 and 60 Å^2/molecule it is clearly nonhomogeneous, and at 45 Å^2/molecule it is very rigid in contrast to the meso film, which was relatively fluid at all these molecular areas as shown by smooth, free motion of the disk.

Discussion

We now can marshal an array of facts about the physical properties of these systems at various states of aggregation for correlation with the stereoselectivity of the photolysis products. It is important to realize at the outset that any interpretation of these results is necessarily ad hoc since there is no direct precedent for this investigation. While many studies of stereochemistry of diazene photolysis in isotropic media exist,[12,14,15] none of them have been carried through such a variety of aggregation states. Correspondingly, few stereochemical studies have been done in micelles or vesicles[16] and none in monolayers. However, the fact that we are comparing stereoisomers means that all other factors that affect inter- and intramolecular forces except shape and symmetry must cancel out and therefore simplify the discussion.

Stereochemistry. (1) In water at high dilution below the cmc, both diastereomers show the same significant retention of stereochemistry in their photolysis products—the original stereochemistry being preferred by a ratio of about 3.5:1.

(2) In water, above the cmc, the (±) isomer shows *steadily increasing* retention of stereochemistry leveling off at a factor of about 6:1 at the highest concentration. This is the same product ratio obtained from photolysis of this isomer in DPPC vesicles.[1]

(3) In water, above the cmc, the meso isomer shows *steadily decreasing* retention of stereochemistry. The product ratio, meso/(±), decreases from about 3.5 at high dilution to about 2 at high micelle concentrations. This is nearly the same meso/(±) ratio from photolysis of this isomer in DPPC.[1]

(4) For the dimethyl esters in chlorobenzene solution, there is no retention of stereochemistry. Both diastereomers give the same 1:1 mixture of meso and (±) products.

(5) For the free diacids in chlorobenzene solution both (±)- and *meso*-diazenes show significant stereoselectivity, with the (±) isomer leading to greater retention of stereochemistry.

Aggregation Properties. All properties related to intermolecular forces show that the (±) diastereomer molecules have a considerably higher driving force for aggregation than the meso. The (±) isomer has a lower cmc, a higher melting point, a tendency to form rigid, patchy monolayers of high surface viscosity, and a higher surface potential (meso mp 109–110 °C; (±) mp 115–116 °C).

Force/area curves show that the meso film is very highly expanded and resists compression even at a molecular area of 200 Å^2. In contrast, the (±) film exerts no pressure against the barrier until shortly before a limiting area of about 50 Å^2/molecule is reached, as though isolated patches of two-dimensional crystals were being gathered which only resisted compression when forced against each other. The high static surface potential for this isomer probably is that for perpendicular carbon chains based on analogy to stearic acid and other single chain fatty acids which have about half the limiting area per molecule as do these two-chain diazenes and about the same surface potential.

The Relation of Observed Stereochemistry to Aggregation. In chlorobenzene solution for the dimethyl esters little or no stereoselectivity is observed in the photolysis products from the diazenes. This means that there is no inherent intermolecular force which binds the radicals formed from expulsion of nitrogen so that they can couple with retained configuration before they escape the initial encounter.

For the free diacid diazenes in chlorobenzene, hydrogen bonding allows association of carboxylic acid head groups in both intramolecular pairing and intermolecular networks. The high stereoselectivity observed in chlorobenzene for the diacids shows unequivocally that (a) radical pair dynamics and the associated

(14) Kopecky, K. R.; Gillan, T. *Can. J. Chem.* **1969**, *47*, 2371.
(15) Koenig, T.; Owens, J. *J. Am. Chem. Soc.*, **1974**, *96*, 4052.
(16) Ueoka, R.; Moss, R. A.; Swarup, S.; Matsumoto, Y.; Strauss, G.; Murakami, Y. *J. Am. Chem. Soc.* **1985**, *107*, 2186.

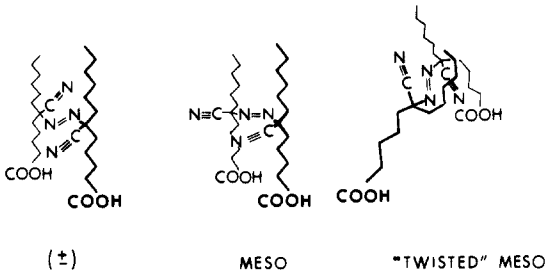


Figure 3. Possible conformations of (±)- and *meso*-diazenes.

stereoselectivity depend dramatically on the state of aggregation of the pair, and that (b) the (±)- and *meso*-diazene and the derivative radical pairs differ significantly in the nature of the aggregates that they form (in this case by carboxylic acid hydrogen bonding). These conclusions can be called upon to relate the sharply differentiated stereochemical results from photolyzing the diastereomeric diazenes in aqueous media to their sharply differentiated tendencies to aggregate. The following interpretation is the simplest we have considered that is sufficient to explain these facts.

At high dilution in water, two forces significantly reduce radical pair mobility compared to that of the pair generated from the methyl esters in chlorobenzene. Hydration of the carboxylate head group or hydrophobic attraction of the hydrocarbon chains of the diazene reduces the mobility of the radicals and enforces increased stereoselectivity in the coupling process. The carboxylate–hydration or hydrophobic association plays the same role here as carboxylate-pair hydrogen bonding plays in chlorobenzene.

As the concentration increases, hydrophobic binding forces begin to cause aggregation by intermolecular attraction. Micelle formation, like monolayer formation, involves an added degree of orientation since all, or most, of the acid head groups must be oriented toward the interface with water while the hydrocarbon chains are oriented more or less parallel to each other. These requirements immediately determine the conformations of both diastereomers and the orientation of their two cyano groups as shown in Figure 3. In the (±) isomer the cyano groups are placed symmetrically on opposite sides of the molecule, and there is nearly perfect C_2v symmetry around the vertical axis between the two hydrocarbon chains. It is arranged ideally for the extended intermolecular packing which it exhibits by its low cmc and rigid monolayer. Jaffe, Skinner, and McBride[17] have performed a single-crystal X-ray analysis of AIBN, the prototype diazene, and find it to be staggered in a S-shaped arrangement with the cyano dipoles trans to each other as in the proposed conformation of the (±)-diazene surfactant shown in Figure 3. This conformation, incidentally, allows a maximum anomeric interaction of the diazene nitrogen lone pairs and the adjacent carbon–cyano bonds.

The *meso*-diazene, on the other hand, cannot adopt an S conformation like the (±) diastereomer and still place the head groups at the same ends of parallel carbon chains. We present here two possible views of *meso*-diazene conformations in molecular aggregates or at the air–water interface. In the first, the meso compound adopts a conformation at the diazene linkage unlike the (±)-diazene S arrangement. This allows the carboxylate head groups to be placed at the ends of parallel chains and demands a conformation where the cyano groups are side by side with parallel dipoles. In the second possibility, the diazene linkage maintains the S arrangement and the carboxylate chains bend to bring both carboxylate groups to the micellar or air–water interface. This "twisted conformation" would result in increased gauche interactions in the carbon chains and would only be adopted if such interactions cost less energetically than what was gained from maintaining the presumably more stable S diazene conformation. While we cannot choose from these two possibilities from our data, we note that the twisted conformation for the meso compound would be consistent with the observation of significant surface pressure at very large areas per molecule in the monolayer. Furthermore, in chlorobenzene a differentiated hydrogen-bonding network for the (±) and meso free diacid diazenes would be expected if the diazene linkage maintained the S conformation.

As the (±) molecules are aggregated in DPPC or micelles they enjoy organizing forces which maintain their radicals in optimum position to retain their original orientation. The meso molecules on the other hand offer some resistance to orientation and aggregation and so are less tightly packed before photolysis and so more easily lose their stereochemistry after expulsion of nitrogen. Of course, in photolysis of both compounds, many radicals leak away from the optimum arrangement for stereoselective coupling to give randomized products.

Conclusion and Significance of These Results. These experiments show definitely that aggregated systems such as micelles, bilayer vesicles, and monolayers provide a milieu for retaining radical stereochemistry that is quite superior to that in isotropic solution. Since many stereoselective biochemical processes also occur in aggregated systems it seems likely that such "hydrophobically enforced" aggregation has survival value. Extensive studies[3] in our laboratories have shown that phosphatidylcholines, the principal lipid component in cell membranes, show remarkably little chiral discrimination but that other chiral molecules can retain their capacities for chiral recognition when mixed with phospholipids. In the present study, stereoselectivity was maintained in micelles and DPPC vesicles as though they provided a rigid or viscous medium in which the chirality of the diazene was maintained during photolysis so that the prochiral radicals produced were held in place before they coupled. We mention the well-studied enzyme cytochrome P-450 as an example of an analogy of this work in biology. It has been suggested that cytochrome P-450 produces radical pairs which couple with high stereoselectivity. The results of this study show that this is the expected result based on molecular aggregation or hydrophobic association of the radical pair.

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Registry No. *meso*-$HOOC(CH_2)_4C(CN)[(CH_2)_5Me]N{=}NC(CN)[(CH_2)_5Me](CH_2)_4COOH$, 86550-44-9; (±)-$HOOC(CH_2)_4C(CN)[(CH_2)_5Me]N{=}NC(CN)[(CH_2)_5Me](CH_2)_4COOH$, 86550-45-0.

(17) Jaffe, A. B.; Skinner, K. J.; McBride, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 8510.