cause of their extremely low acidity.

In summary, we have shown that amine elimination is an effective way to form direct early-late-transition-metal bonds under mild conditions. Formation of compounds with several early-late metal bonds and the reactivity of the early-late metal complexes are now under investigation.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Institute for Mining and Minerals Research (subgrant from the U.S. Bureau of Mines), and Ashland Oil for financial support and Engelhard Industries and Johnson-Matthey for generous loans of $RuCl_3$.

**Supplementary Material Available:** Listings of experimental and calculated structure factors (Table II) and positional and thermal parameters (Table III-V) (20 pages). Ordering information is given on any current masthead page.

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(19) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.)

## Effects of Molecular Organization on Photophysical Behavior. Excimer Kinetics and Diffusion of 1-Pyrenedecanoic Acid in Lipid Monolayers at the Nitrogen-Water Interface[1]

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*Received November 30, 1984*

Here we report the time resolved behavior of pyrenedecanoic acid excimers in spread phospholipid monolayers at the air-water interface. It is well established that pyrene excimer formation is a diffusion-controlled process[2] and prominent use has been made of excimer fluorescence to measure the diffusion of this probe through various host media, especially those related to biological membranes.[3] In the present study, interactions of the pyrene-bearing probe, 1-pyrenedecanoic acid (PDecA), have been compared as functions of probe concentration and hydrocarbon structure of the host lipid to the character of the lipid environment.

A rectangular Teflon Langmuir trough, maintained at 22 °C and 90+% relative humidity, was used. Time-resolved measurements were made with a modified PRA (Photochemical Research Associates) single photon lifetime apparatus using a PRA nitromite laser as the excitation source.[4] Excimer behavior was monitored at 480 nm.

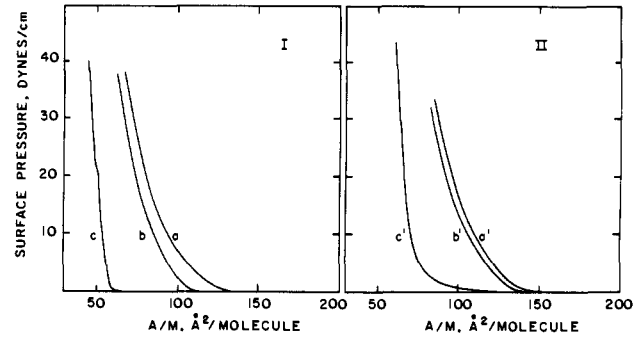


**Figure 1.** Force-area isotherms for DLP (a), DOP (b), and DSP (c) without (I) and then with (II) equimolar PDecA. Horizontal axis, area per lipid molecule.

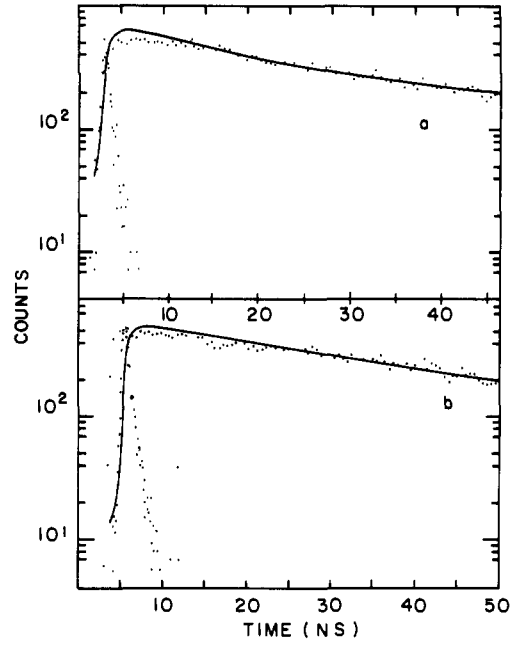


**Figure 2.** Lifetime measurements at the $N_2$-water interface for spread monolayers of PDecA in DOP at ratios of (a) 1:1.5 ($\tau$ = 18 ns) and (b) 1:3 ($\tau$ = 33 ns). Excitation was with a 300-ps $N_2$-laser puluse ($\lambda$ = 337 nm) and emission was monitored at 480 nm. The curve fits provided are based on convolution with a single exponential. Attempts to obtain two exponential fits were unsatisfactory. Measurements were taken at surface pressures of 5 dyn/cm.

Figure 1 illustrates the force-area isotherms—with and without equimolar probe—for monolayers of the three lipid systems examined: dilinoleoyl-L-phosphatidylcholine (DLP), dioleoyl-L-phosphatidylchloline (DOP), and distearoyl-L-phosphatidylcholine (DSP). The pure lipid data agree well with those reported in the literature.[5] The probe itself, at these levels, may be seen to force an increase of about 10-15% in lipid-lipid intermolecular separation under the surface pressures at which lifetime measurements were conducted (5 dyn/cm).

Time-resolved fluorescence measurements of mixed PDecA-lipid monlayers exhibit two features at 480 nm: a very fast rise in excimer intensity and a dependence of the excimer decay on PDecA mole fraction in the layer. Figure 2 illustrates these features (see caption for details). Plots of apparent decay rate vs. mole fraction are given in Figure 3. The lifetime will be subject to an error of ±5%.

An interpretation of this behavior may be made by employing the approach of Birks and co-workers, developed to explain photophysical behavior of pyrene in concentrated hexane solutions.[6]

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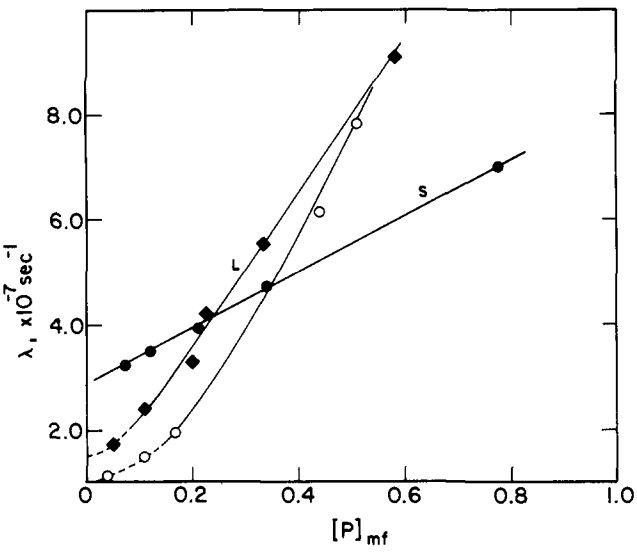


Figure 3. Plots of pseudo-first-order apparent excimer decay rates vs. mole fraction of PDecA in DSP (S), DOP (O), and DLP (L). Measurements were taken at surface pressures of 5 dyn/cm.

Here the time course of apparent excimer emission decay at high probe concentration may be related to excimer behavior via the expression

$$1/\tau = \lambda = k_m + k_{md} + k_{dm}[Py]$$

where $\tau$ is the measured lifetime, $k_m$ is the rate constant for excited monomer emission, $k_{md}$ is excimer dissociation, and $k_{dm}$ is the formation rate constant. It follows that

$$d\lambda/d[Py] = k_{dm}$$

at high concentrations of PDecA. The plots in Figure 3 of $\lambda$ vs. [PDecA] provide essentially linear relationships over most of the data although some curvature is implied at the lowest concentrations used. The intercepts for these plots fall within the region reported in Birk's early pyrene–hexane systems where $\lambda$ as $C \rightarrow 0$ is taken to reflect the sum of all rate constants for disappearance of excimer. In none of these systems have we been able to suitably measure the monomer lifetime (spectral studies have shown that the contribution of monomer fluorescence is very small in these systems).

For comparison to other systems, we have applied the simple relationship of Sackmann[3] ($D_p \approx {}^1/_4\, k_{dm}$) and utilized areas per molecule found in Figure 1. With this relationship and $k_{dm}$ in cm$^2$ molecule$^{-1}$ s$^{-1}$, one arrives at diffusion coefficients of 0.5, 2.4, and 2.2 $\times$ 10$^{-7}$ cm$^2$ s$^{-1}$ for PDecA in DSP, DOP, and DLP, respectively. The diffusion constant found here in DSP is comparable to that reported by Sackmann for PDecA in dipalmitoylphosphatidylcholine bilayer and monolayer vesicles (8 $\times$ 10$^{-8}$ cm$^2$ s$^{-1}$)[7]. The values for the DOL system are, as expected, somewhat lower than for PDodecA in an oleic acid monolayer determined eariler by steady-state methods and application of Monte Carlo simulations to the data (lower limit = 9 $\times$ 10$^{-7}$).[8] Although these measurements were conducted at low surface pressure, it might be considered somewhat surprising that the DSP monolayer exhibited a $k_{dm}$ so comparable with those obtained in the other lipids which incorporate *cis* methylene interrupted double bonds. However, photobleaching studies by Tancrede, et al. indicate a limited dependence on the nature of the lipid alkyl chains alone.[9] Additionally, one may not disregard the perturbations in the lipid packing generated by the presence of the pyrene (or other) probe. While such diffusion constants are not meant to be taken strictly as a measure of lipid fluidity in a pure lipid monolayer, they do demonstrate a rather simple means for characterizing interaction of the probe and provide an insight into spread monolayer behavior at the molecular level. A comprehensive study of temperature, compression, and probe structure effects in such systems is in progress.

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## A New Class of Amino Acid Based Sweeteners

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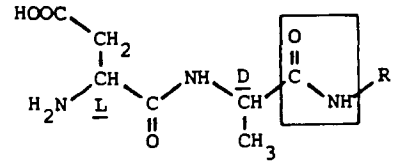
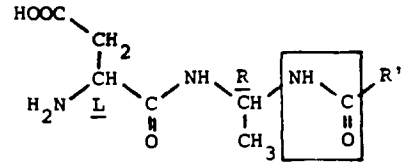
We wish to report the synthesis of a novel class of sweeteners based on the "retro-inverso" peptide modification. It has been reported that certain L-aspartyl-D-alanine amides I are sweet.[1,2]




(I)




(II)

Since the routes to reverse the direction of amide bonds in peptide backbones are now being developed,[3] we utilized this approach to prepare the *N*-(L-aspartyl)-1,1-diaminoalkane-based sweeteners II.[4] In these derivatives, the C-terminal amide bond in the structure I has been formalistically reversed. This was accomplished with complete maintainance of optical purity at the asymmetric center of the diaminoalkane residue. The taste characteristics of these molecules are strikingly similar in quality to sucrose and depend on the nature of the group R′ of the carboxylic acid used to acylate the 1,1-diaminoalkane. The properties of a small selection of a large number of these compounds which have been synthesized and where the nature of the group, R′, of the terminal amide is varied are summarized in Table I. The chirality of the aspartyl residue in these derivatives is L, while the chirality of the 1,1-diaminoalkane is *R*.

The synthesis of these 1,1-diaminoalkane derivatives is outlined in Scheme I. The protected dipeptide III was prepared by using standard peptide chemical techniques. The key step in the synthesis of these novel sweeteners, the Hofmann rearrangement of compound III, was accomplished by using a mild oxidizing agent from the class of iodobenzene compounds, such as [bis(trifluoroacetoxy)iodo]benzene.[5] The monoacylated 1,1-diaminoalkane salt IV was then acylated, under basic conditions, by the

* University of California.
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