(26) S. Wolfe, H. B. Schlegel, I. G. Csizmadia, and F. Bernardi, *J. Am. Chem. Soc.*, **97**, 2020 (1975).

(27) It should be noted that reservations have been expressed concerning the interpretation of these experimental results. See: H. C. E. McFarlane and W. McFarlane, *J. Chem. Soc., Chem. Commun.*, 886 (1975); R. D. Baechler, J. P. Casey, R. J. Cook, G. H. Senkler, Jr., and K. Mislow, *J. Am. Chem. Soc.*, **94**, 2859 (1972). The present theoretical results, while not refuting these criticisms, do tend to support the general validity of the conclusions of Lambert et al.[13]

(28) A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and J. R. Schweiger, *J. Am. Chem. Soc.*, **95**, 6506 (1973); A. H. Cowley, M. J. S. Dewar, J. W. Gilje, D. W. Goodman, and J. R. Schweiger, *J. Chem. Soc., Chem. Commun.*, 340 (1974).

(29) M. Berthelat, R. Mathis, J.-F. Labarre, and M. Mathis, *C. R. Acad. Sci., Ser. C*, 645 (1975); M. Berthelat, R. Mathis, and F. Mathis, *J. Chem. Soc., Chem. Commun.*, 615 (1977).

(30) A more recent CNDO/2 calculation of Borisov[31] yields not only a pyramidal geometry at nitrogen, but also an anti ground state structure (**1**, $\phi = 180°$) for H_2NPH_2. This does not agree with either the ab initio[18] or the earlier CNDO/2 result; it is also incompatible with the experimental data on substituted aminophosphines.

(31) E. V. Borisov, *Zh. Fiz. Khim.*, **51**, 1322 (1977).

(32) M.-H. Whangbo and S. Wolfe, *Can. J. Chem.*, **54**, 949 (1976).

(33) D. Kost, D. J. Mitchell, H. B. Schlegel, and S. Wolfe, *Can. J. Chem.*, **57**, 729 (1979).

(34) S. G. Baxter, D. A. Dougherty, J. P. Hummel, J. F. Blount, and K. Mislow, *J. Am. Chem. Soc.*, **100**, 7795 (1978).

(35) S. Wolfe, *Acc. Chem. Res.*, **5**, 102 (1972).

(36) S. Wolfe, D. J. Mitchell, and M.-H. Whangbo, *J. Am. Chem. Soc.*, **100**, 1936 (1978).

(37) In Hartree–Fock SCF theory, the total energy, E_T, of a closed-shell system is given by $E_T = (2\sum_k \epsilon_k - V_{ee} + V_{nn})$, where the ϵ_k's are the canonical orbital energies, V_{ee} is the electron–electron repulsion energy, and V_{nn} is the nuclear–nuclear repulsion energy.[38] We now speculate that the earlier successes of the PMO method of conformational analysis, when applied to hydrocarbon molecules,[39] were the result of a fortuitous conformational invariance of $(-V_{ee} + V_{nn})$.[40,41]

(38) P. K. Mehrotra and R. Hoffmann, *Theor. Chim. Acta*, **48**, 301 (1978).

(39) J. P. Lowe, *J. Am. Chem. Soc.*, **96**, 3759 (1974); R. Hoffmann, *Pure Appl. Chem.*, **24**, 567 (1970).

(40) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(41) It is useful to comment at this point on the relevance, to a PMO interpretation, of the observation[42] that $E_T^{SCF} = K\Sigma_i^{occ} 2\epsilon_i$, since this relationship is obeyed by the molecules of the present investigation. At the 4-31G level, K is found to be 1.54, 1.62, and 1.61 for hydrazine, diphosphine, and aminophosphine, respectively, and to be conformationally invariant. At the STO-3G level, hydrazine is found to have $K = 1.56$. According to one of the referees, a quantitative PMO analysis within a SCF scheme would have no meaning, unless the above relationship can be shown to exist, with K identical not only for the different molecules, but also for the fragments and the molecule. In our view, if the validity of the PMO analysis were to be dependent upon the existence of a Ruedenberg relationship,[42a] it would become necessary to treat *all possible* orbital interactions between the fragments. The method would thereby be reduced to a problem of bookkeeping, with loss of the (hoped-for) simple picture. To avoid this problem, we assume that the conformational behavior of a molecule is paralleled by the behavior of the HOMO.[43] When this assumption is valid, an understanding of the behavior of the HOMO provides some understanding of the behavior of the molecule. The mathematical formalism presented in ref 21 permits a transformation of the computed molecular orbitals from an atomic orbital basis to a fragment orbital basis. For each conformation, the HOMO is then reconstructed in terms of the fragment orbital interactions that contribute to that HOMO. With this formalism, the first-order term of the perturbational expansion is included in the fragment orbital energy, and the form of the HOMO is then reproduced by the second-order term calculated with eq 1 and 2. Figure 7 illustrates the application of this operational procedure to the rotational potential of diphosphine shown in Figure 1. The various curves in Figure 7 refer to E_T, the two-electron contribution to the HOMO, the four-electron contribution to the HOMO, the total PMO contribution to the HOMO, and ϵ_{HOMO}. The curve for ϵ_{HOMO} has been multiplied by a constant factor of 1/4.66, i.e., $\Sigma\Delta e_{ij} \simeq K'\epsilon_{HOMO}$. Although the two-electron PMO term most closely resembles E_T in the present case, we have no evidence that such behavior will be observed generally. To overcome the charge that the PMO analysis is arbitrary, we therefore advocate that this analysis be based upon the HOMO.[44]

(42) (a) K. Ruedenberg, *J. Chem. Phys.*, **66**, 375 (1977); (b) L. J. Schaad, B. H. Robinson, and B. A. Hess, *ibid.*, **67**, 4616 (1977); (c) N. H. March, *ibid.*, **67**, 4618 (1977); (d) T. Anno and Y. Sakai, *ibid.*, **67**, 4771 (1977); (e) A. B. Sannigrahi, B. R. De, and B. Guha Niyogi, *ibid.*, **68**, 784 (1978); (f) M. A. Whitehead, *ibid.*, **69**, 497 (1978); (g) D. G. Pettifor, *ibid.*, **69**, 2930 (1978); (h) S.-T. Wu, *ibid.*, **69**, 2934 (1978); (i) T. Anno, *ibid.*, **69**, 2935 (1978); (j) M. Kertész, J. Koller, and A. Ažman, *ibid.*, **69**, 2937 (1978).

(43) B. M. Deb, *J. Am. Chem. Soc.*, **96**, 2030, 2040 (1974).

(44) A PMO analysis of rotation in hydrazine based upon "tempered" orbitals[38] predicts the anti conformation of hydrazine to be ca. 30 kcal less stable than the gauche.

(45) A referee has pointed out that such conclusions are basis set dependent, and has urged caution in this regard. We comment that, in terms of our operational procedure, described in footnote 41, a basis set that reproduces an experimental trend should also produce a reliable PMO analysis. To check this point, we repeated the quantitative PMO analysis on the three molecules at the STO-3G (STO-3G) level, with the results shown in parentheses in Table V. It is clear that the *stabilizing interactions* dominate at the STO-3G level. It is also clear that the PMO analysis at this computational level has failed. The 90° conformation is predicted to be more stable in the case of hydrazine, and the 180° conformation is predicted to be more stable in the case of diphosphine. The total energy behavior is just the opposite in both cases. A final calculation was then performed on the 90 and 180° conformations of hydrazine at the 4-31G* (STO-3G) level. The results of these calculations, summarized in footnotes *a* and *b* of Table III and footnote *b* of Table V, indicate that the 4-31G and 4-31G* basis sets lead to the same conclusions concerning both the total energy and the PMO behavior. We therefore suggest that the procedures advocated herein contain proper safeguards concerning the relative importance of stabilizing and destabilizing interactions. We also suggest that much more work will be needed before reliable qualitative rules can be provided for the PMO analysis of molecules containing adjacent electron pairs.

(46) R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, **93**, 773 (1971).

Formation of Stable Monolayer Membranes and Related Structures in Dilute Aqueous Solution from Two-Headed Ammonium Amphiphiles

Yoshio Okahata and Toyoki Kunitake*

Contribution No. 484 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan.
Received March 5, 1979

Abstract: Two-headed, single-chain ammonium amphiphiles in which the hydrophobic chain was made of the flexible decamethylene unit and the rigid diphenylazomethine or biphenyl unit were synthesized. These amphiphiles produced huge (10^6–10^7 daltons) aggregates in dilute aqueous solution. The basic structure of the aggregates was shown by electron microscopy to be the monolayer membrane. A rod-like structure resulted, when the flexible moiety increased. Addition of second components drastically changed the aggregate structure. For instance, rigid lamellae were converted to large single-walled vesicles by incorporation of cholesterol. The present finding is the first example of the formation of stable monolayer membranes.

Stable bilayer membranes have been prepared in dilute aqueous solution from a variety of totally synthetic amphiphiles which contain two higher alkyl chains (C_{10}–C_{18}) as the hydrophobic moiety. The hydrophilic group of these amphiphiles may be cationic,[1-5] anionic,[6,7] nonionic,[8] or zwitterionic.[8] In very recent studies, it is shown that the hydrophobic portion of these bilayer-forming amphiphiles can be replaced by a single-chain unit which contains a rigid segment such as diphenylazomethine[9] or biphenyl group.[10] Figures 1a,b illustrates schematically these bilayer structures.

0002-7863/79/1501-5231$01.00/0

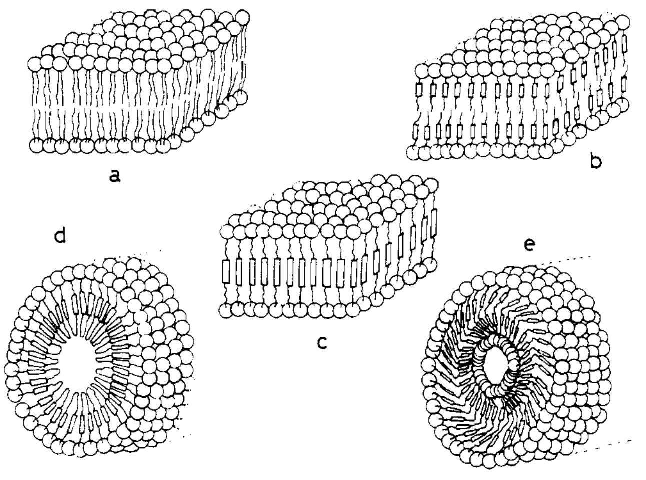
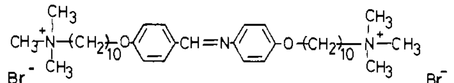


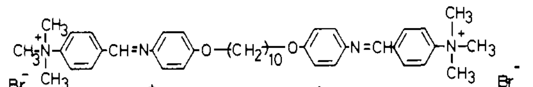
Figure 1. Schematic illustrations of synthetic molecular membranes. Open circle, hydrophilic head group; wavy line, flexible hydrocarbon chain; rectangle, rigid segment. (a) Bilayer membrane formed from one-headed, double-chain amphiphiles. (b) Bilayer membrane formed from one-headed, single-chain amphiphiles. (c) Monolayer membrane formed from two-headed, single-chain amphiphiles. (d) Rod-like structure conceived for the aqueous aggregate of **3**. (e) Tubular structure conceived for the aqueous aggregate of **3**.

As an extention of these studies, we wish to report herein novel monolayer membranes and related structures (see Figures 1c-e) which are formed in water spontaneously from two-headed ammonium amphiphiles. The amphiphile structures are shown below together with abbreviations.

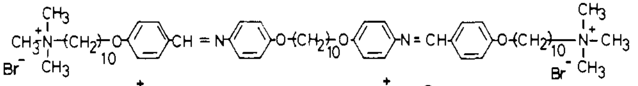
Two-headed Amphiphiles



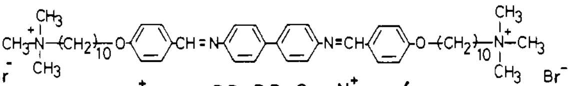
$^{+}N-C_{10}-BB-C_{10}-N^{+}$ **1**



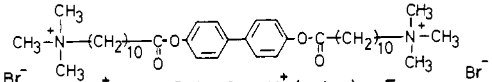
$^{+}N-BB-C_{10}-BB-N^{+}$ **2**



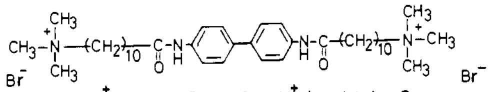
$^{+}N-C_{10}-BB-C_{10}-BB-C_{10}-N^{+}$ **3**



$^{+}N-C_{10}-BB-BB-C_{10}-N^{+}$ **4**



$^{+}N-C_{10}-Bph-C_{10}-N^{+}$ (ester) **5**



$^{+}N-C_{10}-Bph-C_{10}-N^{+}$ (amide) **6**

Results and Discussion

The aqueous solution of these dicationic amphiphiles was prepared by the sonication method or by the injection method. In the first method, 5-7 mg of the amphiphiles was suspended in 1 mL of deionized water and sonicated for 2-5 min by a Branson Sonifier 185 (sonic power 40). The resulting solutions (10 mM) were usually clear or translucent, and freely flowing. The appearance of these solutions was very similar to that of aqueous solutions of lecithin liposomes. A turbid solution was obtained from **6** by this procedure. In the injection method, 10 mg of the amphiphiles was dissolved in dimethylformamide, and the solution was injected by a syringe into 10 mL of hot water and sonicated for 2-5 min. This procedure did not work for **6**, because it was not soluble in dimethylformamide, while clear solutions were obtained from **2**, **4**, and **5**.

Table I summarizes the aggregation behavior of the amphiphiles. The critical micelle concentration is $(1-3) \times 10^{-4}$ M as estimated by the Wilhelmy method and the molecular weight of the aggregates is in the range of 10^6-10^7. Therefore, it is concluded that huge aggregates are formed in *dilute* aqueous solution. These aggregates are stably dispersed in water and the appearance of the solutions did not change for at least several weeks. The azomethine group is known to be hydrolyzed readily at neutral pH in the molecular dispersion. However, it seems to resist hydrolysis when imbedded in the hydrophobic core of the tight aggregate. In fact, identical electron micrographs were obtained after the amphiphile solution (10 mM) had been kept for several weeks. A similar conclusion has been obtained for the ordered aggregate of single-chain amphiphiles which contained the azomethine group.[9]

The fine structure of the aggregates can be elucidated most directly by electron microscopy. Thus, 1 mL of the amphiphile solution (10 mM) was mixed with 1 mL of 2% aqueous uranyl acetate and sonicated for 15-30 s. The mixture was incubated in ice-water for 30 min, applied to the carbon-coated Cu mesh, dried in vacuo, and subjected to electron microscopic examination. Except for **6**, which did not disperse in water, all of the amphiphiles formed well-organized structures in dilute (10^{-2} M) solution. The preparative method of the sample solutions (sonication or injection) did not affect the aggregate structure. Those amphiphiles that possess rigid segments in the middle of the molecule (i.e., **1**, **4**, and **5**) produce well-developed lamellar structures. In particular, very clear lamellar structures were observed for **1** as shown in Figure 2A. This is apparently an edge of a fragment of stacked sheets (membranes). The same structure of varying sizes was viewed abundantly, and no other structures were apparent. The layer thickness is 30-40 Å; therefore it is strongly implied that the layer is composed of the dicationic amphiphiles aligned perpendicular to the layer surface, as illustrated in Figure 1c. These structures may be related to separate lyotropic liquid crystalline phases of the lamellar type such as obtained with concentrated soap solutions.[11] However, an important difference exists in that the present aggregates are stable as monolayers, as can be typically seen in Figure 2D. The lamellar structure is derived not from the formation of separate lyotropic liquid crystalline phases, but from the intrinsic stability of the monolayer.

The lamellar structure appears to become flexible when the hydrocarbon chain occupies the center of the molecule as in **2**. A further increase in the flexible hydrocarbon segment drastically changes the aggregate structure, and **3** produces a rod-like structure as shown in Figure 2B. The diameter of the rod is 70-100 Å, a value larger than the length of the extended molecular chain of **3** (67 Å). A dark streak runs through the middle of the rod. These features are consistent with the molecular arrangements shown in Figures 1d,e. The amphiphilic molecule is folded into two and packed radially in Figure 1d. In Figure 1e, the large area difference between the outer and inner surfaces may be accommodated by assuming bent molecular packing in the outer half of the membrane. This is possible because the flexible chain is present in the middle of the molecule. The dark streak is explained by deposition of uranyl acetate in the inner core in both cases. The formation of the rod-like structure was reported for a mixture of lecithin and cholesterol,[12] but the tubular structure of Figure 1e has not been mentioned in the past literature. We cannot discriminate between these two possibilities at the moment.

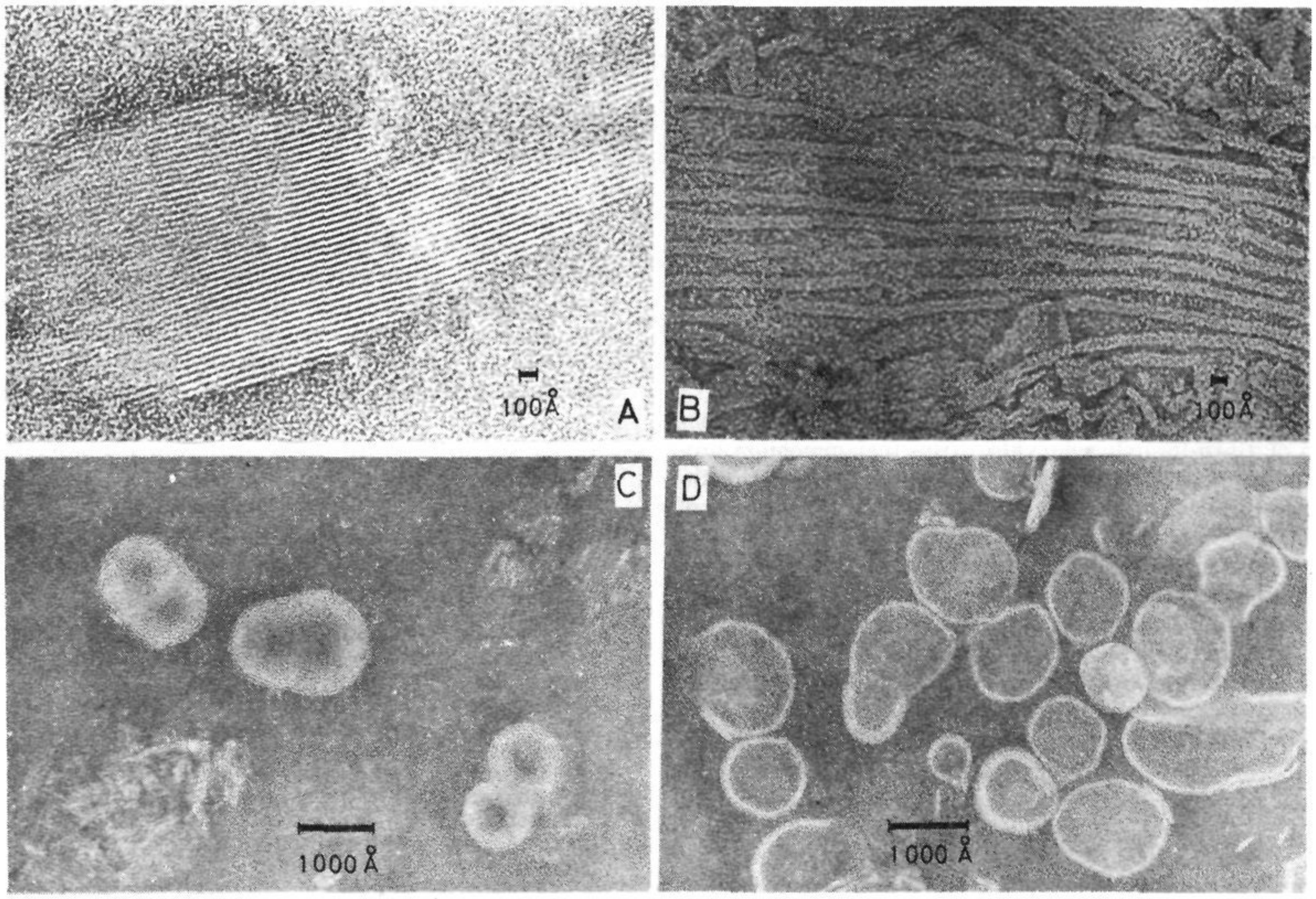


Figure 2. Electron micrograph. (A) **1**, magnification ×360 000. (B) **3**, magnification ×360 000. (C) **1** + $2C_{12}N^+2C_1$ (equimolar mixture), magnification ×180 000. (D) **1** + cholesterol (3:1 molar mixture), magnification ×180 000.

Table I. Aggregation of Dicationic Amphiphiles

	compd	aqueous solution[a] (10 mM)	10^4 cmc[b] M	aggregate weight,[c] dalton ($\times 10^{-6}$)	electron micrograph[d]
1	N^+-C_{10}-BB-C_{10}-N^+	clear	1.4	1.2	lamella
2	N^+-BB-C_{10}-BB-N^+	translucent (clear)	2.5	11	lamella
3	N^+-C_{10}-BB-C_{10}-BB-C_{10}-N^+	clear	3.0	13	rod-like structure
4	N^+-C_{10}-BB-BB-C_{10}-N^+	translucent (clear)	1.0	3.1	lamella
5	N^+-C_{10}-BPh-C_{10}-N^+ (ester)	translucent (clear)	2.5	7.9	lamella
6	N^+-C_{10}-BPh-C_{10}-N^+ (amide)	turbid			

[a] The solution obtained by the sonication method. The description given in parentheses is for those solutions that were obtained by the injection method. [b] The critical micelle concentration (cmc) was determined by the surface tension measurement (Wilhelmy method). Portions of DMF solutions (~2 mL) of the amphiphiles were successively added to 25 mL of water at ambient temperature. The minimal surface tension was 50 ± 2 dyn/cm in all cases. [c] Determined by the light scattering method: Union Giken Co. (Japan) Model LS-600. Light source: He–Ne laser. The aqueous solutions were prepared by sonication; the scattering intensity at 0.5, 0.25, and 0.125 wt % was extrapolated to that at the zero concentration. [d] 10 mM solution prepared by sonication. Hitachi H-500 instrument.

The rigid-looking lamellar structure of **1** can be transformed into totally different structures by adding second components. When 50 mol % of didodecyldimethylammonium bromide was cosonicated (total amphiphile concentration, 15 mM), multiwalled vesicles are formed (Figure 2C). An example of the most remarkable transformation was the predominant formation of seemingly single-walled vesicles by cosonication of 1/3 M cholesterol (Figure 2D). The vesicles are 1000–3000 Å in diameter and their membrane thickness is at least 60–70 Å. It is suspected that cholesterol molecules are mostly located in the outer half of the membrane, thus creating curvature suitable for the vesicle formation.

In conclusion, two-headed (cationic) amphiphiles can form stable monomolecular membranes in dilute aqueous solution, if they possess the hydrophobic moiety composed appropriately of the rigid segment and the flexible hydrocarbon chain. The rigid segment is required for facilitated packing of amphiphilic molecules in dilute solution. It is important that the aggregate structure can be varied drastically by modifying the chemical structure of amphiphiles or by adding second components. A variety of functionalized membranes will be prepared in the future on the basis of the present study.

Experimental Section

The two-headed amphiphiles N^+-C_{10}-BB-C_{10}-N^+ (**1**), N^+-BB-C_{10}-BB-N^+ (**2**), N^+-C_{10}-BB-C_{10}-BB-C_{10}-N^+ (**3**), and N^+-C_{10}-BB-BB-C_{10}-N^+ (**4**) were prepared by condensation of appropriate benzaldehydes and aromatic amines.

10-(*p*-Aminophenoxy)decyltrimethylammonium Bromide. According to a general procedure,[13] 10-(*p*-acetamidophenoxy)decyl bromide (white granules from ethanol, mp 90–95 °C) was obtained from *p*-acetamidophenol and excess 1,10-dibromodecane. The product was quaternized by trimethylamine in ethanol in a sealed ampule at 80 °C for 36 h. Solvent was then removed in vacuo and the precipitates were hydrolyzed for 3 h in a refluxing mixture of ethanol and concentrated hydrochloric acid. The reaction mixture was neutralized to pH 8–9, solvent was removed in vacuo, and precipitates were extracted with hot ethanol. White granules obtained upon cooling were recrystallized from ethanol, yield 71%, mp 175–180 °C.

1,10-Bis(*p*-aminophenoxy)decane. 1,10-Bis(*p*-acetamidophenoxy)decane (mp 160–170 °C) as obtained similarly from 1,10-dibromodecane and excess *p*-acetamidophenol was hydrolyzed in a mixture of ethanol and concentrated hydrochloric acid as pale brown granules from ethanol, mp 70–71 °C.

Amphiphiles 1–4. N^+-C_{10}-BB-C_{10}-N^+ (**1**) was prepared by condensation of 10-(*p*-formylphenoxy)decyltrimethylammonium bromide[9] (mp 117–118 °C) and 10-(*p*-aminophenoxy)decyltrimethylammonium bromide in refluxing ethanol for 1 h in the presence of a small amount of acetic acid: yield 56%; mp 225 → 260 °C (the liquid crystalline behavior was observed during the melting point measurement as indicated by arrow); NMR ($CDCl_3$-Me_2SO-d_6) δ 3.1 (s, 18 H, N^+-CH_3), 7.0 (m, 8 H, phenyl), 8.3 ppm (1 H, -CH=N-). Anal. ($C_{39}H_{67}N_3O_2Br_2{\cdot}H_2O$) C, H, N.

N^+-BB-C_{10}-BB-N^+ (**2**) was prepared similarly from 1,10-bis(*p*-aminophenoxy)decane and *p*-formylphenyltrimethylammonium bromide (mp 208–210 °C):[9] yield 96%; mp 195–200 °C (from ethanol); NMR (Me_2SO-d_6) δ 3.8 (s, 18 H, N^+-CH_3), 7.3 (m, 16 H, phenyl), 8.2 ppm (2 H, -CH=N-). Anal. ($C_{42}H_{56}N_4O_2Br_2{\cdot}H_2O$) C, H, N.

N^+-C_{10}-BB-C_{10}-BB-C_{10}-N^+ (**3**) was similarly prepared from 1,10-bis(*p*-aminophenoxy)decane and 10-(*p*-formylphenyl)decyltrimethylammonium bromide:[9] yield 60%; mp 245–250 °C (from ethanol). Anal. ($C_{62}H_{96}N_4O_4Br_2{\cdot}2H_2O$) C, H, N.

N^+-C_{10}-BB-BB-C_{10}-N^+ (**4**) was similarly prepared from benzidine and 10-(*p*-formylphenoxy)decyltrimethylammonium bromide:[9] yield 80%; mp 150 → 270 °C. Anal. ($C_{52}H_{76}N_4O_2Br_2{\cdot}1.5H_2O$) C, H, N.

N^+-C_{10}-BPh-C_{10}-N^+ (ester) (5). Excess 11-bromoundecanoyl chloride (2.2 equiv, bp 180 °C (10 mm))[14] was allowed to react with *p,p′*-dihydroxybiphenyl in dimethylformamide at 0–40 °C for 90 min in the presence of triethylamine. *p,p′*-Bis(11-bromoundecanoyloxy)biphenyl (mp 75–80 °C, recrystallized from acetone) thus obtained was quaternized with trimethylamine in ethanol-benzene at 90 °C for 72 h: colorless granules from ethanol; mp 130–132 °C; NMR ($CDCl_3$-Me_2SO-d_6) δ 1.2 (m, 32 H, -CH_2-), 3.1 (s, 18 H, N^+-CH_3), 6.8 and 7.3 ppm (m, 8 H, phenyl). Anal. ($C_{40}H_{66}N_2O_4Br_2$) H; C: calcd, 60.15; found 63.61. N: calcd, 3.51; found 2.69.

N^+-C_{10}-BPh-C_{10}-N^+ (amide) (6). Excess 11-bromoundecanoyl chloride and benzidine were similarly allowed to react in chloroform in the presence of triethylamine, and resulting *p,p′*-bis(11-bromoundecanoyl)benzidine (mp 220 °C, recrystallized from chloroform–ethanol) quaternized by trimethylamine in a sealed ampule: colorless granules; mp 245 °C. Anal. ($C_{40}H_{68}N_4O_2Br_2{\cdot}H_2O$) C, H, N.

Acknowledgment. The authors are grateful to Professor M. Takayanagi of Kyushu University for the use of an electron microscope.

References and Notes

(1) T. Kunitake and Y. Okahata, *J. Am. Chem. Soc.*, **99**, 3860 (1977).
(2) T. Kunitake, Y. Okahata, K. Tamaki, F. Kumamaru, and M. Takayanagi, *Chem. Lett.*, 387–390 (1977).
(3) T. Kunitake and Y. Okahata, *Chem. Lett.*, 1337–1340 (1977).
(4) C. D. Tran, P. L. Klahn, A. Romero, and J. H. Fendler, *J. Am. Chem. Soc.*, **100**, 1622 (1978).
(5) K. Deguchi and J. Mino, *J. Colloid Interface Sci.*, **65**, 155–161 (1978).
(6) T. Kunitake and Y. Okahata, *Bull. Chem. Soc. Jpn.*, **51**, 1877–1879 (1978).
(7) R. A. Mortara, F. H. Quina, and H. Chaimovich, *Biochem. Biophys. Res. Commun.*, **81**, 1080–1086 (1978).
(8) Y. Okahata, S. Tanamachi, M. Nagai, and T. Kunitake, *Polym. Prepr. Jpn.*, **27**, 231 (1978).
(9) T. Kunitake and Y. Okahata, *J. Am. Chem. Soc.*, submitted.
(10) T. Kunitake and Y. Okahata, *Bull. Chem. Soc. Jpn.*, to be submitted.
(11) S. Friberg, "Lyotropic Liquid Crystals", *Adv. Chem. Ser.*, **No. 152** (1976).
(12) A. D. Bangham and R. W. Horne, *J. Mol. Biol.*, **8**, 660–668 (1964).
(13) M. E. Neubert, S. J. Laskos, Jr., L. J. Maurer, L. T. Carlino, and J. P. Ferrato, *Mol. Cryst. Liq. Cryst.*, **44**, 197–210 (1978).
(14) F. J. Buckle, F. L. M. Pattison, and B. C. Sanders, *J. Chem. Soc.*, 1471 (1949).