

Models for Photochemical Electron Transfer at Fixed Distances. Porphyrin-Bicyclo[2.2.2]octane-Quinone and Porphyrin-Bibicyclo[2.2.2]octane-Quinone

Alvin D. Joran, Burton A. Leland, George G. Geller,
John J. Hopfield,*† and Peter B. Dervan*

Contribution No. 7046, Division of Chemistry
and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

Received June 11, 1984

Models of the photosynthetic reaction center can help elucidate the structural and chemical features that govern the electron-transfer processes essential for biological charge separation. Many synthetic models exist which consist of porphyrins covalently bound to quinones by flexible and semirigid linkers.¹ Kinetic studies of intramolecular electron transfer have been complicated by reactions occurring from more than one conformation. There is a general need for the construction of structurally less ambiguous porphyrin-linker-quinone molecules (PLQ) for studies on the dependence of variables such as distance, orientation, and energy gap between donor and acceptor molecules in electron-transfer processes.²

We report the syntheses of three rigidly linked side-by-side porphyrin-quinone molecules 2-4 whose edge-to-edge distances are fixed at 6, 10, and 14 Å (Figure 1).³ The spacer units bicyclo[2.2.2]octane and bibicyclo[2.2.2]octane prevent translational displacement and only allow rotational freedom.⁴ Our preliminary studies of the fluorescence yields of both the free base PLQ 2a-4a and Zn PLQ 2b-4b systems, relative to 1, a similar porphyrin not equipped with a quinone, reveal a distance dependence. This suggests that 2-4 will be useful systems for studying the incremental effect of distance on photochemical electron transfer from excited-state porphyrins to quinones.

The syntheses of 1-4 were based on the method of condensing linear tetrapyrroles and aldehydes to form *meso*-substituted porphyrins (Figure 2).⁵ (Arylbicyclo[2.2.2]octyl)benzaldehyde

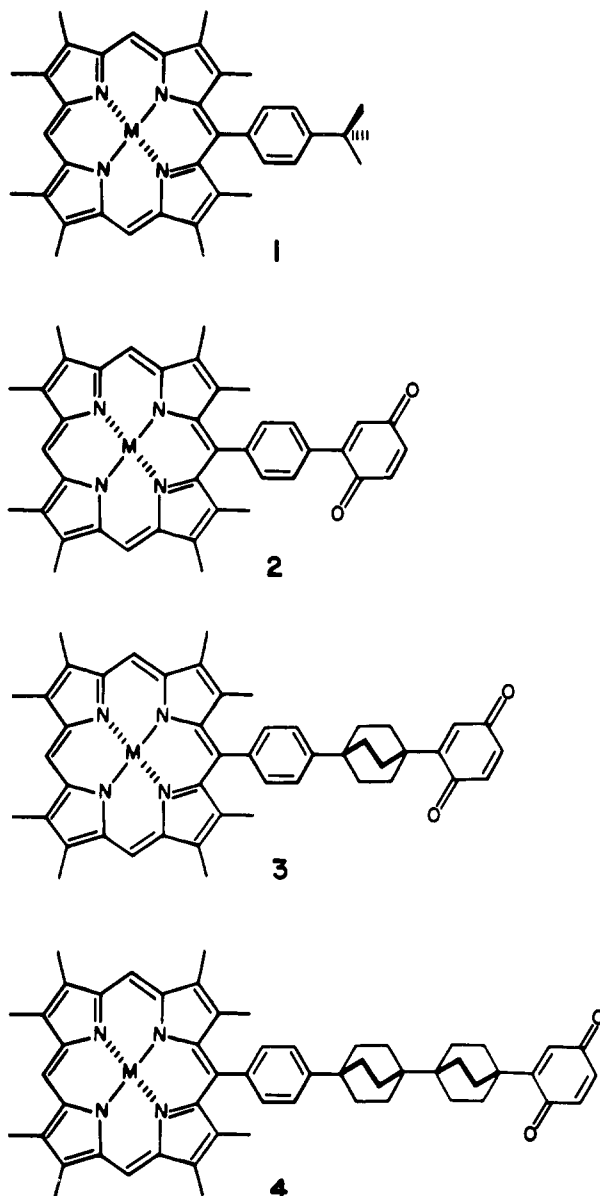


Figure 1. Substituted porphyrin 1a-4a, M = H₂; 1b-4b, M = Zn.

Table I. Relative Fluorescence Yields from Free Base PLQ 2a-4a and ZnPLQ 2b-4b^a

PLQ	solvent	I/I ₀ ^b
2a	n-PrCN	0.02
2a	C ₆ H ₆	0.01
3a	n-PrCN	0.63
3a	C ₆ H ₆	0.80
4a	n-PrCN	0.90
4a	C ₆ H ₆	0.94
2b	n-PrCN	0.035
2b	C ₆ H ₆	0.003
3b	n-PrCN	0.26
3b	C ₆ H ₆	0.27
4b	n-PrCN	0.95
4b	C ₆ H ₆	0.97

^a Energy gap for electron transfer estimated to be 0.55 V for 2a-4a and 0.97 V for 2b-4b in CH₂Cl₂.^{13,14} ^b We estimate an uncertainty of ±5% in these values.

7, obtained in five steps from the 4-phenylbicyclo[2.2.2]octane ethyl ether 5,^{4b} was allowed to react with *ac*-biladiene 8⁶ to afford porphyrin-bicyclo[2.2.2]octane-dimethoxybenzene 9a in 40% yield (Figure 2). Similarly (arylbicyclo[2.2.2]octyl)benzaldehyde 12

(6) Johnson, A. W.; Kay, I. T. *J. Chem. Soc.* 1965, 1620.

* Also: Division of Biology, California Institute of Technology and Bell Laboratories, Murray Hill, NJ.

(1) (a) Tabushi, I.; Koga, N.; Yanagita, M. *Tetrahedron Lett.* 1979, 257-260. (b) Dalton, J.; Milgrom, L. R. *J. Chem. Soc., Chem. Commun.* 1979, 609-610. (c) Kong, J. L. Y.; Loach, P. A. *J. Heterocycl. Chem.* 1980, 17, 737. (d) Ho, T.-F.; McIntosh, A. R.; Bolton, J. R. *Nature (London)* 1980, 286, 254-256. (e) Ganesh, K. N.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* 1980, 1129-1131. (f) Harriman, A.; Hosie, R. J. *J. Photochem.* 1980, 15, 163-167. (g) Netzel, T. L.; Bergkamp, M. A.; Chang, C. K.; Dalton, J. *Ibid.* 1981, 451-460. (h) Nishitani, S.; Kurata, N.; Sakata, Y.; Misumi, S.; Migita, M.; Okada, T.; Mataga, N. *Tetrahedron Lett.* 1981, 2099-2102. (i) Migita, M.; Okada, T.; Mataga, N.; Nishitani, S.; Kurata, N.; Sakata, Y.; Misumi, S. *Chem. Phys. Lett.* 1981, 84, 263-266. (j) Kong, J. L. Y.; Spears, K. G.; Loach, P. A. *Photochem. Photobiol.* 1982, 35, 545-553. (k) Ganesh, K. N.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* 1982, 1611-1615. (l) Ganesh, K. N.; Sanders, J. K. M.; Waterton, J. C. *Ibid.* 1982, 1617-1624. (m) Bergkamp, M. A.; Dalton, J.; Netzel, T. L. *J. Am. Chem. Soc.* 1982, 104, 253-259. (n) Lindsey, J. S.; Mauzerall, D. C. *Ibid.* 1982, 104, 4498-4500. (o) Lindsey, J. S.; Mauzerall, D. C. *Ibid.* 1983, 105, 6528-6529. (p) McIntosh, A. R.; Siemiarz, A.; Bolton, J. R.; Stillman, M. J.; Ho, T.-F.; Weedon, A. C. *Ibid.* 1983, 105, 7215-7223. (q) Siemiarz, A.; McIntosh, A. R.; Ho, T.-F.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *Ibid.* 1983, 105, 7224-7230. (r) Nishitani, S.; Kurata, N.; Sakata, Y.; Misumi, S.; Karen, A.; Okada, T.; Mataga, N. *Ibid.* 1983, 105, 7771-7772. (s) Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J.-C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Liddell, P. A.; Lehman, W. R.; Nemeth, G. A.; Moore, A. L. *Nature (London)* 1984, 307, 630-632. (t) Wasielewski, M.-R.; Niemczyk, M. P. *J. Am. Chem. Soc.* 1984, 106, 5043-5045.

(2) (a) For recent rigid PLQ systems see ref 1, o.t. (b) For a recent example of the effect of free energy on the rates of electron transfer in 16-biphenyl-5- α -androstane-acceptor molecules, see: Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* 1984, 106, 3047.

(3) Estimated distances from Dreiding models.

(4) (a) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* 1980, 45, 3933. (b) Zimmerman, H. E.; McKelvey, R. D. *J. Am. Chem. Soc.* 1971, 93, 3698. (c) Beechcroft, R. A.; Davidson, R. S.; Goodwin, D.; Pratt, J. E. *Pure Appl. Chem.* 1982, 9, 1605. (d) Davidson, R. S.; Bonneau, R.; Jousset-Dubien, J.; Toyne, K. T. *Chem. Phys. Lett.* 1979, 63, 269.

(5) Harris, D.; Johnson, A. W.; Gaete-Holmes, R. *Bioorg. Chem.* 1980, 9, 63-70.

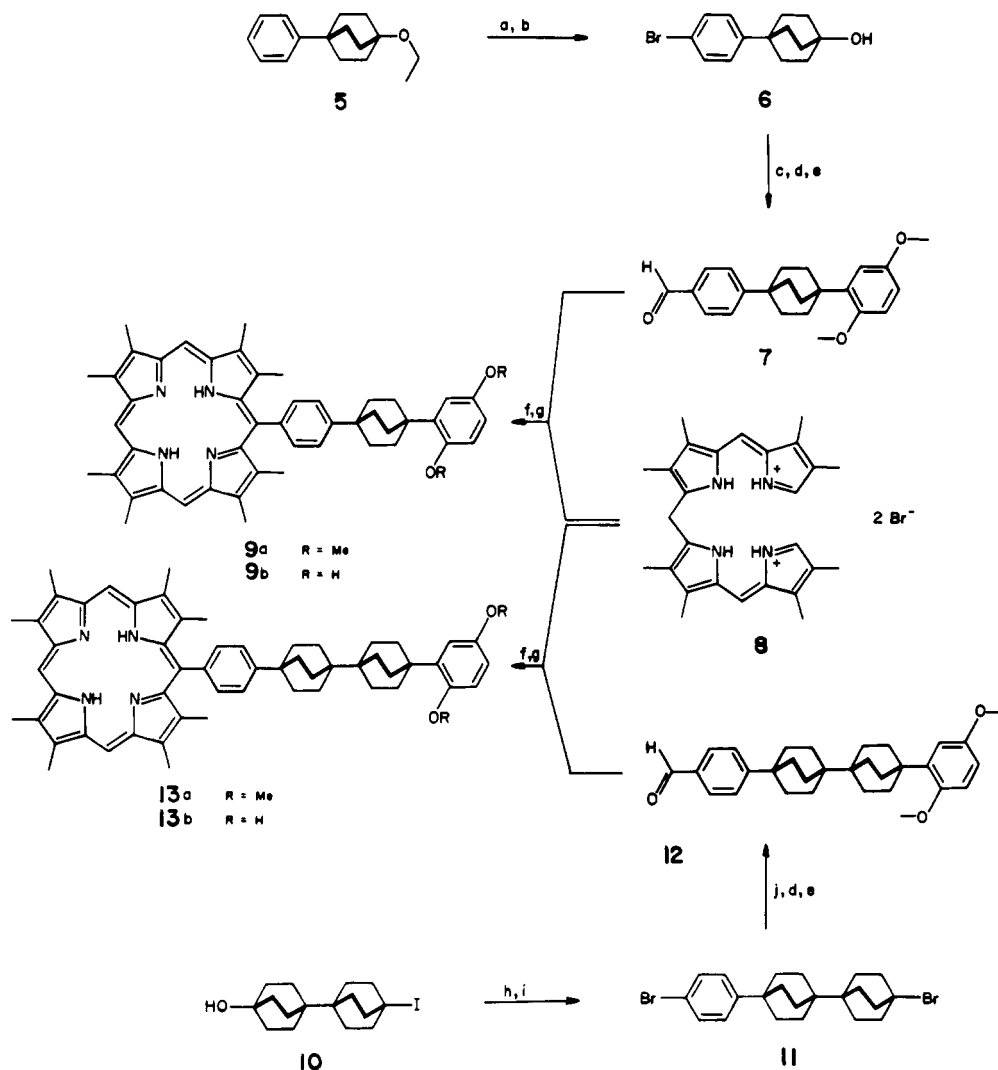


Figure 2. Synthetic scheme. (a) Br_2 , $\text{LiOCOC}_6\text{H}_5$, CH_3CN , 81°C . (b) KOH , H_2O , 100°C . (c) 1,4-Dimethoxybenzene, BF_3 , $p\text{-TsOH}$, $\text{CCl}_2\text{CHCl}_2$, 87°C . (d) $n\text{-BuLi}$, THF , -78°C . (e) DMF , -78°C . (f) HBr , HOAc , CH_3OH , 65°C . (g) BBr_3 , CH_2Cl_2 , 25°C . (h) BF_3 , $p\text{-TsOH}$, C_6H_6 , 60°C . (i) Br_2 , Fe , CCl_4 , 70°C . (j) 1,4-dimethoxybenzene, AlBr_3 , $\text{ClCH}_2\text{CH}_2\text{Cl}$, 83°C .

obtained in five steps from 4'-iodo-1,1'-bibicyclo[2.2.2]octan-4-ol (10),⁴ was treated with *ac*-biladiene 8 to afford porphyrin-biladiene 13a in 30% yield. The dimethyl ethers 9a and 13a were deprotected by treatment with BBr_3 , oxidized with PbO_2 , and purified by flash chromatography (silica gel, $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$, 1:9) to afford 3a and 4a, respectively.⁷

Irradiation of matched solutions of each of the porphyrin-quinones 2–4 and the reference porphyrin 1 in benzene and butyronitrile solvents at $<10^{-6}$ M concentrations in the Soret region (404 nm) afforded the fluorescence intensity (I) of porphyrin-quinones 2–4 relative to the fluorescence intensity (I_0) of porphyrin 1 (Table I).^{9,10} In benzene we find that for free base PLQ 2a–4a

the relative fluorescence yields (I/I_0) are 0.01, 0.80, and 0.94, respectively. Likewise for the ZnPLQ 2b–4b, in benzene, I/I_0 are 0.003, 0.27, and 0.97, respectively (Table I). The trend in the fluorescence yields obtained for the two series of three PLQ molecules is consistent with a marked distance effect on the rate of intramolecular electron transfer from the porphyrin excited singlet state to the quinone moiety. Assuming the singlet state is competitively quenched by electron transfer and using appropriate values for the porphyrin fluorescence lifetime,¹¹ rate constants for the three distances examined can be estimated. The estimated electron-transfer rate constants (k_{ET}) in benzene for 2a–4a would be 5.8×10^9 , 1.5×10^7 , and $\leq 4 \times 10^6 \text{ s}^{-1}$, respectively, and for 2b–4b would be 2.2×10^{11} , 1.8×10^9 , and $\leq 2 \times 10^7 \text{ s}^{-1}$, respectively.¹¹ For 3a and 3b, which have energy gap values that differ by $\sim 0.4 \text{ eV}$, the forward rate constants in benzene appear to differ by a factor of 120, the Zn PLQ being faster.^{13,14}

(7) 3a: UV-vis (CH_2Cl_2) 248, 401, 500, 533, 569, 623 nm; IR (CHCl_3) 1655 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 10.17 (s, 2 H), 9.97 (s, 1 H), 7.94 (d, 2 H, $J = 7.9 \text{ Hz}$), 7.72 (d, 2 H, $J = 7.9 \text{ Hz}$), 6.73 (s, 2 H), 6.66 (s, 1 H), 3.63 (s, 6 H), 3.60 (s, 6 H), 3.54 (s, 6 H), 2.44 (s, 6 H), 2.24 (m, 6 H), 2.15 (m, 6 H), -3.39 (br s, 2 H); MS (FAB) 712 (M^+ , 62), 713 ($\text{M}^+ + 1$, 73), 714 ($\text{M}^+ + 2$, 35).

(8) 4a: UV-vis (C_6H_6) 404, 502, 534, 574, 628 nm; ^1H NMR (500 MHz, CDCl_3) δ 10.10 (s, 2 H), 9.90 (s, 1 H), 7.89 (d, 2 H, $J = 8.2 \text{ Hz}$), 7.62 (d, 2 H, $J = 8.2 \text{ Hz}$), 6.67 (s, 2 H), 6.52 (s, 1 H), 3.59 (s, 6 H), 3.57 (s, 6 H), 3.49 (s, 6 H), 2.39 (s, 6 H), 2.07 (m, 6 H), 1.80 (m, 6 H), 1.66 (m, 6 H), 1.58 (m, 6 H); MS (FAB) 821 (M^+ , 53), 822 ($\text{M}^+ + 1$, 63).

(9) Fluorescence yields were independent of exciting wavelength and concentration (10^{-6} – 10^{-7} M). Fluorescence yields were measured under aerobic conditions. Benzene was distilled from CaH_2 . *n*-PrCN was allowed to stand over K_2CO_3 and distilled from P_2O_5 .

(10) We thank Professor H. B. Gray and his group for generous assistance in carrying out the fluorescence measurements.

(11) For PLQ 2–4, the estimate of k_{ET} was calculated from $I_0/I = 1 + k_{\text{ET}}\tau_0$, where $\tau_0(\text{C}_6\text{H}_6) = 17 \times 10^{-9} \text{ s}$ and $\tau_0(\text{PrCN}) = 18 \times 10^{-9} \text{ s}$ for 1a and $\tau_0(\text{C}_6\text{H}_6) = 1.5 \times 10^{-9} \text{ s}$ and $\tau_0(\text{PrCN}) = 1.6 \times 10^{-9} \text{ s}$ for 1b in degassed solutions.¹² From dynamic quenching data currently in progress¹² we believe the estimated k_{ET} values for 4a and 4b will be upper limits.

(12) Felker, P. M.; Joran, A. D.; Leland, B. A.; Hopfield, J. J.; Dervan, P. B.; Zewail, A. H., California Institute of Technology, unpublished results.

(13) Low solubility of PLQ 2–4 in *n*-PrCN and large uncompensated resistance in C_6H_6 precluded electrochemical measurements in these solvents. However, we were able to obtain electrochemical data in CH_2Cl_2 .¹⁴ Unfortunately, fluorescence yield measurements for PLQ 2–4 in CH_2Cl_2 were complicated by photoreactions not yet characterized.

Quantitative comparison and further interpretation must await direct optical studies. This series of compounds is the first reported system in which incremental distance effects on electron-transfer rates have been observed in rigid models of the photosynthetic primary process. Theoretical studies aimed at determining the role of the bicyclooctane spacer are under way.

Acknowledgment. We are grateful to the National Science Foundation (CHE-8305790 and DMR-8107494) and to the Southern California Regional NMR Facility (NSF Grant 7916324) for generous support of this research.

(14) From differential pulse voltammetry, the oxidation potential E_o of the free base porphyrin **3a** in CH_2Cl_2 (0.1 M TBAP) is +0.79 V vs. SSCE. The redox potential for the reduction of the quinone **3a** is -0.64 V vs. SSCE. From the singlet excitation energy (W^*) of 1.98 eV we calculate the driving force for the forward electron transfer to be $\Delta G \sim 0.55$ V from $-E_o(\text{P/P}^+) + W^*(\text{P/P}^+) + E_o(\text{Q/Q}^-)$. For ZnPLQ **3b**, $E_o(\text{P/P}^+) = +0.54$ V, $E_o(\text{Q/Q}^-) = -0.64$ V vs. SSCE, $W^* = 2.15$ eV and $\Delta G = +0.97$ V. We thank Professor F. Anson and Dr. M. Sharp for generous assistance in carrying out the electrochemical measurements.

Silicoaluminophosphate Molecular Sieves: Another New Class of Microporous Crystalline Inorganic Solids

Brent M. Lok,* Celeste A. Messina, R. Lyle Patton, Richard T. Gajek, Thomas R. Cannan, and Edith M. Flanigen

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

Received June 29, 1984

The well-known classes of molecular sieves comprise the aluminosilicate zeolites,¹ including phosphorus-substituted aluminosilicates,^{2,3} the microporous silica polymorphs,⁴ and the recently discovered aluminophosphate molecular sieves.⁵ Now another novel class of crystalline microporous framework oxide molecular sieves, the silicoaluminophosphates, has been synthesized.⁶ These new materials have properties both of zeolites and of aluminophosphates yet are unique in many ways. They should find uses as adsorbents for separation and purification of molecular species, as catalysts or catalyst supports, and as ion-exchange agents.

The new family of silicoaluminophosphate materials (SAPO-n)⁷ exhibits structural diversity with some 13 three-dimensional microporous framework structures known to date. These include novel structures, SAPO-40, SAPO-41, and SAPO-44, structures topologically related to the zeolites, chabazite (SAPO-34), levynite (SAPO-35), faujasite (SAPO-37), and A (SAPO-42), structures topologically related to the novel structure types found in the aluminophosphates, including SAPO-5, SAPO-11, SAPO-16, and

SAPO-31,⁵ and topological relatives of structures found in both zeolites and aluminophosphates, erionite (SAPO-17) and sodalite (SAPO-20).

Members of the new class of molecular sieves are synthesized hydrothermally, as are the synthetic zeolites and aluminophosphates. The materials crystallize at 100–200 °C from reactive mixtures containing organic amine or quaternary ammonium templates (R) which are retained within the products. Reactive alumina, phosphate, and silica sources, such as hydrated aluminum oxide, phosphoric acid, and silica sol, were used in synthesis. The species R appears essential to the synthesis of these novel phases since in its absence amorphous or dense crystalline materials form.

The silicoaluminophosphates encompass a wide compositional range of $0-0.3\text{R} \cdot (\text{Si}_x\text{Al}_y\text{P}_z)_2\text{O}_2$ in the anhydrous form, where x , y , and z represent the mole fractions of silicon, aluminum, and phosphorus and range from 0.01 to 0.98, 0.01 to 0.60, and 0.01 to 0.52, respectively, with $x + y + z = 1$.

Table I lists the SAPO species, the templates used in their synthesis, and the structure type determined from X-ray powder diffraction patterns. The template-structure relationships observed in the aluminophosphate molecular sieves^{5,9} are again found here. SAPO-17 and SAPO-20 are formed in the presence of the templates quinuclidine and tetramethylammonium ion, respectively, as were the aluminophosphates AlPO_4 -17 and AlPO_4 -20. However, the presence of silica in the reaction mixture also influences structure formation. For example, the tetraethylammonium ion is a template for AlPO_4 -5 and AlPO_4 -18 in the aluminophosphates but produces SAPO-34, a chabazite-type structure, in the silicoaluminophosphate system. Tetrapropylammonium ion, tetrabutylammonium ion, and cyclohexylamine yield novel silicoaluminophosphate structure types which were not reported in the aluminophosphate family.

Most three-dimensional silicoaluminophosphates exhibit excellent thermal and hydrothermal stabilities. All remain crystalline after the 400–600 °C calcination necessary to remove the organic template and free the intracrystalline-void volume for adsorption or catalysis. Like aluminophosphates, most of the silicoaluminophosphates retain their structures at 1000 °C in air and at 600 °C under 20% steam.

The silicoaluminophosphate molecular sieves have intracrystalline pore volumes (H_2O) from 0.18 to 0.48 cm^3/g and adsorption pore diameters from 0.3 to 0.8 nm, spanning the range of pore volumes and pore sizes known in zeolites and in silica and aluminophosphate molecular sieves. The uniform pore dimensions defined by the crystal structure enable the use of these new materials for size- and shape-selective separations and catalysis. Properties of selected SAPO molecular sieves are given in Table I.

There are two very small pore (six-membered ring) molecular sieves, SAPO-16 and SAPO-20, which admit only small molecules such as water and ammonia. The silicoaluminophosphates that admit normal paraffins and exclude isoparaffins with eight-ring pore openings of about 4.3 Å are SAPO-17, SAPO-34, SAPO-35, SAPO-42, and SAPO-44.

SAPO-11, -31, -40, and -41 are intermediate to large in pore size. Both SAPO-11 and SAPO-41 more readily admit cyclohexane (kinetic diameter, 6.0 Å) than 2,2-dimethylpropane (kinetic diameter, 6.2 Å). SAPO-31 and SAPO-40 adsorb 2,2-dimethylpropane but exclude the larger triethylamine (kinetic diameter, 7.8 Å). The pore sizes of these structures are defined by either open 10-rings as in silicalite (6 Å) or puckered 12-rings, with 12-rings most probable for SAPO-31 and -40. The largest pore structures include SAPO-5 and SAPO-37, which have known structural analogues with circular 12-ring pore openings.

SAPO molecular sieves have tetrahedral oxide frameworks containing silicon, aluminum, and phosphorus. Mechanistically, we can consider their composition in terms of silicon substitution into hypothetical aluminophosphate frameworks. The substitution can occur via (1) silicon substitution for aluminum, (2) silicon substitution for phosphorus, or (3) simultaneous substitution of

(1) Breck, D. W. "Zeolite Molecular Sieves"; Wiley: New York, 1974.

(2) Flanigen, E. M.; Grose, R. W. *Adv. Chem. Ser.* 1971, No. 101, 76–101.

(3) Artioli, G.; Pluth, J. J.; Smith, J. V. *Acta Crystallogr., Sect. C* 1984, C40, 214–217.

(4) For example, Silicalite: Grose, R. W.; Flanigen, E. M. U.S. Pat. 4061 724, 1977. Flanigen, E. M.; Bennett, J. M.; Grose, R. W.; Cohen, J. P.; Patton, R. L.; Kirchner, R. M.; Smith, J. V. *Nature (London)* 1978, 271, 512–516.

(5) (a) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* 1982, 104, 1146–1147. (b) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. "Intrazeolite Chemistry"; The American Chemical Society: Washington, DC, 1983; pp 79–106.

(6) Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannan, T. R.; Flanigen, E. M. U.S. Pat. 4440 871, 1984.

(7) The acronym SAPO is derived from $(\text{Si}_x\text{Al}_y\text{P}_z)_2\text{O}_2$. The suffix "n" denotes a specific structure type.

(8) Bennett, J. M.; Cohen, J. P.; Flanigen, E. M.; Pluth, J. J.; Smith, J. V. "Intrazeolite Chemistry"; The American Chemical Society: Washington, DC, 1983; pp 110–118.

(9) Lok, B. M.; Cannan, T. R.; Messina, C. A. *Zeolites* 1984, 3, 282–291.