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Guest/Host Relationships in the Synthesis of Large Pore Zeolite SSZ-26 from a Propellane Quaternary Ammonium Compound

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Abstract: Quaternary ammonium compounds based upon propellane ring systems [*n*.3.3.0] were prepared for use as guest molecules in molecular sieve synthesis. The objective was to create microporous systems with intersecting pores greater than 7 Å. Using 8,11-diquaternary ammonium derivatives of the [4.3.3.0]propellane, a new crystalline phase was obtained, an aluminosilicate, SSZ-26. Two distinct isomeric organic salts were successful. Template I (one of the isomers) crystallized from acetonitrile/H_2O in the orthorhombic space group $P2_12_12_1$ with a = 9.573 (6) Å, b = 13.875 (7) Å, c = 16.912 (9) Å (at 130 K), and Z = 4. Template III crystallized from H_2O in the monoclinic space group $P2_1/n$ with a = 14.681 (4) Å, b = 12.172 (6) Å, c = 14.613 (4) Å, β = 103.79 (2) Å (at 130 K), and Z = 4. The zeolite product SSZ-26 was characterized by microporosity measurements and catalytic cracking. All data are consistent with a material with pores >7 Å and a multidimensional channel system.

Inorganic molecular sieves are finding ever-broadening applications in chemical catalysis and separation.[1] Much of the utility of these materials, traditionally aluminosilicates (zeolites) and more recently aluminum phosphates, comes from the shape-selectivity they impart to catalytic reactions.[2] The known materials have pore apertures ranging from 3–10 Å and very high surface areas (300–800 m^2/g). Therefore, a large number of organic molecules can be selectively transformed. Most of the materials are stable to at least 600 °C, yielding considerable temperature flexibility for their use as catalysts.

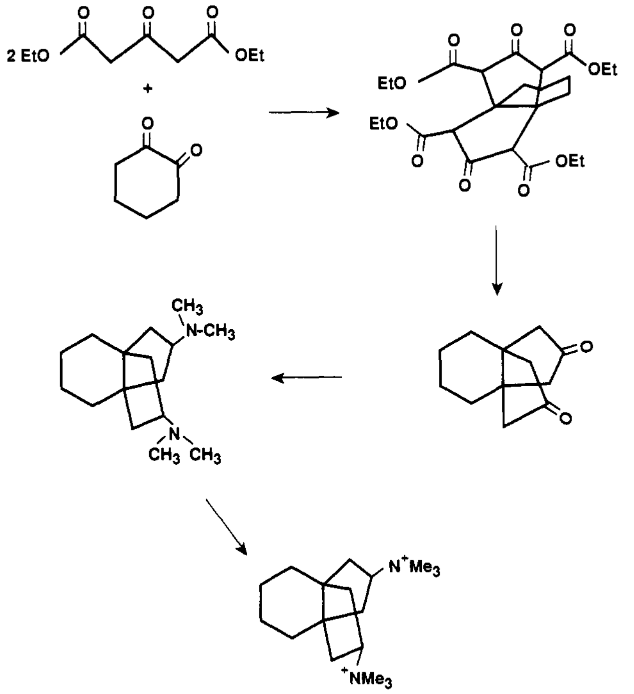
The search for new molecular sieve structures continues based upon a consideration that each new structure may provide enhanced selectivity for an industrial chemical process (i.e., hydrocracking,[3] *p*-xylene isomerization,[4] cumene synthesis,[5] arylamine synthesis,[6] syngas on to gasoline,[7] and so on). Much of the proliferation of inorganic molecular sieves has come from their hydrothermal synthesis in the presence of space-filling polar organic guests. Although each unique organic polar guest does not necessarily generate a novel inorganic host structure (some restrictions are imposed on bonding possibilities for the host structures), the synthesis of new guest molecules has been fruitful in leading to new molecular sieves. Because of charged interactions between the guest and the anionic host structure, most polar guest molecules have come from quaternary ammonium compounds, or amines with p*K*a's high enough to experience some protonation at the basic pH values of aluminosilicate zeolite synthesis. Charge also provides enough polarity to solvate these molecules in reactions of relatively high ionic strength. Aluminophosphates crystallize in a range of slightly acidic to slightly basic conditions (pH 3–8) and can utilize a broader range of amines.

Only a few molecular sieves are known with both large pores and pore systems which intersect. This type of pore system can increase resistance to fouling and allow reactants to diffuse more readily through the crystal lattice. Two such structures have proved to be of commercial value. Y zeolite[8] is the mainstay of cracking catalyst inventory.[9] β zeolite[10] is of value in a variety of emerging process technologies including isomerization dewaxing under mild hydrocracking conditions.[11] With this knowledge we wanted to synthesize a template or guest molecule which could produce a novel molecular sieve with large, intersecting pores. A new structure should have unique catalytic selectivity. In this report we describe the use of a propellane template to synthesize zeolite SSZ-26,[12] a novel phase found in the aluminosilicate regime.

Experimental Section

A. Organic Synthesis. The synthesis of *N,N,N,N′,N′,N′*-hexamethyl-8,11-[4.3.3.0]dodecane diammonium diiodide is described in ref 12. The product is a potential mixture of isomers arising from the use of a reductive amination via a Leuckart reaction[13] on the 8,11-dione of the same skeleton.[14] (See Scheme I.) Careful recrystallization from methanol separates the diquaternary isomers from the chief impurity, the

Scheme I. Synthetic Sequence for Propellane Synthesis



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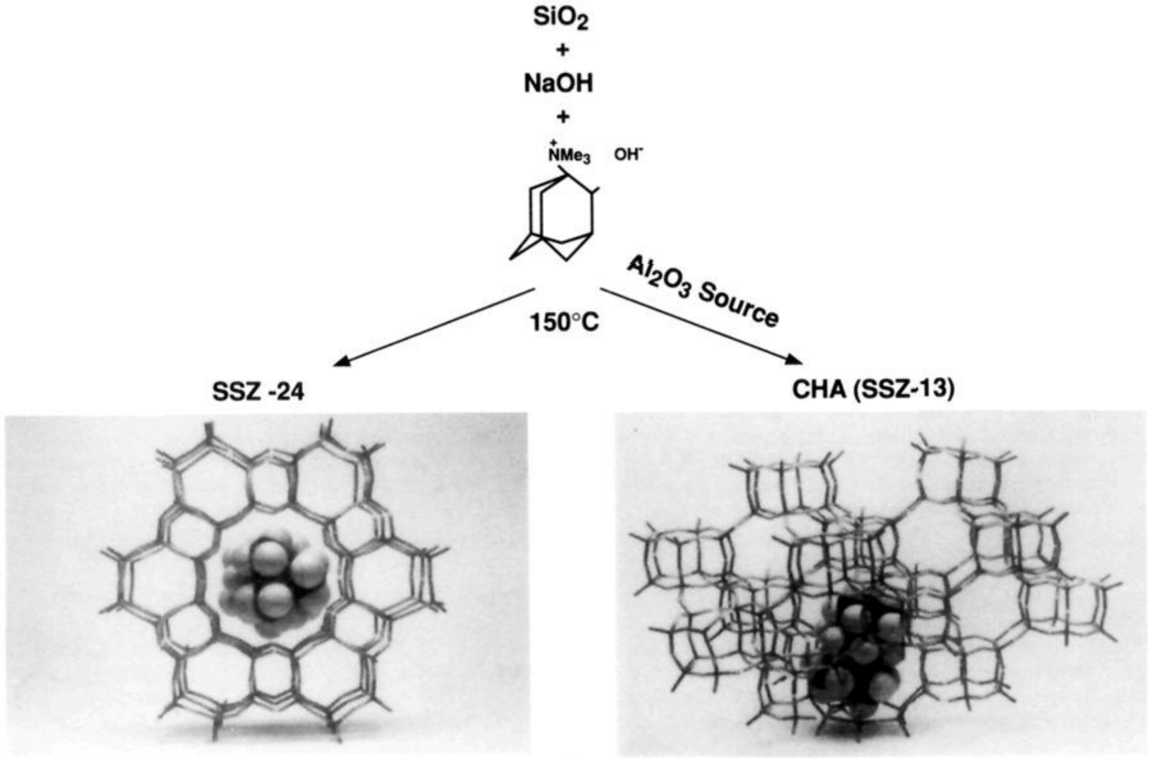

Figure 1. Crystalline zeolite phases obtained from an adamantane organocation as inorganic parameters are changed. Introduction of aluminum produces cavities rather than parallel channels.

monoquaternary ammonium iodide. Two diquaternary ammonium isomers were isolated by recrystallizing the mixed product from either a 90/10 solvent of acetonitrile/H_2O or ethanol/H_2O. (The single crystal work on the latter was done on a specimen from H_2O alone.) Both isomers give correct microanalyses and melting points of 304 °C.

1-Azonia[3.3.3.0]undecane chloride was purchased from Aldrich Chemical Company. A synthesis has been described as well.[15] *N*,*N*′,*N*″-trimethyl-3,7,10-triaza[3.3.3.0]undecane was synthesized according to the method of Knowles et al.[16] Conformations of charged species have been described by Ginsberg et al.[17]

B. Single-Crystal X-ray Data Collection, Solution, and Refinement of Structures. X-ray Conformational Analysis of Organocations. Crystals of template I (the diquaternary ammonium propellane from ETOH/H_2O) were coated with a light hydrocarbon oil to prevent cracking upon exposure to air. The crystal was mounted on a glass fiber with silicon grease and placed in the nitrogen cold stream of a Siemens R3m/V diffractometer equipped with a locally modified Enraf-Nonius low temperature apparatus. Crystals of template III (from acetonitrile/H_2O) were handled in a similar manner, with the data being collected on a Syntex $P2_1$ diffractometer and the cooling accomplished with a locally modified LT-1 low temperature apparatus. Both data sets were collected at 130 K.

Only random fluctuations of <2% in the intensities of two standard reflections were observed during the course of data collection on template I, while template III exhibited a 3.5% decay. The latter data were scaled to compensate for the observed decay. The structures were solved by direct methods and refined using full-matrix, least-squares methods.[18] Hydrogen atoms bonded to the carbon atoms were included at calculated positions using a riding model, with C–H of 0.96 Å and fixed isotropic thermal parameters. An absorption correction was applied using Program XABS.[19] In the final cycles of refinement, non-hydrogen atoms were assigned anisotropic thermal parameters. The largest feature on a final difference map was 1.27 e $Å^{-3}$ in height for template I and 1.71 e $Å^{-3}$ for template III; in each case this density was close to an iodide. Crystal data and additional data collection and refinement parameters are summarized in Table I. Final positional parameters, anisotropic thermal parameters, calculated hydrogen positions, and listings of observed and calculated structure factors have been included as supplementary material.

C. Zeolite Synthesis and Characterization. SSZ-26 was synthesized as described in a U.S. patent,[12] and subsequent calcination and ion-exchange steps were also described in that reference. (See supplementary material.) β zeolite,[10] ZSM-5,[20] and SSZ-24[21] were synthesized according to the literature. Y zeolite was purchased as LZ Y82 or Y52 from Union Carbide Corporation. All zeolites were analyzed by X-ray diffraction using Cu Kα and a Siemens powder diffractometer.

D. Adsorption. The use of a pore probe apparatus to measure the steady concentration of various hydrocarbons in zeolite pores (equilibrium dynamic, competitive) was described by Santilli.[22] The data obtained for various zeolites was at 125 °C. Determination of pore-filling for liquid nitrogen was determined on a Micromiretics instrument. Data were obtained by the BET method.[23] Micropore volumes for 2,2-dimethylbutane were determined on a vacuum line system at $P/P_0 = 0.148$ and 23 °C. All hydrocarbons were greater than 99% pure and used as received.

E. Catalysis. Zeolite catalysts were studied in a downflow reactor at atmospheric conditions using He as carrier gas and hydrocarbon feed delivered by dual injection Brownlee pumps. The zeolite catalysts were tableted, crushed, and meshed to 20–40 grade. The catalyst was loaded in a stainless steel reactor with glass wool on either side of the bed. HCL-washed inert alundum was packed above the bed, and a thermocouple supporting the catalyst charge came below. The catalyst was dried at 1000 °F before cooling to the run temperature. The feed was passed through the catalyst bed at $WHSV^{-1} = 0.68$. Products were periodically analyzed by means of an in-line gas chromatographic loop with analysis carried out on a capillary column in a Hewlett-Packard GC. The detector was FID.

F. Spectroscopy. Proton NMR studies were performed in D_2O for the isomeric templates using a GE 300 Instrument. Magic angle spinning

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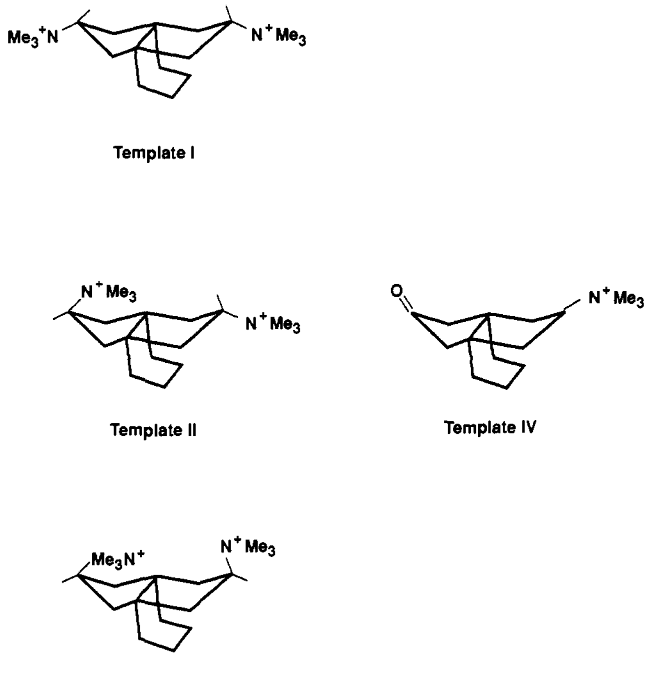
Table I. Abridged Summary of Data Collection, Structure Solution and Refinements for Templates I and III

	I	III
formula	$[C_{18}H_{36}N_2]^{2+}2I^{-}\cdot H_2O$	$[C_{18}H_{36}N_2]^{2+}2I^{-}\cdot 4H_2O$
fw	552.3	606.3
T, K	130	130
cryst system	orthorhombic	monoclinic
a, Å	9.573 (6)	14.681 (4)
b, Å	13.875 (7)	12.172 (6)
c, Å	16.912 (9)	14.613 (4)
α, deg		
β, deg		103.79 (2)
γ, deg		
V, Å^3	2239 (2)	2536.1 (16)
space group	$P2_12_12_1$	$P2_1/n$
Z	4	4
$D_{(calc)}$ Sm/cm^3	1.64	1.567
λ	Mo Kα	Mo Kα
linear absorb. coeff	2.785 mm^{-1}	2.473 mm^{-1}
2θ range, deg	0.0–55.0	0.0–50.0
obsd redl	2643 ($F > 4.06(F)$)	3626 ($F > 4.06(F)$)
no. of params refined	208	232
R, R_w	0.045, 0.059	0.0369, 0.0388



Template I

Template II

Template IV

Template III

Figure 2. Organocations produced in the reductive amination of the 8,11-[4.3.3.0]dodecanedione.

NMR studies of the as-made zeolites were carried out on a Bruker 300 using established spinning parameters.[24]

Results and Discussion

A. Propellane Choice and Synthesis. Most molecular sieves do not contain both large pores and an intersecting channel system. There is a virtual competition during the hydrothermal synthesis to produce either open continuous parallel channels, or cavities which can be large but are only connected by small windows into adjacent cavities. For example, the oblong, rigid N,N,N-trimethyl-1-adamantylammonium cation can produce either type of zeolite depending upon inorganic parameters and synthesis conditions.[25] Figure 1 compares these structural examples.

More generally, whole groups of diquaternary ammonium compounds with a major linear axis will produce one-dimensional channels. Smaller, cyclic and polycyclic, saturated hydrocarbon-based guests often yield cavity type materials. Our effort was aimed at disrupting the linear orientation in such a way that a channel intersection might be introduced. We thought D_{3h} symmetry might be helpful in a prospective guest molecule. Propellane molecules seemed good candidates.

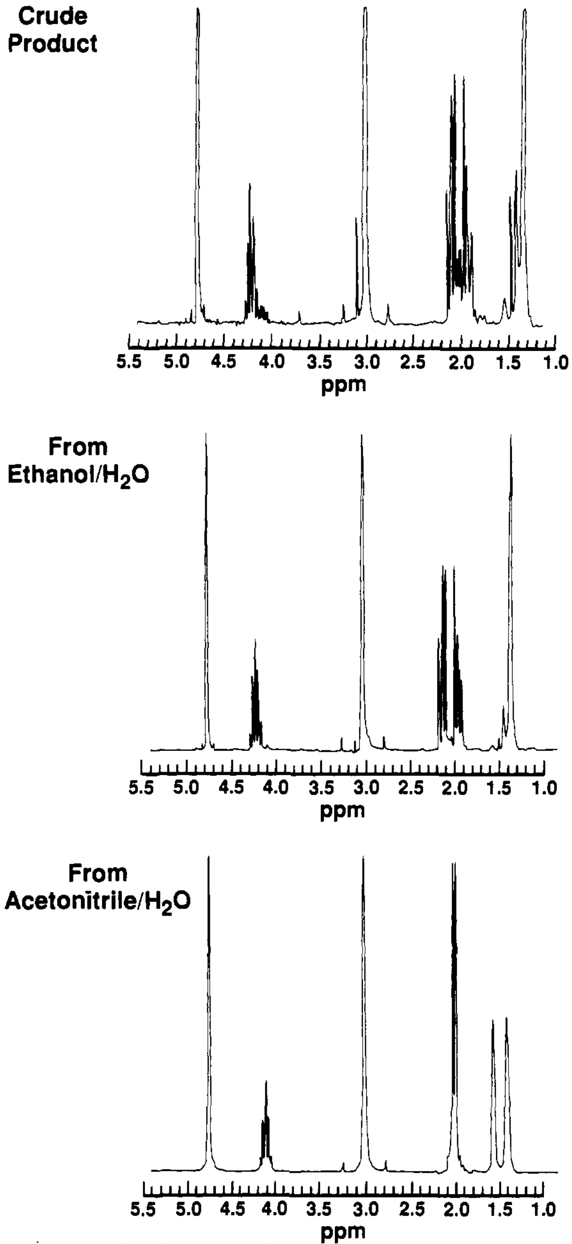


Figure 3. Proton NMR spectra for (a) the mixture of diquaternary propellane isomers, (b) template I (see Figure 2), and (c) template III.

Y zeolite crystallizes with a high aluminum content and requires no organic guest at all. β zeolite was first discovered using tetraethylammonium cation which actually does not exhibit a high structure/fit correlation. This organocation can also be used as a guest molecule for several other molecular sieve syntheses.[26-28] Although β zeolite is produced with the pores essentially filled with this organocation, the spacial role the latter plays in the zeolite synthesis has yet to be elaborated. So the previous two multidimensional large pore zeolites had not been discovered by using a designed guest or template component.

Returning to the propellane strategy, a simple starting point, using the Weiss–Cook reaction,[29] was described by Ginsberg[14]

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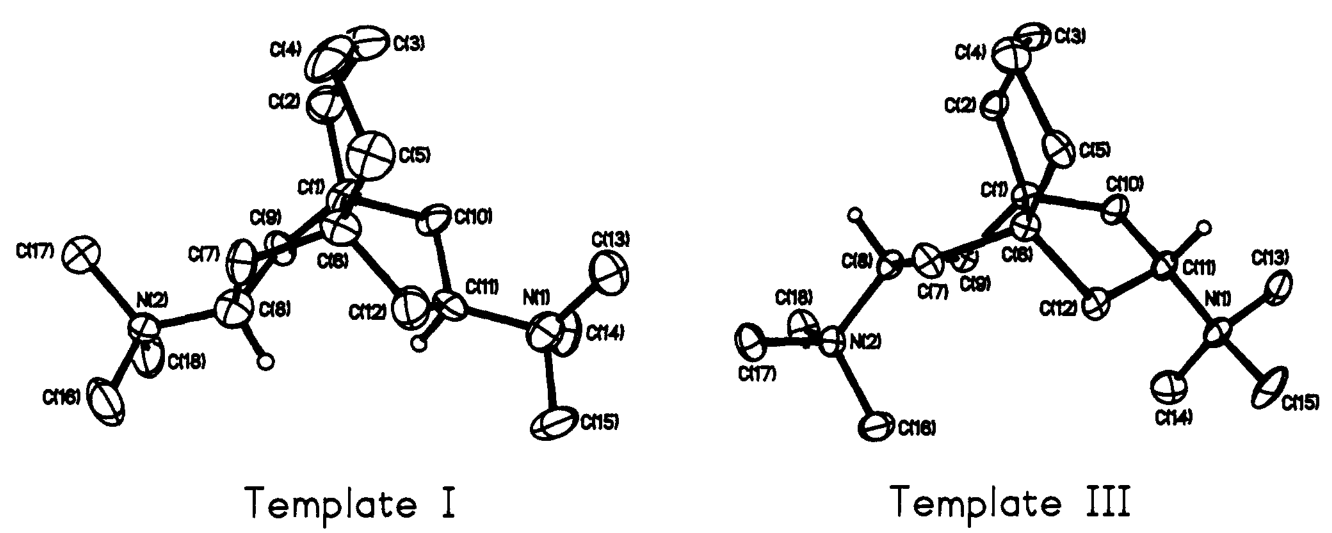

Template I

Template III

Figure 4. Comparison of conformations of templates I and III from X-ray crystal data.

and produced a [4.3.3.0]dodecanedione with at least pseudo C_{2v} symmetry. We converted the dione to the diquaternary ammonium compound. Scheme I shows the synthetic steps. Because of the particular reductive amination route chosen by us, three isomeric products (I–III in Figure 2) were possible.

By varying mixed polar solvent systems we were able to separate some of the isomeric possibilities by recrystallization. Figure 3 shows the NMR spectra for the mixture and the products isolated from an acetonitrile or ethanol-based system. X-ray diffraction was carried out on each separate isomer. Table I gives a summary of the parameters for structure determination.

Figure 4 shows a comparison of the conformations of isomers, templates I and III. Surprisingly, whether the conformations are syn,syn or anti,anti, the nitrogen–nitrogen charged center distances are not too different. This appears to result from different puckering conformations for the five-membered ring (C_6–C_9) in each structure. The distance from charged nitrogen to C_3–C_4 in the cyclohexyl ring is also not much changed in the two conformations. The similarity of conformations may be why each pure isomer is capable of producing SSZ-26 in the zeolite synthesis. For both isomers one can imagine the necessity of a branched pore system to accommodate the three ring structures built on the C_1–C_6 axis in the propellane.

Figure 5 shows the unit cell packing for template III. It is interesting to note the arrangement of H_2O molecules as a layer with the propellane diquaternary ammonium molecules arranged end-to-end in a sheet.

Template IV (Figure 2) a byproduct of the synthesis, is not able to produce the desired product, however. This demonstrates the importance of both trimethylammonium sites on the polycyclic skeleton.

B. Molecular Sieve Synthesis. While it is generally known that the most open structure will form at the lower synthesis temperatures, this system is an exception requiring temperatures above 150 °C. By contrast, the FAU structure (Y zeolite) can be crystallized below 100 °C and is difficult to stabilize above 100 °C for long periods; it also has only hydrated sodium cations as guest molecules. β zeolite requires temperatures closer to 150 °C and both β zeolite and SSZ-26 are considerably richer in SiO_2, which is also probably a factor in the need for higher synthesis temperatures. SSZ-26 crystallizes at 160 °C after several days.

The SSZ-26 product forms most easily in the SiO_2/Al_2O_3 range of 20–50. Useful synthetic ratios are $N^+/SiO_2 = 0.15$, $Na/Si = 0.15$, $H_2O/Si = 27$, and $OH^-/Si = 0.30$. The product contained 11.4 wt % carbon and 1.4% nitrogen. The molar C/N value of 9.4 is slightly higher than the expected value of 9.0 for the propellane. ^{13}C MAS-NMR of SSZ-26 also shows that the guest organocation is probably intact (Figure 6). Previously, it had been demonstrated in some zeolite syntheses that the molecular sieve product is formed from byproducts of degradation of the organocation via the Hofmann elimination route.[25] The product made from template III shows a greater number of carbon lines which may be consistent with the lowered symmetry because of conformational differences for the two five-membered rings (see Figure 4).

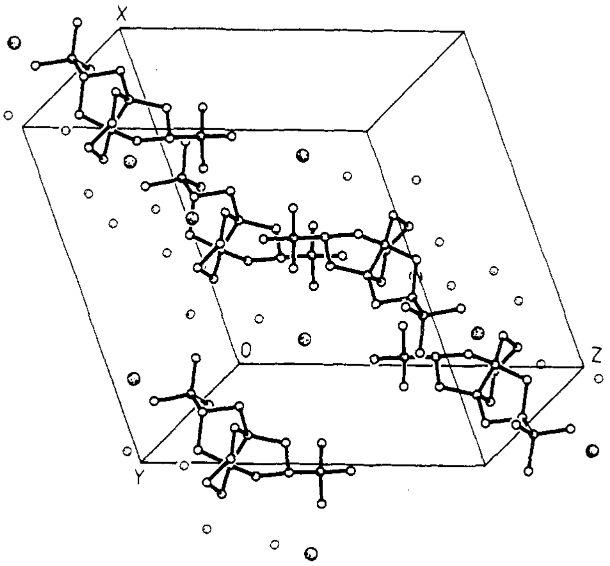

Figure 5. Unit cell packing of template III including water molecules associated with the crystal.

The product is crystalline as determined by powder X-ray diffraction. Figure 7 shows diffraction patterns for both the organic-containing and organic-free SSZ-26. They are unique when compared with patterns for known molecular sieve materials.

C. Molecular Sieve Properties. 1. Adsorption. The molecular sieve features of the crystalline product can be explored once the guest molecule is removed. In general, in most molecular sieve reactions the polar guest molecules are trapped, even in open pore systems. Thermal decomposition up to 600 °C yields a stable, inorganic SSZ-26 molecular sieve. Figure 7 shows that the positions of reflections are not much changed by heating to this temperature. Any residual sodium cations can be removed by heating the zeolite in an aqueous solution of ammonium nitrate. A subsequent thermal treatment decomposes the NH_4^+ cations leaving only protons to balance charge in the zeolite.

The mass loss on calcination is about 20 wt %, consistent with a pore system running in more than one dimension. Losses are closer to 10 wt % for one-dimensional systems. Even one-dimensional systems with enlarged cavities usually do not exceed

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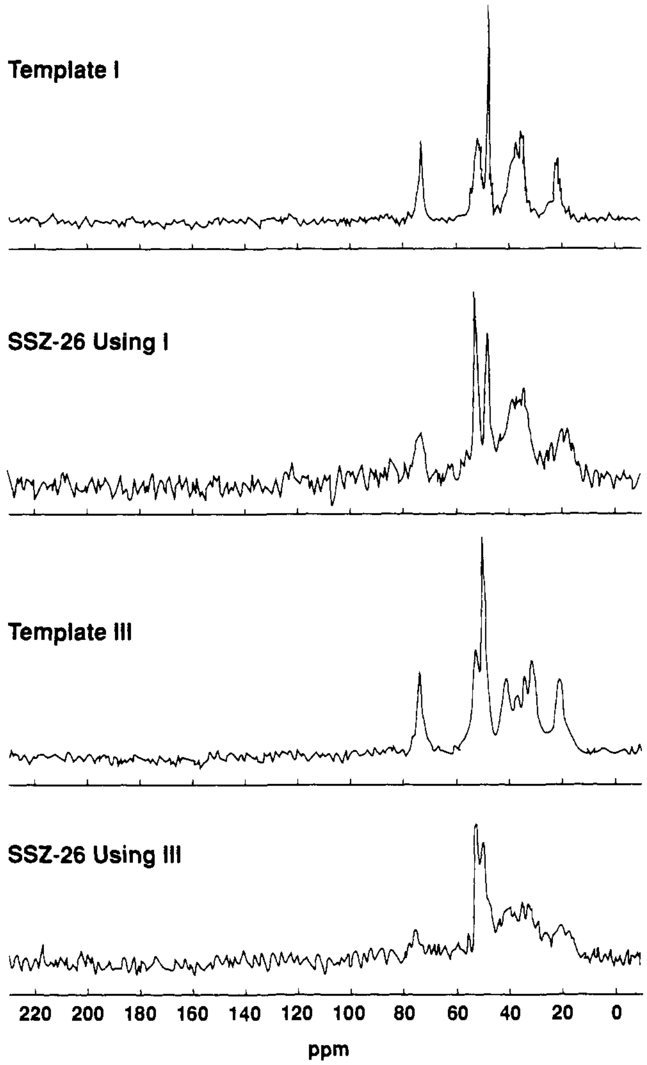

Figure 6. Carbon-13 NMR spectra (magic angle spinning) for the organocations in the solid state and then as incorporated into the crystalline zeolite.

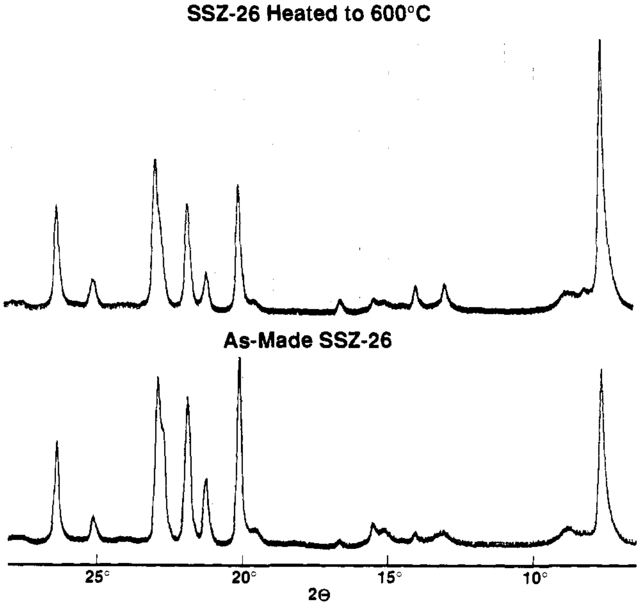

Figure 7. X-ray diffraction patterns for the organozeolite SSZ-26 and for the calcined zeolite.

Table II. Micropore Filling in Zeolites[a]

zeolite	*n*-hexane	3-methylpentane	2,2-dimethylbutane	total[b]	N_2[c]
Y	38	37	26	101	0.27
β	57	37	20	114	0.25
SSZ-26	31	22	18	71	0.19
SSZ-24	12	15	26	53	0.12
ZSM-5	25	7	5	37	0.14

[a] Conditions: feed = 1:1:1 *n*-hexane:3-methylpentane:2,2-dimethylbutane; feed rate was 17 μL/min at 1 atm with the helium carrier gas = 20 mL/min. Feed is run until steady state filling is observed. [b] μg/g molecular sieve at 125 °C. [c] cc/gm molecular sieve.

Table III. Micropore Filling by 2,2-Dimethylbutane in Zeolites

zeolite	cc/g (at $P/P_0 = 0.148$)	zeolite	cc/g (at $P/P_0 = 0.148$)
Y-52	0.24	SSZ-26	0.20
β	0.27	SSZ-24	0.11

Table IV. Catalytic Cracking of 50/50 *n*-Hexane/3-Methylpentane by Acidic Zeolites at 600 °F[a]

zeolite	time onstream (min)	conversion	SiO_2/Al_2O_3
Y	10	85	5
β	10	>99	25
SSZ-26	10	>99	22
SSZ-24	10	70[b]	100
ZSM-5	10	50	70

[a] Atmospheric pressure with feed delivered at 0.68 WHSV-1 with He as carrier (20 mL/min). [b] Data for 700 °F.

15 wt %. Table II shows the micropore filling for SSZ-26 using a mixture of three C_6 isomers. The values are the steady state quantities of the three isomers in the pores of SSZ-26. Also shown for comparison are the values for Y, β, ZSM-5, and SSZ-24 zeolites. Micropore volumes for nitrogen are also shown.

ZSM-5 zeolite has interconnecting channels, but they are smaller (5.5 Å)[30] than in the other zeolites shown. SSZ-24 has the AFI structure[31] and pores ~7.5 Å. 2,2-Dimethylbutane is freely admitted, but the pores run in only one dimension so the total micropore is slightly lower than even ZSM-5. An important discovery is that considerable amounts of 2,2-dimethylbutane go into SSZ-26. This shows that at least one pore system is large (i.e., 12 ring aperature).

A key question is whether the large pore runs in more than one dimension in SSZ-26. Table III gives pore filling at $P/P_0 = 0.148$ for several large pore zeolites with 2,2-dimethylbutane alone.[32] ZSM-5 does not adsorb this component under these conditions. Now it is more clearly seen that the large pore, micropore capacity of SSZ-26, is almost double that of the one-dimensional SSZ-24.

2. Catalytic Cracking Activity. Zeolites as a group of molecular sieves are highly active cracking catalysts with the activity showing some relationship to the number of aluminum lattice substitution centers.[33] As such, SSZ-26 was expected to be quite active, and the conversion of a 50/50 weight *n*-hexane/3-methylpentane feed demonstrated this. Table IV shows conversion at 600 °F as the catalyst first comes onstream. Comparison with other zeolites under discussion is also given. As can be seen, the cracking activity of SSZ-26 was at least as great as β zeolite. The high activity for both catalysts is consistent with the large pores and optimal SiO_2/Al_2O_3 ratios of 20–30.

D. Evidence for a Multidimensional Channel System in SSZ-26. Our experimental design was to produce a template molecule which would lead to developing a multichannel host lattice. In

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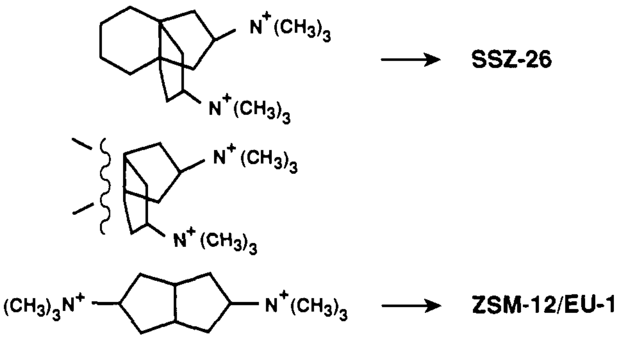

Figure 8. Structure of the diquaternary ammonium compound *N*,*N*,*N*,*N'*,*N'*,*N'*-hexamethyl-3,7-[3.3.0]octane. Note that the third fused ring, which defines a propellane, is missing.

the absence of having elucidated the structure of SSZ-26, can we infer that we have succeeded? Preliminary high resolution electron microscopy indicates that pores may be seen in more than one orientation.[34] We do not know yet whether there is more than one large pore system.

The most encouraging results are from adsorption. But they must be examined in view of some structual data which can be gleaned from X-ray powder data. The largest reflection observed for SSZ-26 is at $2\Theta = 7.8°$ (Figure 7) at a d-spacing of 11.28 Å. It might be possible to have very large adsorption data and unidimensional channels in a material with very large pores such as the 18 rings found in VPI-5.[35] But then d-spacings are larger, 16.1 Å in that case. The largest d-spacing in SSZ-26 is much more consistent with a 12-ring aperture.

Given the micropore volume of 0.20 cc/gm for 2,2-dimethylbutane (this same value is also obtained for cyclohexane) it cannot be rationalized that the microporosity is entirely due to one set of 12 ring channels. The data for such a material, SSZ-24, gives only about 60% as much micropore filling. What about side pockets or larger cavities off a main channel? EU-1 is a one-dimensional channel system with large side pockets.[36] The reported micropore filling for this zeolite, using *n*-hexane, is 0.15 cc/gm.[37] The micropore volume is still 25% less than for SSZ-26. It would also seem that side pockets or cavities cannot get too much larger within a structure before they protrude into other cavities making a multidimensional pore system. The framework density for EU-1 is about 18 TO_2/1000 Å^3. The ZSM-5 zeolite also has a micropore volume of close to 0.15 cc/gm for adsorbates and a TO_2 framework density[30] of 17.9/1000 Å^3. ZSM-5 is a multidimensional channel system of 10-ring apertures. Mordenite has a 12-ring pore system with distorted 8-ring cross channels. Its framework density[30] is 17.2 TO_2/1000 Å^3. Given the 25% micropore volume increase for hydrocarbons for SSZ-26 over EU-1 or ZSM-5, its framework density must be significantly lower. Considering the properties of mordenite, the SSZ-26 must have a larger cross channel system off a main 12 ring. Because the micropore volume of 2,2-dimethylbutane is as large as it is for nitrogen, it seems most likely that a second channel system in SSZ-26 must also be a 12-ring pore.

E. Other Propellane Guests. A choice of a particular propellane organocation has led to a new molecular sieve material. This is also the only molecular sieve product that this organocation produces. From the adsorption behavior, a large pore multidimensional network is indicated. Preliminary high resolution electron microscopy also indicates more than one pore system. The pore-filling by the organocation is also indicative of such a result. But, while the rationale for such a guest choice has been borne out in some of the results, the key factors responsible in the synthesis are not fully understood.

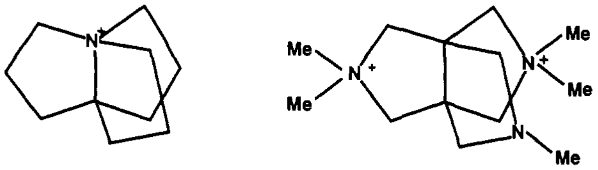

Figure 9. Two symmetric propellanes based upon aza substitution into the [3.3.3.0]undecane system.

As in previous syntheses involving large organocations, keeping a reasonably low concentration of alkali cation proved important.[25] The interplay between cation types, use of silicates, and how the resulting product forms are still being studied.[38] The importance of disrupting linear orientation in the organocation is seen in analyzing the behavior of the fused bicyclic [3.3.0] guest shown in Figure 8. This molecule is exactly the same structure as our propellane but lacking the third ring, the cyclohexyl entity. In molecular sieve synthesis this guest (mixture of isomers) produces sizeable but only one-dimensional pores in phases like ZSM-12[39] or EU-1.

On the other hand, the use of the [4.3.3.0] derivative has some paradoxes. The monoquaternary compound (template IV, Figure 3) does not produce the SSZ-26 structure. The second quaternary site is needed. But is it needed as a charge consideration, for solubility, or to produce the size of the organocation? The spatial requirements cannot be quite so rigid, because more than one isomeric conformation can be used (templates I and III, Figure 3).

A fortuitous choice may have been made in the diquaternary [4.3.3.0]propellane. Figure 9 shows two other propellanes from the more symmetric [3.3.3.0] system. The 1-azonia derivative[15] which is closer to D_{3h} symmetry produces a cage type product, SSZ-29 (isostructural with SGT).[40] The more polar 3,7,10-triaza derivative[16] is also unsuccessful in producing an open pore system. The distention of the two trimethylammonium groups in the [4.3.3.0]propellane may be vital to forming an open channel system. The function may be simply to make the guest too large to reside in a cavity. Cavity formation may be a more preferable route for the use of organocation guests and formation of silica-rich hosts at higher temperatures. Recently, large-pore aluminophosphate materials have been described which do not require organic components to stabilize the structure.[35] Under even more acidic conditions, organics are not needed in the synthesis,[41] but these reactions were carried out in acidic, phosphate-based reactions. Such open pore stabilization by water alone has not been observed for high silica zeolites formed under alkaline conditions.

Conclusion

A novel molecular sieve has been discovered using a sizeable propellane diquaternary ammonium template or guest. As in many previous syntheses, the guest molecule fills the void regions of the inorganic host crystalline phase. This is particularly true for phases formed at higher temperatures which are silica-rich. Adsorptive and catalytic measurements on the new molecular sieve support a view of large pores (>7 Å, or 12 tetrahedral atoms lining the pore) which probably run in more than one dimension. This is consistent with the design of the guest molecule. Our intention was to avoid making cavity-only sieves (some of which are termed clathrasils[42]) and sieves with one-dimensional linear pores. More than one isomeric guest configuration could produce the new sieve,

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but several other propellane candidates were not successful.

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Supplementary Material Available: Listing of crystal data, solution and refinement data, atomic coordinates, bond angles, bond lengths, and X-ray diffraction data (14 pages). Ordering information is given on any current masthead page.

Preparation and Characterization of $1,1\text{-}W_2(CCMe)_2Cl_2(PMe_3)_4$. Structural and Spectroscopic Manifestations of $\delta(MM)\text{-}\pi(CC)$ Conjugation

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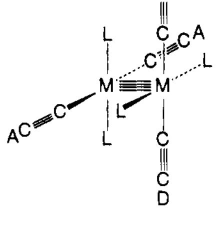
Abstract: The compound $W_2\text{-}1,1\text{-}(CCMe)_2\text{-}2,2\text{-}Cl_2\text{-}(PMe_3)_4$ (denoted $1,1\text{-}W_2(CCMe)_2Cl_2(PMe_3)_4$, **1**) has been prepared from the reaction between $W_2Cl_4(PMe_3)_4$ and LiCCMe (2 equiv). The asymmetric substitution pattern has been confirmed by X-ray crystallography (space group $P2_1/c$; $a = 15.383$ (3) Å, $b = 10.417$ (2) Å, $c = 19.038$ (4) Å, $\beta = 103.15$ (3)°, $V = 2971$ Å^3, $Z = 4$, $D_c = 1.836$ g cm^{-3}, $T = -69$ °C). The most noteworthy structural parameters of **1** are the W–C distances (2.13 Å), which are 0.19 Å shorter than those of $W_2(CH_3)_8^{4-}$; these short distances are consistent with strong $\delta(MM)\text{-}\pi(CC)$ conjugation, since only a 0.08-Å contraction is predicted from the difference between the covalent radii of sp- and sp^3-hybridized carbon. The $CCCH_3$ resonance in the ^1H-NMR spectrum of **1** is a pseudoseptet; selective ^{31}P-decoupling experiments indicate that this is the result of coupling, over five and six bonds, to the phosphorus nuclei on both metal centers, the six-bond coupling being facilitated by the $\delta\text{-}\pi$ orbital pathway. The energy and intensity of the $^1(\delta\rightarrow\delta^*)$ electronic-absorption band of **1** are also consistent with $\delta\text{-}\pi$ conjugation: the band red shifts and intensifies as the conjugated chain length increases across the series $W_2Cl_4(PMe_3)_4$ (δ) < **1** ($\delta\text{-}\pi$) < $W_2(CCMe)_4(PMe_3)_4$ ($\pi\text{-}\delta\text{-}\pi$). These results indicate that there are strong similarities among the electronic structures of these conjugated transition-metal complexes and those of analogous organic compounds.

Introduction

Conjugated molecules and polymers that contain transition metals as an integral part of their unsaturated backbones should possess electrical and optical properties that are enhanced relative to their numerous and extensively studied organic counterparts. Few such metal compounds are known,[1-3] however, and their physical properties are largely unexplored. As part of our studies directed at elucidating the electronic and structural analogies among conjugated organic and transition-metal systems,[2,3] we recently described the preparation and characterization of a series of symmetrically substituted dimetallapolyynes of the type $M_2(CCR)_4(PMe_3)_4$ (M = Mo, W; R = alkyl, aryl), for which we inferred the presence of $\pi(CC)\text{-}\delta(MM)\text{-}\pi(CC)$ conjugation from resonance-Raman and electronic-spectroscopic data.[2] In light of these findings, an interesting question is whether this $\pi\text{-}\delta\text{-}\pi$ orbital pathway will facilitate donor–acceptor interactions in differentially substituted dimetallapolyynes of the type $M(CCD)_2L_2\overset{4}{\text{—}}M(CCA)_2L_2$, where CCD and CCA are η^1-alkynyl ligands that are capped by electron donating and accepting groups, respectively; such interactions have significant structural and electronic consequences for organic polyynes.[4] Unfortunately, asymmetrically substituted, quadruply bonded compounds are rare,[5] and general synthetic routes to them have not been developed. Herein we report the synthesis of $W_2\text{-}1,1\text{-}(CCMe)_2\text{-}2,2\text{-}Cl_2\text{-}(PMe_3)_4$ (hereafter denoted $1,1\text{-}W_2(CCMe)_2Cl_2(PMe_3)_4$, **1**), an important precursor to such species, as well as new structural and spectroscopic evidence for $\delta\text{-}\pi$ conjugation that independently substantiates and significantly strengthens our earlier conclusions[2] concerning the electronic structures of dimetallapolyynes.



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