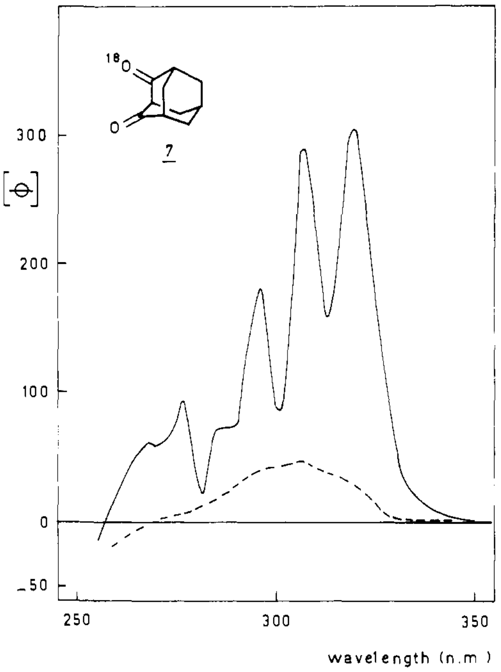

**Figure 1.** Circular dichroism spectrum (solid line) of (1*S*)-2,4-adamantanedione-*4*-$^{18}O$ (7) (concentration 2.1 g/L) in cyclohexane at room temperature.[19] The spectrum is recorded with a sample which has an enantiomeric excess of 69% and an isotopic purity of 65%. This spectrum is **not** corrected to 100% optical and isotopic purity. The dotted line represents the spectrum recorded after oxygen exchange and should be regarded as the zero base line.

Thus the spectroscopic data were obtained with a sample of **7** which had a 41 ± 3% isotopic purity. On the assumption that no change in optical purity had occurred during the entire synthesis,[14] the optical purity of **7** is identical to that of the 3*R*-acid **1**, i.e., 76 ± 3%.

The circular dichorism spectrum (Figure 1) of the optically active (1*S*)-2,4-adamantanedione-*4*-$^{18}O$ (**7**) is characterized by three bands at 320, 307, and 297 nm and small bands at lower wavelength. No immediate conclusion should be drawn about the considerable differences between the CD spectrum of **7** and that of the only other two optically active rigid 1,3-diketones,[3,15] since temperature and solvent effects can influence these spectra strongly as has been clearly demonstrated by Lightner[15] and was found for **7**.[19] It is reasonable to assume that the bands belong to different electronic transitions.[3,16,20]

In the light of the fast reaction of enol ethers with oxygen[12,17] and the high yield of 1,2-dioxetane, even when the "ene-reaction" is possible,[18] possible,[18] this synthetic route is unique and could be generally useful in the preparation of oxygen-18 ketones. The route is especially suitable for diketones in which one carbonyl is to be labeled with oxygen 18.

**Supplementary Material Available**: Physical properties and experimental details of the synthesis of **1**–**5** and **7** (5 pages). Ordering information is given on any current masthead page.

---

[13] The mass spectrum of 7 showed a percentage $^{18}O$ of 41 ± 3 one night after the preparation of 7; storage of cyrstalline 7 at room temperature in a closed ($^{16}O_2$ containing air) vessel for 72 h provided material with a mass spectrum identical with the $^{16}O$ analogue !

[14] During the entire synthesis no crystallizations were performed.

[15] Lightner, D. A.; Christiansen, G. D.; Melquist, J. L. *Tetrahedron Lett.* **1972**, 2045–2048.

[16] Spafford, R.; Baiardo, J.; Wrobel, J.; Vala, M. *J. Am. Chem. Soc.* **1976**, *98*, 5217–5225.

[17] Meijer, E. W.; Wynberg, H. *Tetrahedron Lett.* **1981**, 785–788.

[18] Asveld, E. W. H.; Kellogg, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 3644–3646.

[19] When the CD spectrum of 7 was recorded in EPA (ether, isopentane, ethanol, 5:5:2) at room temperature and at 92 K, the amplitudes of several bands had changed dramatically and bands with negative signs appeared.

[20] For an excellent recent review on isotopically engendered chirality see: Barth, G.; Djerassi, C. *Tetrahedron* **1981**, *37*, 4123–4142.

---

# Aluminophosphate Molecular Sieves: A New Class of Microporous Crystalline Inorganic Solids

Stephen T. Wilson,* Brent M. Lok, Celeste A. Messina,
Thomas R. Cannan, and Edith M. Flanigen*

*Union Carbide Corporation, Tarrytown Technical Center*
*Tarrytown, New York 10591*

*Received October 27, 1981*

A novel class of crystalline, microporous, aluminophosphate phases has been discovered that represents the first family of framework oxide molecular sieves synthesized without silica. The most widely known molecular sieves are the aluminosilicate zeolites[1] and the microporous silica polymorphs.[2] The novel aluminophosphate molecular sieves are similar to zeolites in some properties and may find many uses as adsorbents for separations of molecular species and as catalysts or catalyst supports.

The new family of aluminophosphate materials ($AlPO_4$-*n*)[3] currently includes about 20, three-dimensional framework structures, of which at least 14 are microporous and 6 are two-dimensional layer-type materials. Most of the three-dimensional structures are novel; however, three appear to be structurally related to the zeolite family, with framework topologies of the erionite/offretite type ($AlPO_4$-17), the sodalite type ($AlPO_4$-20), and the analcime type ($AlPO_4$-24).[1] One of the novel three-dimensional structures, that of $AlPO_4$-5, has been determined by single-crystal X-ray methods.[4] $AlPO_4$-5 has hexagonal symmetry with $a = 1.372$ nm and $c = 0.847$ nm and contains one-dimensional channels oriented parallel to the *c* axis and bounded by 12-membered rings composed of alternating $AlO_4$ and $PO_4$ tetrahedra. It has the framework topology of the hypothetical 4-connected three-dimensional net no. 81 (4.6.12) proposed by Smith.[5]

The novel materials are synthesized hydrothermally at 100–250 °C from reaction mixtures containing an organic amine or quaternary ammonium salt (R) which becomes entrapped or clathrated within the crystalline products of composition: $x\text{R}\cdot Al_2O_3\cdot(1.0 \pm 0.2)P_2O_5\cdot yH_2O$. The quantities $x$ and $y$ represent the amounts needed to fill the microporous voids within the neutral $AlPO_4$ framework. The species R appears to fulfill an essential templating or structure-directing role in the synthesis of these novel microporous phases since without R dense $AlPO_4$ structures or known hydrates, $AlPO_4\cdot nH_2O$, form.

The direct relationship between a templating agent and the resulting structure is illustrated in the synthesis of $AlPO_4$-17, with a proposed erionite framework topology, by using quinuclidine, neopentylamine, or cyclohexylamine. In each case chemical analysis corresponds to two template molecules per large cavity. Model building experiments indicate that (1) the three templating agents are similar in size, (2) two template molecules essentially fill the large cavity, and (3) there are no further voids in the erionite-type structure of sufficient volume to contain these templates. Similarly, tetramethylammonium hydroxide (TMAOH) templates the $AlPO_4$-20 sodalite framework topology with a template stoichiometry near 1 per sodalite cage. The spherical TMAOH molecule, with a 0.62-nm diameter, fits neatly into the sodalite cage.

Some structures are much less template specific. $AlPO_4$-5 can be synthesized with 23 different amine and quaternary ammonium compounds. The large one-dimensional cylindrical pore system perhaps imposes fewer constraints on the template fit. Because of the neutrality of the $AlPO_4$ network, the template is not needed as a charge-balancing agent; therefore, its incorporation into the structure is more a function of its size and shape relative to the channel volume to be filled.

---

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

[2] For example, silicalite: U.S. Patent 4 061 724, 1977. Flanigen, E. M.; Bennett, J. M.; Grose, R. W.; Cohen, J. P.; Patton, R. L.; Kirchner, R. M.; Smith, J. V. *Nature* **1978**, *271*, 512–516.

[3] The suffix *n* denotes a specific structure type.

[4] Cohen, J. P.; Bennett, J. M., to be submitted for publication.

[5] Smith, J. V. *Am. Mineral.* **1978**, *63*, 960–969.

0002-7863/82/1504-1146$01.25/0

Table I. Properties of Selected $AlPO_4$ Molecular Sieves

| | adsorption properties[a] | | | |
|---|---|---|---|---|
| | | | intracrystalline pore vol, $cm^3/g$ | |
| structure[c] | pore size, nm | ring[b] size | $O_2$ | $H_2O$ |
| $AlPO_4$-5 determined, novel[d] | 0.8 | 12 | 0.18 | 0.3 |
| $AlPO_4$-11 unknown | 0.61 | 10 or puckered 12 | 0.11 | 0.16 |
| $AlPO_4$-14 unknown | 0.41 | 8 | 0.19 | 0.28 |
| $AlPO_4$-16 unknown | 0.3 | 6 | 0 | 0.3 |
| $AlPO_4$-17 erionite/offretite type | 0.46 | 8 | 0.20 | 0.28 |
| $AlPO_4$-18 unknown | 0.46 | 8 | 0.27 | 0.35 |
| $AlPO_4$-20 sodalite type | 0.3 | 6 | 0 | 0.24 |
| $AlPO_4$-31 unknown | 0.8 | 12 | 0.09 | 0.17 |
| $AlPO_4$-33 unknown | 0.41 | 8 | 0.23 | 0.23 |

[a] Determined by standard McBain–Bakr gravimetric techniques after calcination (500–600 °C in air) to remove R; pore size determined from measurements on molecules of varying size (kinetic diameter from ref 1); pore volumes near saturation, $O_2$ at −183 °C, $H_2O$ at ambient temperature. [b] Number of tetrahedral atoms (Al or P) in ring that controls pore size; when structure not known, estimated from adsorption measurements. [c] Structures distinguished by their characteristic X-ray powder diffraction patterns. [d] See text.

In the two-dimensional layer structures the organic R is presumed to be intercalated between $AlPO_4$ layers. The layer structures undergo crystallographic collapse and structural rearrangement to dense phases when the interlayer organic species is removed by thermal treatment.

In contrast, many of the three-dimensional aluminophosphates exhibit excellent thermal stability. Most remain crystalline after the 400–600 °C calcination necessary to remove the organic template and free the intracrystalline void volume for adsorption or catalysis. Indeed, many retain their structure after calcination at 1000 °C. Several materials tested for hydrothermal stability show virtually no structural loss when treated with 16% steam at 600 °C.

The aluminophosphate molecular sieves exhibit intracrystalline pore volumes ($H_2O$) from 0.04 to 0.35 $cm^3/g$ and adsorption pore sizes from 0.3 to 0.8 nm, spanning the entire range of pore volumes and pore sizes known in zeolites and silica 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 $AlPO_4$ molecular sieves are given in Table I.

Some of the aluminophosphate molecular sieves are small pore materials. $AlPO_4$-20, like its zeolite analogue sodalite, is a small-pore molecular sieve that admits only water. $AlPO_4$-14 and $AlPO_4$-33 adsorb xenon (0.40 nm) but not *n*-butane (0.43 nm). $AlPO_4$-17 and $AlPO_4$-18 have a slightly larger pore size of 0.46 nm, adsorbing *n*-paraffins but excluding isoparaffins.

$AlPO_4$-11, whose structure has not yet been determined, is intermediate in pore size. It adsorbs molecules as large as cyclohexane (0.60 nm) but not 2,2-dimethylpropane (0.62 nm). This pore size is similar to that of silicalite[2] and indicates that the $AlPO_4$-11 structure contains voids bounded by 10-rings or puckered 12-rings.

Large-pore structures include $AlPO_4$-5, known to have 12-ring channels which allow adsorption of molecules at least as large as 2,2-dimethylpropane (0.62 nm). $AlPO_4$-31, with unknown structure, has a pore size like that of $AlPO_4$-5 and must also contain 12-ring pores.

Nearly all of the aluminophosphate molecular sieves with pore sizes from 0.4 to 0.8 nm (8-, 10-, or 12-rings) exhibit a characteristic adsorption pore volume for oxygen (and in some cases hydrocarbons) that is only 50–80% that of the water pore volume. This requires that their framework structures contain both large-pore voids and voids accessible through small pores (6-rings) which admit only water. In the case of the known $AlPO_4$-5 structure, the excess water volume is associated with small voids outlined by columns of twisted chains of 4-rings and 6-rings parallel to the *c* axis.[4]

Zeolites are hydrophilic due to the interaction of the dipole of the water molecule with the electrostatic fields of the anionic aluminosilicate framework and the balancing nonframework cations. The molecular sieve silicalite, with a neutral $SiO_2$ framework and no extra-framework cations, is hydrophobic. In contrast, the neutral aluminophosphate frameworks with no extra-framework cations are moderately hydrophilic, apparently due to the difference in electronegativity between aluminum (1.5) and phosphorus (2.1). They exhibit less affinity for $H_2O$ than the hydrophilic zeolites such as type A and type X zeolites yet substantially more than hydrophobic silicalite.

The aluminophosphate materials have interesting properties for potential use in adsorptive and catalytic applications, due to both their unique surface selectivity characteristics and novel structures. The discovery of this new family opens the door to a new era in molecular sieve materials.

**Acknowledgment.** We dedicate this paper to the late Donald W. Breck, a pioneer in the discovery of new molecular sieve materials, whose encouragement and chemical and structural insights supported us throughout the course of this work. We thank R. L. Patton for many fruitful discussions and critical review of the manuscript, P. A. Burtis and R. T. Gajek for their excellent technical assistance, and Union Carbide Corp. for permission to publish this article.

---

# An Unusual Ground-State Di-π-methane Rearrangement in the Thermal Isomerization of Homoazulene

Lawrence T. Scott* and Ihsan Erden

*Department of Chemistry*
*University of Nevada, Reno, Nevada 89557*

*Received November 16, 1981*

Homoazulene (**1**, 1,5-methano[10]annulene), a nonbenzenoid aromatic hydrocarbon with an extraordinarily twisted π system, has recently become available in sufficient quantity to permit extensive physical and chemical investigations.[1] Preliminary spectral analysis reveals a distinct resemblance between the electronic properties of **1** and those of azulene.[2] Our interest in the thermal rearrangements of azulene[3] and aromatic compounds in general[4] has prompted us to examine the behavior of **1** at elevated temperatures. Some unusual transformations have been discovered, including one which appears to represent the first example of a ground-state di-π-methane rearrangement (Scheme II).

Flash vacuum pyrolyses (FVP) were conducted in a 10-cm vertical quartz tube (12-mm i.d.) at ca. 0.01 torr. At 300 °C, homoazulene passed through unchanged. Such thermal stability was not anticipated. At 435 °C, five isomeric products were formed in high overall yield (reaction 1), although a small amount of **1** still survived even at this temperature. Phenylcyclopentadienes **2** and **3** have been reported previously and interconvert by 1,5-hydrogen shifts at temperatures well below 435 °C.[5] Their presence in the pyrolysate was obvious from the $^1H$ NMR spectrum; however, further confirmation was obtained by GC

---

(1) (a) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I., *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 274–279. (b) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216–5220. (c) For an earlier synthesis, see: Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, 3239–3240. (d) For a discussion of the geometry of **1**, see: Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893–3907.

(2) Scott, L. T., unpublished results. See also ref 1b.

(3) Scott, L. T.; Kirms, M. A.; Minton, M. A. *Croat. Chem. Acta* **1980**, *53*, 643–647; Scott, L. T.; Kirms, M. A.; Minton, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 5875–5879.

(4) Scott. L. T. *Acc. Chem. Res.*, in press.

(5) Riemschneider, R.; Nehring R. *Monatsh. Chem.* **1960**, *91*, 829–835. Wahren, R., *J. Organomet. Chem.* **1973**, *57*, 415–422. See also ref 10d.

0002-7863/82/1504-1147$01.25/0