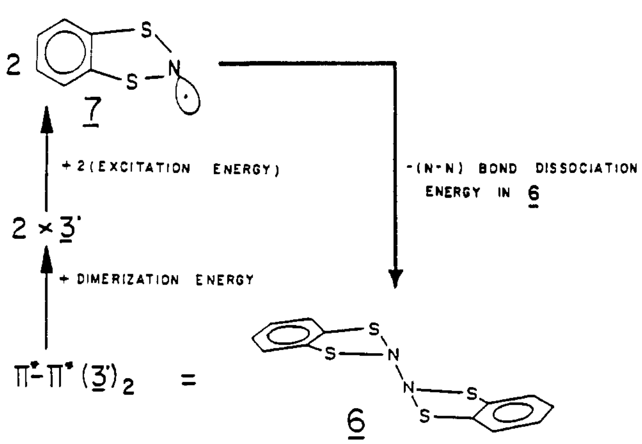
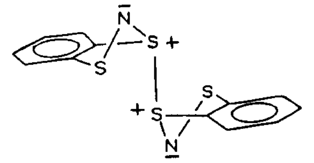


Figure 14. Energy cycle for the formation of **6** from the dimer $(3^\bullet)_2$.

therefore the calculation does not suggest the direction in which donation is preferred. It is possible that both interactions occur.

Thermodynamic Stability of the π-Bonded $(3^\bullet)_2$. The dimer $(3^\bullet)_2$ is thermodynamically more stable than alternative structures in which the monomers are joined by either an S^+–S^+ σ bond, **5**, or an N–N σ bond, **6** (included in Figure 14). The N–N



5

σ-bond strength (35–45 kcal mol^{-1})[48] is likely greater than that of S^+–S^+ (66 kcal mol^{-1} in HSSH)[49] due to the electrostatic repulsion of the adjacent charged sulfur atoms. Therefore, the energy change between $(3^\bullet)_2$ and **6** may be depicted by the energy cycle in Figure 14, in which the excited-state **7** is half of **6**, with the unpaired electron localized on the nitrogen center. Then

$$\Delta H = 2(\text{excitation energy}) + \text{dimerization energy} - \text{N–N bond dissociation energy in } \mathbf{6}$$

The excitation energy is equal to the difference in the sums of the bond energies of $3^\bullet$ and **7**, approximately the π-bond energy of the $-\overline{\mathrm{CSNSC}}-$ portion of $3^\bullet$. This approximates to half the energy of an NS π bond per monomer unit but is greater than this due to bond delocalization (see SOMO of $3^\bullet$, Figure 10). The localized NS π-bond energy (42 kcal mol^{-1})[49] is very similar to N–N σ-bond energy (35–45 kcal mol^{-1}). Observed dimerization energies in related dimers in solution are very small (0–9 kcal mol^{-1}; see above). The dimerization energy is $(3^\bullet)_2$ is probably not greater than 5 kcal mol^{-1}.[50] Thus, the π-bond delocalization of the SN bond in $3^\bullet$ is critical to the stability of the observed $(3^\bullet)_2$ configuration. Therefore, $(3^\bullet)_2$ and other related parallel-planar dimer molecules and ions form π bonds at the expense of σ bonds, reminiscent of radicals of second-row elements, such as $NO^\bullet$, O_2, and the nitroxides.[45]

Acknowledgment. We thank the NSERC (Canada) for financial support, the Canadian Commonwealth Scholarship and Fellowship Committee for a graduate scholarship (S.P.), Prof. F. Grein (UNB) for invaluable discussions and patient guidance in the theoretical work and the use of his programs, Dr. D. J. Williams (Imperial College, London) for kindly supplying bond distances and angles for $C_6H_4S_2N^+Br^-/Br_3^-$ for comparison with the present data, and Dr. C.-M. Wong for help in obtaining crystallographic figures.

Supplementary Material Available: Tables of thermal parameters and crystallographic data for $C_6H_4S_2N^+Cl^-\cdot SO_2$ and $C_6H_4S_2N^\bullet$ and magnetic susceptibility data for $C_6H_4S_2N$ and text detailing compound preparation (10 pages); listings of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Notes

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The Molecular Sieve VPI-5: A Precursor to $AlPO_4$-8†

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The present work shows that the largest pore molecular sieve VPI-5, in its as synthesized form, is a precursor to $AlPO_4$-8, which is obtained by calcining the former in inert atmosphere or in vacuum in the temperature range 388–773 K.

Both VPI-5 and $AlPO_4$-8 are synthesized from identical gel compositions by using tetrabutylammonium hydroxide, *n*-dibutylamine, or *n*-dipentylamine as a templating agent at 423 K.[1-3] In addition, VPI-5 can also be synthesized by using *n*-dipropylamine.

The reported differences between the syntheses of VPI-5 and $AlPO_4$-8 are only with respect to the aging and longer crystallization period required, respectively, in the two cases. However, the procedure referred to by Grobet et al.[3a] eliminates steps involving aging and yields VPI-5 in a shorter crystallization period. Also, the only role of templating agents appears to be to provide the optimum pH conditions.[2,4] Thus, all synthesis factors are

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† $(Al_{0.5}P_{0.5})O_2$.

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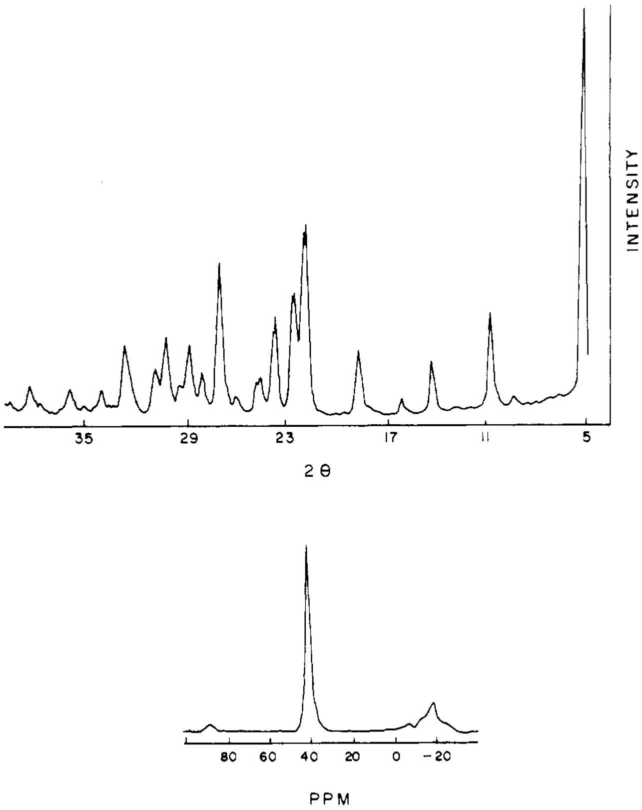

Figure 1. XRD pattern and ^{27}Al MASNMR spectrum of VPI-5.

common for both syntheses and the end products should therefore have the same identity.

Experimental Section

VPI-5 was synthesized by using *n*-dibutylamine as the template.

XRD patterns were recorded with a PW 1730 Philips instrument using nickel-filtered Cu Kα radiation. MASNMR spectra were recorded in the solid state with a Bruker MSL 300 spectrometer operating at a field of 7 T. ^{27}Al MASNMR spectra were run at 78.2 MHz, with a pulse length of 2 μs, a pulse interval of 500 ms, and a spinning speed of 3–5 kHz. The chemical shift was measured relative to aqueous $AlCl_3$ solution.

Samples of VPI-5 were calcined at different temperatures (388–773 K) in dry nitrogen or vacuum.

Results and Discussion

The VPI-5 sample, as synthesized, was air-dried and its identity confirmed by XRD and ^{27}Al MASNMR measurements. The XRD pattern matches closely with that reported;[5] the ^{27}Al MASNMR spectrum shows the presence of tetrahedrally and octahedrally coordinated Al in the ratio 2:1 (Figure 1).

Figure 2A shows the XRD pattern and ^{27}Al MASNMR spectrum of the sample calcined at 773 K. The former matches closely with the data reported for $AlPO_4$-8.[2] The MASNMR spectrum is devoid of the signal attributed to octahedral coordination of Al(VI), and it now shows only the Al(IV) signal at ~40 ppm characteristic of all $AlPO_4$ materials. The observations were identical with respect to samples calcined at intermediate temperatures. In the light of this study, it is suggested that the changes in the ^{31}P MASNMR spectra of VPI-5 on calcination reported by Grobet et al. may be associated with the transformation to $AlPO_4$-8. Recently, Davis et al. have examined $AlPO_4$-8 and shown that it is a distinct phase.[6]

A sample of VPI-5 after calcination at 773 K was cooled in dry atmosphere and exposed to moisture for rehydration. Figure 2B shows the XRD pattern and ^{27}Al MASNMR spectrum of the sample. The XRD pattern shows a shift in the *d* values and also a reduction in the peak intensity at d = ~16 Å. The multiple resonance maxima of the Al(IV) peak may be explained as being due to aluminum atoms in different crystallographic sites.[7] Rehydration also restores the Al(VI) peak in the MASNMR spectrum. These changes in the spectra may be interrelated and indicative of transformation of Al(IV) to Al(VI).[3a]

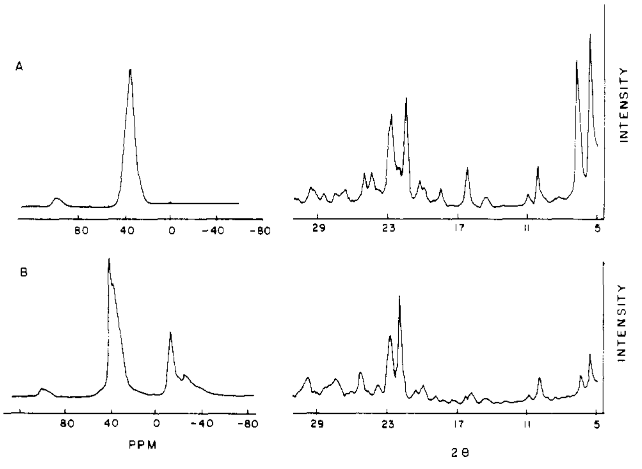

Figure 2. (A) XRD pattern and ^{27}Al MASNMR spectrum of calcined VPI-5 at 773 K in dry nitrogen. (B) XRD pattern and ^{27}Al MASNMR spectrum of calcined rehydrated VPI-5.

The effect of calcination and rehydration of the sample can be schematically represented as follows:

$$\text{VPI-5} \xrightarrow[-H_2O]{\text{heat}} AlPO_4\text{-8} \underset{-H_2O}{\overset{+H_2O}{\rightleftarrows}} AlPO_4\text{-8 (hydrated)}$$

It is significant to note, in this context, that there has been, as yet, no publication outside of the patent report on the synthesis of $AlPO_4$-8. If this fact is taken along with our observations, the conclusion that VPI-5 is only a precursor to $AlPO_4$-8, to which it transforms irreversibly upon calcination, seems justified. This would, of course, mean that the largest pore molecular sieve (VPI-5) was originally synthesized by Flanigen et al., who missed identifying it because the product was dried at 388 K!

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Molecular Structure of $Ru(CO)_3Cl_2H_2O$·Diglyme: Hydrogen Bonding of Diglyme to Coordinated Water

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and Joseph S. Merola

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During the course of an investigation of the reactions of ruthenium carbonyl chlorides adsorbed on metal oxide surfaces,[1] we obtained crystals of the complex $Ru(CO)_3Cl_2H_2O$-diglyme (**1**). This complex serves as a simple model for the structure of the surface species $Ru(CO)_3Cl_2$(surface).[1] The complex is also unique since water as a ligand in 18e organometallic complexes is rare. The recent report of water bound to iridium in [IrH_2-

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