A High-resolution Synchrotron X-Ray Powder Diffraction Study of *trans*-Stilbene in Zeolite ZSM-5†

J. B. Parise,*[a] J. A. Hriljac,*[b] D. E. Cox,*[b] D. R. Corbin[c] and V. Ramamurthy[c]

[a] *Earth and Space Sciences, SUNY, Stony Brook, NY 11794-2100, USA*
[b] *Department of Physics, Brookhaven National Laboratory, Upton, NY 11973, USA*
[c] *Central Research and Development, Du Pont Company, Wilmington DE 19880-0262, USA*

Upon adsorption of two molecules of stilbene per unit cell, the apparent symmetry of ZSM-5 changes to tetragonal, but the true symmetry is orthorhombic with a very small difference between *a* and *b*, which becomes progressively more pronounced with $b > a$ as the sample is cooled to 25 K; the stilbene molecule is located in the straight channels, with one phenyl ring on the mirror plane, at the intersection of the straight and sinusoidal channels.

The aluminosilicate framework designated ZSM-5[1] is widely proposed as a highly selective catalyst and as an agent for the synthesis of fine chemicals.[2] Its selectivity ensues from a unique structure[1] consisting of two intersecting channels which have cross sections consisting of ten $(Al,Si)O_4$ tetrahedra and free diameters of *ca.* 5.5 Å. One of these, the 'straight channel', runs parallel to the *b*-axis while the other 'sinusoidal channel' runs parallel to the *a*-axis (Fig. 1).

As synthesized (Na, TPA)-ZSM-5[1] is orthorhombic, *Pnma*, where TPA represents the tetrapropylammonium cation added to the precursor gel as a structure-directing agent. Upon removal of the TPA from the framework, the symmetry is lowered to monoclinic, $P2_1/n$. Heating[3] causes the empty framework to undergo a reversible phase transition back to *Pnma* symmetry. A number of crystallographic studies have been carried out on ZSM-5–sorbate complexes, with mixed success.[4–7] The most fruitful of these investigations was carried out by van Koningsveld *et al.*[4] on a single crystal sample of ZSM-5 fully loaded with *p*-xylene. They found the sorbate to be well ordered in space group $P2_12_12_1$. Except for this case, the space group *Pnma* has been used for structural studies of loaded ZSM-5.[5–7]

Recently, the shape-selective properties of this material have inspired organic chemists to use it as a platform for a variety of polymeric and photochemical reactions.[8,9] One of these studies[8] involved the sorption of *trans*-stilbene into Na-ZSM-5, and demonstrated the generation of long-lived cation radicals stabilized within the framework. Preliminary ^2H NMR results[8] suggested little dynamic disorder at room temperature for the sorbed stilbene and that the molecule retained its *trans*-conformation and planarity after adsorption. This contrasts with the situation in the large-pore zeolite Y, where the NMR results indicate free motion for stilbene; the free diameter for channels in zeolite Y is 7.4 Å while that for the cages is 11 Å. This study was undertaken to determine the structure of the ZSM-5–stilbene system, in particular to locate the sorbed molecules and to investigate the effects on the framework geometry. For our study, the prohibitively slow adsorption rates for stilbene into single crystals necessitated the use of powdered samples. We find that structure modelling based on high resolution synchroton X-ray powder diffraction data,[10] at temperatures between 25 and 300 K, offers novel insights into how the ZSM-5 framework accommodates stilbene.

trans-Stilbene was obtained commercially and was crystallized several times from ethanol. (Na,TPA)-ZSM-5 was prepared according to the procedure of Rollman and Valyocski.[11] The stilbene was introduced into a sample with an Si : Al ratio of 550 : 1 according to the procedure described previously.[8] The samples were stored under ambient conditions. A thermogravimetric analysis (TGA) was consistent with a composition of two molecules of stilbene and one molecule of water per unit cell of ZSM-5.

The sample was loaded into thin-walled 1 mm diameter quartz capillaries and measurements were performed in the high resolution mode[10] at the X-7A beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. A wavelength of 1.1965 Å was used, with a Ge(111)/Ge(220) monochromator–analyser combination, a Kevex detector and incident beam-defining slits of 1.1 mm × 8.0 mm. The variation in the diffraction pattern was followed from 25 K to room temperature using a Displex cryogenic unit with a Be window. Step scans were carried out over selected angular regions covering the (110), (020/200), (321/231), (040/400), and (410) reflections at several temperatures. Further, these same reflections were monitored to 440 K, the temperature at which stilbene was lost. More extensive X-ray data were collected at 25 K from 5 to 70° in 2θ with a step size

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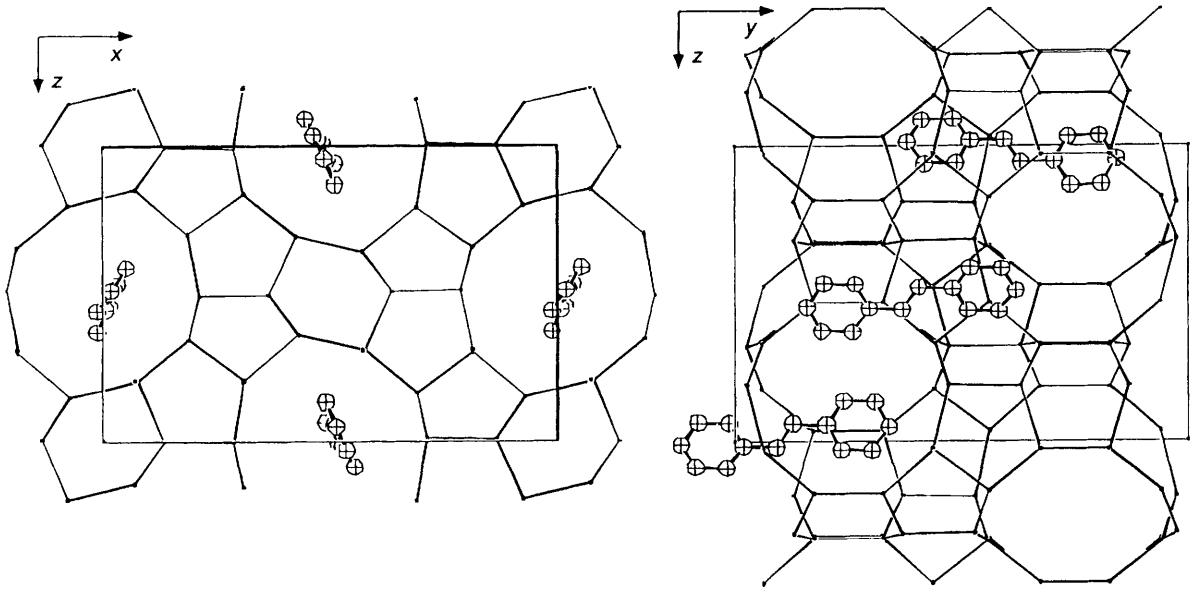

Fig. 1 (*a*) Projection of the structure of ZSM-5 along *b*. The position of the sorbate molecule, *trans*-stilbene, is that obtained from the structure modelling procedure (see text). (*b*) Projection along the *a*-axis of ZSM-5. For clarity, only selected orientations of the molecule, which is disordered about the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$, are shown. The oxygen atoms are omitted and straight lines drawn between the tetrahedrally coordinated cations in the framework.

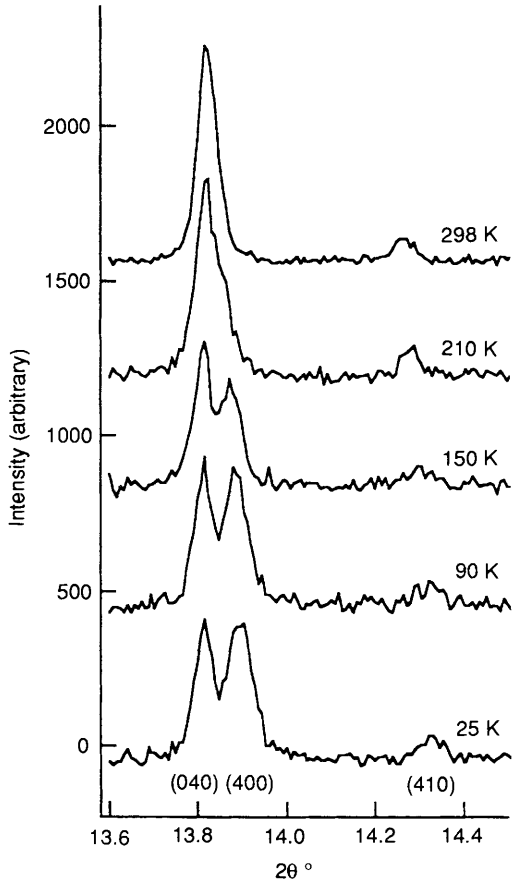

Fig. 2 Synchrotron X-ray scans through the (040/400) and (410) reflections from stilbene-loaded ZSM-5 as a function of temperature. The wavelength is 1.1956 Å. The (140) reflection, absent for diffraction symbol *Pn-a*, is not observed. It would appear just to the low angle side of the (410) reflection. Note that the *b*-axis is almost invariant with temperature.

of 0.008° in 2θ and a counting time of 4 s for low angle and 5 s for data above 30°. The wavelengths used for the experiments were obtained by calibration with a reference sample of CeO_2.

Diffraction data for the (410/140) and (040/400) reflections are reproduced in Fig. 2 to show the relative changes in the *a*- and *b*-axes in the temperature range 50 to 300 K. The assignment of the (040) to the lower angle peak in the (040/400) pair in Fig. 2 is made uniquely on the basis of the final Rietveld refinement.[12] The relative lengths of the *a*- and *b*-axes are unusual in that all other orthorhombic cells reported for ZSM-5[1-9] have $a > b$. It should be noted that because of the pseudo-tetragonal nature of this material, the positions of a few weak reflections of the type $hk0$; $h = 2n$, are important in defining the unit cell. With laboratory-based diffractometers these reflections can be easily lost in the background or appear as poorly resolved shoulders. This situation is exacerbated at room temperature where, even with the superior resolution afforded by the X-7A diffractometer,[10] the *a* unit cell parameter is indistinguishable from *b* (Fig. 2). In this case a full pattern analysis[12] is required to resolve the ambiguity.

At 25 K the orthorhombicity of the cell is clearly evident (Fig. 2). Further, there is no broadening of (111), which would indicate monoclinic symmetry. Instead, the diffraction pattern was fully indexed on the basis of an orthorhombic cell [a = 19.8526(1), b = 19.9801(2) and c = 13.3921(2) Å] with absences corresponding to diffraction symmetry *Pn-a*. The mirror plane perpendicular to the *b*-axis was assumed throughout the subsequent investigations. Upon warming to room temperature the cell derived from a preliminary Rietveld-type refinement was a = 19.9601(2), b = 19.9907(2) and c = 13.4155(2) Å; this represents a linear expansion of 0.54%, 0.05% and 0.17% along a, b and c, respectively.

A starting model for full pattern refinement[12] was obtained from real-time simulation of the 25 K powder diffraction data using molecular graphics software.[13] Stilbene, fixed at an occupancy of 0.25 to correspond to the two molecules per unit cell obtained from the TGA data, was placed into a ZSM-5 framework whose geometry had been optimized[14] based upon

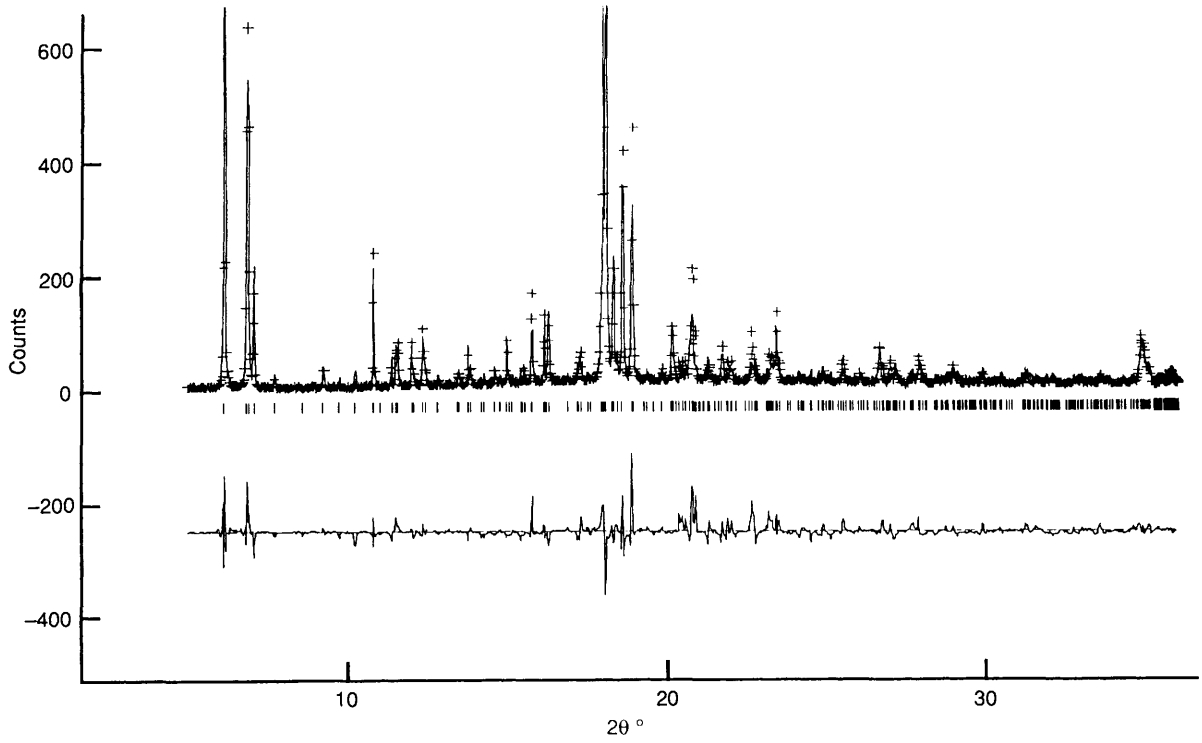

Fig. 3 Calculated (continuous line) and observed X-ray powder diffraction profiles for *trans*-stilbene (occupancy = 0.25) in Na-ZSM-5. The difference pattern is given below. Note that the intensity is truncated at 600 counts normalized to 100 mA. The strongest peak in the pattern, the (011), has an intensity of 1500 counts.

the observed unit cell parameters. The calculated diffraction pattern was monitored as the position of the *trans*-stilbene molecule was varied manually within the rigid framework. Inspection suggested the observed data were best modelled when stilbene was located in the straight, rather than the sinusoidal channels. Translation along this channel located the molecule with one phenyl ring close to the intersection of the straight and sinusoidal channels with its centre at $y \approx \frac{1}{4}$ and the other at $y \approx \frac{1}{2}$ (Fig. 1); this is close to the position found for *p*-dichlorobenzene.[5] In this position the stilbene molecule must be disordered about the mirror plane. The length of the *trans*-stilbene molecule is estimated to be 13.2 Å, assuming a van der Waals radius for hydrogen of 1 Å. If the ≈20 Å translational repeat along the *b*-axis is imposed on the sorbed molecule this would limit the number of stilbene per unit cell to two (Fig. 1). In space group *Pnma* this corresponds to 0.25 occupancy of the eightfold general position. An equivalent model with an ordered molecule in the space group $Pn2_1a$ cannot be ruled out, but is much more complex to analyse and would not offer additional information on the siting preference.

With this starting model a series of preliminary Rietveld refinements[12] were carried out. The diffraction data were supplemented with 140 interatomic Si–O, O–O and Si–Si distances taken from a recent accurate single crystal study of orthorhombic ZSM-5 loaded with *p*-xylene.[4] The positions of all framework atoms were varied; overall thermal parameters (U) of 0.01 and 0.03 Å^2 were employed for the Si and O atoms, respectively. The positional parameters for the stilbene molecule were fixed at values obtained from the molecular modelling study. The diffractometer zero, lattice parameters and five profile coefficients[12] were also varied. Background was estimated and not refined. Fig. 3 gives a graphical representation of the fit in the low-angle region of the 25 K data. The usual discrepancy indices[12] were $R_{wp} = 0.185$ and $\chi^2 = 3.2$.

In summary, at a loading of two molecules per unit cell, *trans*-stilbene resides in the straight channels of ZSM-5 with one phenyl ring close to $y = \frac{1}{4}$ and the other at $y \approx \frac{1}{2}$. It is disordered about the mirror plane in space group *Pnma*. Upon heating to room temperature from 25 K the thermal expansion of the $a : b : c$ axes are in the ratios 3.2 : 0.3 : 1. A neutron study is underway better to define the relationship between the *trans*-stilbene and the ZSM-5 framework.

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