On the Location and Disorder of the Tetrapropylammonium (TPA) Ion in Zeolite ZSM-5 with Improved Framework Accuracy

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Abstract

$Si_{11.96}Al_{0.04}O_{24} \cdot \frac{1}{2}NC_{12}H_{28}OH + nH_2O$ (+0·04Na$^+$?), $M_r = 822·65 + (n \times 18)$, orthorhombic, *Pnma* (assumed), $a = 20·022$ (2), $b = 19·899$ (2), $c = 13·383$ (1) Å, $V = 5332$ (4) Å^3, $Z = 8$, $D_x = 2·06$ (including TPAOH), $D_x = 1·80$ g cm^{-3} (for the anhydrous framework), $\lambda(Mo~K\alpha) = 0·71069$ Å, $\mu = 6·91$ cm^{-1}, $F(000) = 3343·7$, $T = 293$ K, $R = 0·042$ for 4523 observed reflections with $I > 2·0\sigma(I)$. The framework topology agrees with earlier descriptions. Straight channels and sinusoidal channels run parallel to [010] and [100], respectively. The symmetry of the framework atoms is too close to *Pnma* to permit refinement in $Pn2_1a$. In the straight channel an approximate mirror plane through N and the channel axis, perpendicular to the crystallographic mirror plane, exists. The tetrapropylammonium ion lies at the intersection of the straight and sinusoidal channels in two different orientations. The two orientations, populated in a ratio of 3:2, are nearly related by the approximate mirror plane. Contrary to literature data the propyl–N–propyl fragments pointing into the sinusoidal and straight channel, respectively, both have CNCC torsion angles around 60°. No evidence is obtained for the tetrapropylammonium ion breaking the *m* symmetry and extra disorder around *m* is assumed. The mean C–C and C–N distances and mean CCC, CCN and CNC angles, averaged over both ions, are 1·55 and 1·57 Å and 109, 113 and 109°, respectively. Contact distances smaller than 4·0 Å, between terminal C atoms of adjacent template ions, are in the range 3·56 (7)–3·75 (2) Å.

Introduction

The catalytic and adsorption properties of the highly siliceous ZSM-5 zeolites, crystalline aluminosilicates and of silicalite, the aluminium-free end member, have received much attention (*e.g.* Flanigen *et al.*, 1978; Olson, Haag & Lago, 1980; Haag, Lago & Weisz, 1984). Differences in physical and chemical behaviour are often discussed in terms of differences in structure and composition of the zeolites (von

Ballmoos, 1981; Auroux, Desepert, Leclercq & Vedrine, 1983; Gilson & Derouane, 1984). Several papers on the crystal structure of ZSM-5 have been published recently using space group *Pnma* (Olson, Kokotailo, Lawton & Meier, 1981; Price, Pluth, Smith, Bennett & Patton, 1982; Baerlocher, 1984; Lermer, Draeger, Steffen & Unger, 1985; Chao, Lin, Wang & Lee, 1986). The positions of the framework atoms agree well with a tetrahedral environment of oxygen around silicon. The template molecule, tetrapropylammonium (TPA$^+$) fluoride or bromide or hydroxide, required for growth and stabilization (Keijsper, Mackay, van den Berg, Kortbeek & Post, 1986) of the ZSM-5 crystals and present in the crystals as synthesized, is not always located. Two papers (Price *et al.*, 1982; Chao *et al.*, 1986) describe the template ion at the intersection of the straight and sinusoidal channels (Fig. 1). The $N(C_3H_7)_2$ part in the sinusoidal channel is in a folded conformation in the crystallographic mirror plane. The other two (C_3H_7) groups, pointing into the straight channel, are related by *m*. Relevant torsion angles, calculated from the published coordinates, are listed in Table 3. The TPA$^+$ ion has *m* symmetry rather than $\bar{4}$ as found in solid TPA$^+$.Br$^-$ (Zalkin, 1957). However, the reported refined C–C and C–N bond distances in TPA$^+$ vary from 0·79 to 1·88 Å, the bond angles are not as expected for tetrahedral C and N atoms and several temperature factors are extremely high. In addition, the *m* symmetry of TPA$^+$ with extended propyl groups at both sides of *m* inevitably leads to very short contacts in the straight channel between terminal C atoms in adjacent ions. And, finally, a folded conformation of the propyl-N-propyl group *in m* (see Fig. 1*a*) seems very unlikely because of the inherent substantial conformational strain caused by unfavourable short H···H contacts. Two other papers (Olson *et al.*, 1981; Lermer *et al.*, 1985) do not report the location of TPA$^+$. These authors describe two non-framework atoms, called Ox1 and Ox2, with low occupancy. Baerlocher (1984) refined the silicalite structure, including the TPA$^+$ ion with *m* symmetry at $y = \frac{1}{4}$, with powder data using geometric restrictions on all distances and angles. The author suggests

disorder of TPA$^+$ in m at $y = \frac{1}{4}$ but does not investigate this possibility any further. The present paper reports a detailed structure analysis of the occluded template ion in ZSM-5, without any constraints on the atoms.

Experimental

Single crystal grown according to a procedure described recently (Lermer *et al.*, 1985). Molar composition reaction mixture: SiO$_2$ (12·2), NaAlO$_2$ (1·0), NaOH (43·3), TPABr (43·5), H$_2$O (2452). Al (and possibly Na) content by electron microprobe analysis (EMPA). Homogeneous Al distribution. IR measurements indicate the presence of H$_2$O, OH$^-$ and possibly Si–OH groups in the channels. Preliminary TGA measurements point to almost full occupancy of TPA$^+$ at the four channel intersections. Unit-cell contents: Na$_{0.3?}$Si$_{95.7}$Al$_{0.3}$O$_{192}$.4TPAOH + nH$_2$O. Full details on the growth experiments, the EMPA measurements, IR and TGA data will be published elsewhere (Jansen, van Koningsveld, Schalkoord & van Bekkum, 1987). Crystal dimensions: $230 \times 200 \times 150$ μm. CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell parameters from 25 reflections with $10 < \theta < 17°$. Data collected to $\theta_{max} = 30\cdot0°$ ($h0 \rightarrow 28$, $k0 \rightarrow 27$, $l0 \rightarrow 18$), $\omega/2\theta$ scan, width = $(0\cdot85 + 0\cdot35 \tan\theta)°$, max. recording time 240 s, $\sigma_{count}(I)/I < 0\cdot02$ requested in a scan. Three reference reflections measured every 2 h of X-ray measuring time; no change in intensity observed. Lorentz and polarization corrections (none for extinction or absorption) applied. 7944 independent reflections, 4528 with $I > 2\cdot0\sigma(I)$. Initial positions of framework atoms taken from literature (Olson *et al.*, 1981). All T atoms (Al, Si) treated as Si. Structure refined in

Fig. 1. Conformation of TPA$^+$ as reported in the literature. (*a*) Folded propyl–N–propyl fragment: C(α')NC(α)C(β) = 0°. (*b*) Extended propyl–N–propyl fragment C(α')NC(α)C(β) between 97 and 127°.

Pnma by (blocked) full-matrix least squares on F; all non-C atoms with anisotropic thermal parameters. N and C atoms located from several difference Fourier maps. H atoms not located. Attempts to locate OH$^-$, required for electroneutrality, and Na$^+$ failed. Disordered model converged with 4523 observations [$I > 2\cdot0\sigma(I)$; five low-order reflections, possibly affected by extinction, left out] to $R = 0\cdot042$, $wR = 0\cdot044$, $w = 1$, $S = 0\cdot48$, 410 parameters; $\Delta/\sigma < 0\cdot14$ for Si, O and N and $< 0\cdot40$ for C.* Final ΔF synthesis has six peaks above $0\cdot50$ e Å^{-3} near C(5) ($0\cdot65$ e Å^{-3}), O(14) ($0\cdot61$ e Å^{-3}), C(10) ($0\cdot58$ e Å^{-3}), O(11) ($0\cdot56$ e Å^{-3}) and O(5) ($0\cdot55$ e Å^{-3}). No residual density around Si atoms observed. Twenty peaks (between $0\cdot41$ and $0\cdot49$ e Å^{-3}) can all be attributed to O atoms of the framework. A refinement of the framework atoms using space group $Pn2_1a$ failed. Apparently the deviation of the framework symmetry from *Pnma* is too small to permit refinement in the lower-symmetry space group $Pn2_1a$. Refinement of TPA$^+$ in $Pn2_1a$ (with fixed framework atoms in *Pnma*) results in a difference Fourier map containing the mirror image of TPA$^+$. Apparently, the influence of the TPA$^+$ ion on the intensity distribution is too small to break the *Pnma* symmetry, or disorder around m really exists. Disorder around m is assumed by refining the whole structure in *Pnma*. All calculations performed with *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972); atomic scattering factors of zero-valent Si, O, N and C from Cromer & Mann (1968).

Discussion

The final positional and isotropic thermal parameters of the framework and the template are given in Tables 1 and 2,† respectively. A comparison with the structural data published by several authors on the same kind of structures is given in Table 3, together with some experimental details.

The framework

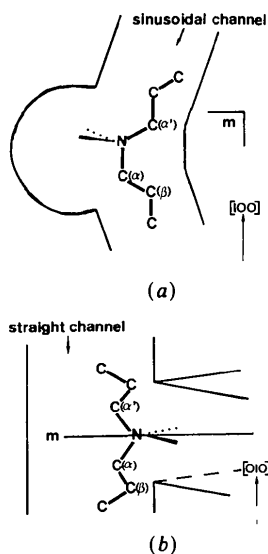The geometry of the framework is the same in all structures. The accuracy of the framework distances

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* A constraint refinement, using Waser constraints [C–C = 1·53(2), C–N = 1·54(2) Å, CCN = CNC = 110(3) and CCC = 110(2)°] gave $R = 4\cdot3\%$. These calculations were performed using *SHELX*76 (Sheldrick, 1976) on the Cyber855 computer of the University of Utrecht with the kind cooperation of Dr A. L. Spek. The final coordinates and template geometry have been deposited.

† Lists of structure factors, anisotropic thermal parameters, bond lengths and bond angles involving framework atoms, final coordinates and template geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43299 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* (×10⁴) *and* U_{eq} *values* (Å²×10³) *for the framework atoms*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
Si(1)	4223·8 (5)	565·0 (6)	−3359·8 (9)	17·6 (3)
Si(2)	3071·6 (6)	277·2 (6)	−1893·0 (9)	20·7 (3)
Si(3)	2791·1 (6)	612·7 (6)	312·0 (9)	19·3 (3)
Si(4)	1221·5 (6)	629·8 (6)	267·0 (9)	18·1 (3)
Si(5)	712·8 (6)	272·2 (6)	−1855·1 (9)	16·0 (3)
Si(6)	1864·1 (5)	589·6 (6)	−3281·8 (8)	17·8 (3)
Si(7)	4226·5 (6)	−1725·0 (6)	−3271·8 (9)	18·5 (3)
Si(8)	3077·8 (6)	−1301·6 (6)	−1854·8 (9)	19·9 (3)
Si(9)	2755·4 (6)	−1727·9 (6)	310·9 (9)	17·6 (3)
Si(10)	1205·8 (6)	−1731·0 (6)	297·9 (9)	19·3 (3)
Si(11)	704·4 (6)	−1303·7 (6)	−1820·0 (9)	19·3 (3)
Si(12)	1870·6 (6)	−1732·7 (6)	−3193·3 (9)	20·0 (3)
O(1)	3726 (2)	534 (3)	−2442 (3)	49 (1)
O(2)	3084 (2)	587 (2)	−789 (2)	40 (1)
O(3)	2007 (2)	592 (3)	289 (4)	64 (2)
O(4)	969 (2)	611 (2)	−856 (3)	44 (1)
O(5)	1149 (2)	541 (2)	−2763 (2)	34 (1)
O(6)	2435 (2)	553 (3)	−2460 (3)	46 (1)
O(7)	3742 (2)	−1561 (2)	−2372 (3)	47 (1)
O(8)	3085 (2)	−1552 (2)	−728 (3)	44 (1)
O(9)	1980 (2)	−1554 (2)	288 (3)	40 (1)
O(10)	910 (2)	−1614 (2)	−777 (3)	58 (2)
O(11)	1169 (2)	−1578 (2)	−2694 (3)	48 (1)
O(12)	2448 (2)	−1594 (3)	−2422 (3)	55 (2)
O(13)	3047 (3)	−510 (2)	−1866 (4)	71 (2)
O(14)	768 (2)	−519 (2)	−1769 (3)	47 (1)
O(15)	4161 (2)	1276 (2)	−3896 (3)	44 (1)
O(16)	4086 (2)	−17 (2)	−4136 (3)	46 (1)
O(17)	4020 (2)	−1314 (2)	−4239 (3)	40 (1)
O(18)	1886 (2)	1298 (2)	−3836 (3)	36 (1)
O(19)	1940 (2)	7 (2)	−4082 (3)	45 (1)
O(20)	1951 (2)	−1291 (2)	−4190 (3)	43 (1)
O(21)	−37 (1)	502 (2)	−2080 (2)	33 (1)
O(22)	−40 (2)	−1528 (2)	−2078 (3)	40 (1)
O(23)	4192 (3)	−2500	−3540 (4)	44 (2)
O(24)	1884 (3)	−2500	−3538 (4)	34 (1)
O(25)	2883 (3)	−2500	579 (4)	33 (1)
O(26)	1085 (3)	−2500	611 (4)	30 (1)

Table 2. *Fractional coordinates* (×10³), U_{iso} *values* (Å²×10³) *and population parameters* (PP) *of the atoms in the* TPA⁺ *ions*

	x	y	z	U_{iso}	PP
N	476·2 (5)	250	−109·5 (6)	69 (4)	1·00
C(1)	495 (1)	233 (1)	−221 (2)	58 (8)	0·30 (1)
C(2)	568 (2)	250	−241 (2)	97 (9)	0·60
C(3)	578 (2)	250	−362 (2)	98 (9)	0·60
C(4)	399 (1)	274 (1)	−100 (2)	64 (8)	0·30
C(5)	355 (1)	228 (1)	−150 (2)	136 (10)	0·30
C(6)	278 (2)	250	−147 (3)	104 (10)	0·60
C(7)	505 (2)	319 (2)	−89 (2)	65 (8)	0·30
C(8)	473 (2)	334 (2)	19 (3)	83 (9)	0·30
C(9),C(9')	496 (1)	412 (1)	45 (2)	88 (6)	0·50
C(10),C(10')	508 (1)	199 (1)	−32 (2)	121 (9)	0·50
C(11),C(11')	490 (1)	124 (1)	−45 (2)	109 (7)	0·50
C(12),C(12')	529 (1)	88 (1)	33 (1)	72 (4)	0·50
C(1')	413 (2)	229 (2)	−166 (4)	83 (16)	0·20
C(2')	355 (1)	272 (1)	−150 (2)	136 (10)	0·20
C(3')	285 (3)	250	−195 (4)	110 (16)	0·40
C(4')	534 (2)	279 (2)	−185 (3)	67 (12)	0·20
C(5')	546 (2)	225 (2)	−263 (4)	73 (13)	0·20
C(6')	601 (3)	250	−332 (5)	129 (21)	0·40
C(7')	468 (2)	315 (2)	−60 (3)	61 (11)	0·20
C(8')	516 (2)	335 (2)	20 (3)	61 (10)	0·20

and angles, reported in this paper, has been significantly improved (Table 3). On average, all twelve SiO₄ groups agree well with the ideal tetrahedral environment of Si atoms. In each tetrahedron, the average Si–O distance and O–Si–O angle are 1·587 Å and 109·47°, respectively, without any significant scatter. ZSM-5 has a three-dimensional channel system defined by ten-membered rings [of T ($=$ Si, Al) atoms]. There are straight channels parallel to [010] and sinusoidal channels along [100] (see Fig. 2). The

Table 3. *Comparison between several ZSM-5-like structures*

Reference	(a)	(b)	(c)	(d)	(e)	This work
Crystal data						
Dimensions (μm)	20×30×40	180×50×50	Powder	260×130×120	200×70×50	230×200×150
Al/unit cell	1·1	0·0	0·0	8·0	3·7	0·3
Reflections with $I \geq 2\sigma(I)$	1026*	1645	2246	2217	1508	4528
θ_{max} (°)	Not given	27·5	45·0	32·5	25·0	30·0
$R(F)$	11·9	6·7	6·9	9·7	7·9	4·2
Framework geometry						
T–O range (Å)	1·50 (4)–1·67 (3)	1·51 (3)–1·69 (3)	1·55–1·65†	1·54 (2)–1·62 (2)	1·52 (2)–1·66 (2)	1·567 (4)–1·605 (4)
O–T–O range (°)	96 (2)–129 (2)	100 (2)–119 (2)	104–113	105·6 (7)–113·7 (8)	103·9 (8)–115·5 (8)	106·0 (2)–112·0 (2)
Av. T–O/tetrahedron (Å)	1·56–1·63	1·57–1·61	1·57–1·62	1·57–1·60	1·57–1·62	1·584–1·591
Av. O–T–O/tetrahedron (°)	109–110	109–110	109·5	109·4–109·5	109·4–109·5‡	109·5
TPA⁺-ion geometry						
C–N range (Å)	TPA not	1·5 (1)–1·9 (1)	1·54–1·55†	TPA not	1·5 (1)–1·9 (1)	1·46 (3)–1·64 (4)
C–C range (Å)	localized§	0·8 (2)–1·8 (2)	1·51–1·55	localized§	1·0 (1)–1·7 (1)	1·45 (4)–1·65 (4)
CNC range (°)		73 (12)–140 (12)	106–112		102 (4)–116 (4)	93 (2)–122 (2)
CCN range (°)		140 (12)–179 (12)	108–113		104 (8)–160 (6)	100 (2)–119 (3)
CCC range (°)		134 (12)–174 (12)	109–112		111 (8)–144 (7)	104 (3)–119 (3)
C(α')NC(α)C(β) torsions (°):						
CNCC (straight channel)		124 (15)	127		97 (8)	67 (2), 31 (2)¶
CNCC (sinusoidal channel)		0	0		0	51 (2), 55 (2)¶
C–C** (straight channel)		2·7 (2)	3·16		3·6 (2)	≥3·67 (3)
C–C** (sinusoidal channel)		3·1 (2)	4·46		3·6 (2)	≥3·56 (7)

References: (a) TPAOH–ZSM-5 (Olson *et al.*, 1981); (b) TPAF–silicalite (Price *et al.*, 1982); (c) TPAOH–silicalite (Baerlocher, 1984); (d) TPAOH–ZSM-5 (Lermer *et al.*, 1985); (e) TPAOH–ZSM-5 (Chao *et al.*, 1986).

* For $F_o \geq 3\sigma(F_o)$.
† Constraint values; standard deviations doubtful, assumed by the author to be of the same order of magnitude as in (a) and (b).
‡ There is a misprint in the reported av. O–Si–O angle (107·9°) and in the reported x coordinate of C(6): 0·1258; the correct values are 109·5° and 0·5128.
§ Non-framework atoms Ox1 and Ox2 localized instead. [Coordinates of Ox2 are different in reports (a) and (d). See text.]
¶ Values in both TPA⁺ ions are listed. The torsion angles measuring the 'folding' are given: C(8)C(7)NC(10) in the straight channel and C(1)NC(4)C(5) in the sinusoidal channel.
** Contact distances between terminal C atoms in adjacent TPA⁺ ions.

Table 4. *Bond lengths (Å) and bond angles (°) in the two TPA⁺ ions in ZSM-5*

	(TPA⁺)	(TPA⁺)′		(TPA⁺)	(TPA⁺)′
N–C(1)	1·57 (2)	1·53 (5)	C(1)NC(4)	111 (1)	112 (2)
N–C(4)	1·62 (3)	1·64 (4)	C(1)NC(7)	106 (1)	111 (2)
N–C(7)	1·52 (3)	1·46 (4)	C(1)NC(10)	113 (1)	119 (2)
N–C(10)	1·59 (3)	1·59 (3)	C(4)NC(7)	94 (1)	93 (2)
Mean	1·58	1·56	C(4)NC(10)	122 (2)	112 (2)
			C(7)NC(10)	108 (2)	111 (2)
C(1)–C(2)	1·53 (4)	1·46 (5)	Mean	109	110
C(2)–C(3)	1·63 (5)	1·58 (6)			
C(4)–C(5)	1·45 (4)	1·52 (6)	NC(1)C(2)	111 (2)	116 (3)
C(5)–C(6)	1·59 (4)	1·52 (7)	NC(4)C(5)	111 (2)	107 (3)
C(7)–C(8)	1·61 (5)	1·50 (6)	NC(7)C(8)	100 (2)	119 (3)
C(8)–C(9)	1·65 (4)	1·62 (5)	NC(10)C(11)	117 (2)	117 (2)
C(10)–C(11)	1·53 (4)	1·53 (4)	Mean	110	115
C(11)–C(12)	1·48 (3)	1·48 (3)			
Mean	1·56	1·53	C(1)C(2)C(3)	107 (2)	119 (3)
			C(4)C(5)C(6)	114 (2)	107 (3)
			C(7)C(8)C(9)	105 (2)	104 (3)
			C(10)C(11)C(12)	106 (2)	106 (3)
			Mean	108	109

Table 5. *Framework-to-TPA⁺ distances less than 3·81 Å*

C(1)–O(15)	3·47 (2)	C(11)–O(5)	3·74 (2)
O(21)	3·77 (2)	O(21)	3·63 (3)
O(26)	3·60 (2)	C(12)–O(7)	3·63 (2)
C(2)–O(18)	3·78 (3)	O(8)	3·57 (2)
O(25)	3·78 (3)	O(22)	3·74 (2)
C(3)–O(17)	3·73 (3)	C(1′)–O(1)	3·74 (4)
O(23)	3·80 (3)	O(15)	3·62 (5)
C(4)–O(2)	3·80 (2)	O(26)	3·70 (5)
O(20)	3·63 (3)	C(2′)–O(1)	3·71 (3)
O(24)	3·77 (3)	O(2)	3·62 (3)
C(5)–O(1)	3·71 (3)	O(20)	3·80 (3)
O(2)	3·62 (3)	C(3′)–O(25)	3·62 (5)
O(20)	3·80 (3)	C(4′)–O(5)	3·74 (4)
C(7)–O(5)	3·80 (3)	O(18)	3·70 (4)
O(21)	3·76 (3)	O(21)	3·77 (4)
C(8)–O(11)	3·37 (4)	C(5′)–O(5)	3·70 (5)
O(20)	3·55 (4)	O(15)	3·66 (5)
O(22)	3·72 (4)	O(21)	3·63 (5)
C(9)–O(11)	3·64 (3)	C(8′)–O(7)	3·65 (4)
O(22)	3·56 (3)	O(8)	3·59 (4)
		O(22)	3·66 (4)

straight channel locally has an approximate mirror plane through the channel axis, Si(1) and Si(7). The pseudo mirror plane contains N as illustrated in Fig. 3(*a*) and might explain the observed disorder of TPA⁺. The Si-atom numbering is given in Figs. 3(*a*) and 4(*a*) together with the numbering of some O atoms involved in short framework-to-TPA⁺ contacts (see Table 5). The thermal vibration of the Si atoms* is essentially isotropic. The O atoms, however, have very anisotropic thermal parameters (see Figs. 3 and 4). These results might indicate a deviation of the O atoms from the assumed *Pnma* symmetry. The deviation, however, is too small to allow refinement in the lower-symmetry space group *Pn2₁a* (see *Experimental*).
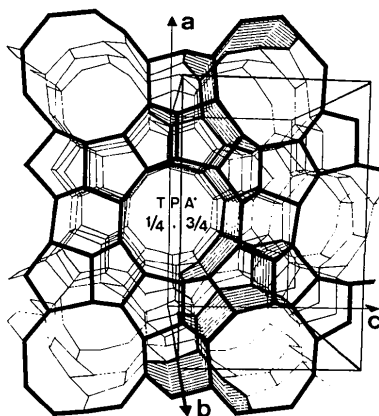
* See deposition footnote.

Fig. 2. View of the framework along **b**. *T* atoms are at the intersections of lines. O atoms (not drawn) are about midway between *T* atoms. Ten-membered rings of *T* atoms in the straight channels are clearly visible. Some ten-membered rings, taking part in the sinusoidal channel, are hatched. Location of TPA⁺ ions in the channels indicated by the *y* coordinate of N atoms.

The TPA⁺ ion

The TPA⁺ ion is located at the intersection of the straight and sinusoidal channels in two different orientations populated in a ratio of 3:2. The two orientations are nearly related by the approximate mirror plane in the straight channel. Bond lengths and bond angles in the two TPA⁺ ions are listed in Table 4. Relevant data are summarized in Table 3. The atom numbering used is depicted in Figs. 3 and 4. Contrary to recently published results (see Table 3) the TPA⁺ ion does not lie exactly in the crystallographic mirror plane. Probably, atom C(4), in both TPA⁺ ions, is refined too far from *m* at *y* = ¼. If the refinement had allowed C(4) to be closer to *m*, the angle C(4)NC(7) would have opened, the angle C(4)NC(10) would have closed and the distance N–C(4) would have become smaller, thus giving values closer to the averaged ones (109° and 1·57 Å). The relatively large *U* values of C(5), C(10) and C(6′) (where the prime indicates atoms in the second TPA⁺ ion) reflect the possibility that C(5) and C(10) do not exactly coincide with C(2′) (repeated *via m*) and C(10′) and that C(6′) is not exactly in *m* at *y* = ¼. A split-atom model for C(5) [C(5) and C(2′)], gives larger C(4)–C(5) and C(1′)–C(2′) distances and smaller C(4)C(5)C(6) and C(1′)C(2′)C(3′) angles, but *does not converge satisfactorily*.

The propyl–N–propyl fragments pointing into the sinusoidal and straight channels (Figs. 3 and 4) are both in a non-extended conformation. The relevant CNCC torsion angles are given in Table 3. The observed conformation of the propyl–N–propyl fragment in the sinusoidal channel has considerably less conformational strain (CNCC ≃ 60°) than the reported folded conformation (CNCC = 0°). Therefore, the *m* symmetry of TPA⁺, found by Price *et al.* (1982), Baerlocher (1984) and Chao *et al.* (1986), does not really exist. The observed conformation of TPA⁺ in

ZSM-5 is completely different from the fully extended conformation of TPA$^+$ (symmetry $\bar{4}$) in solid TPA$^+$.Br$^-$ (Zalkin, 1957). The C–C contacts between terminal C atoms in neighbouring TPA$^+$ ions in the straight channel and in the sinusoidal channel are summarized in Table 3. In the present structure disorder is observed and there are three CC contacts in the straight channel: C(9)–C(12) 3·67 (3) C(9)–C(9') 3·70 (4) and C(12)–C(12') 3·75 (2) Å. Because of the actual conformation and the tilting of the TPA$^+$ ion with respect to m the contact distances are close to the expected van der Waals distances and are not as short as given in Table 3 for (b), (c) and (e). There are four CC contacts in the sinusoidal channel: C(6)–C(6') 3·56 (7), C(6)–C(3) 4·01 (5), C(3')–C(3) 4·21 (6) and C(3')–C(6') 3·70 (8) Å. The shortest contacts involve C(6') at $y = 0·250$, an atom with a large

temperature factor. The distances increase if C(6') is not exactly in the mirror plane. The framework-to-TPA$^+$ distances less than 3·81 Å are given in Table 5 and illustrated in Figs. 3 and 4. The C–C and C–O contacts are different for the two TPA$^+$ ions. This might explain the population difference of the two TPA$^+$ ions.

The coordinates of the non-framework atoms Ox1 and Ox2, found by Olson et $al.$ (1981), correspond to those of the centre of gravity of atoms C(3) and C(6') and of atoms C(6) and C(3') in our study, respectively. The Ox1 and Ox2 atoms given by Lermer et $al.$ (1985) are identical with C(6) [and C(3')] and N in the present work, respectively. These observations strongly suggest that the template ion is also present in the structures studied by Olson et $al.$ and Lermer et $al.$
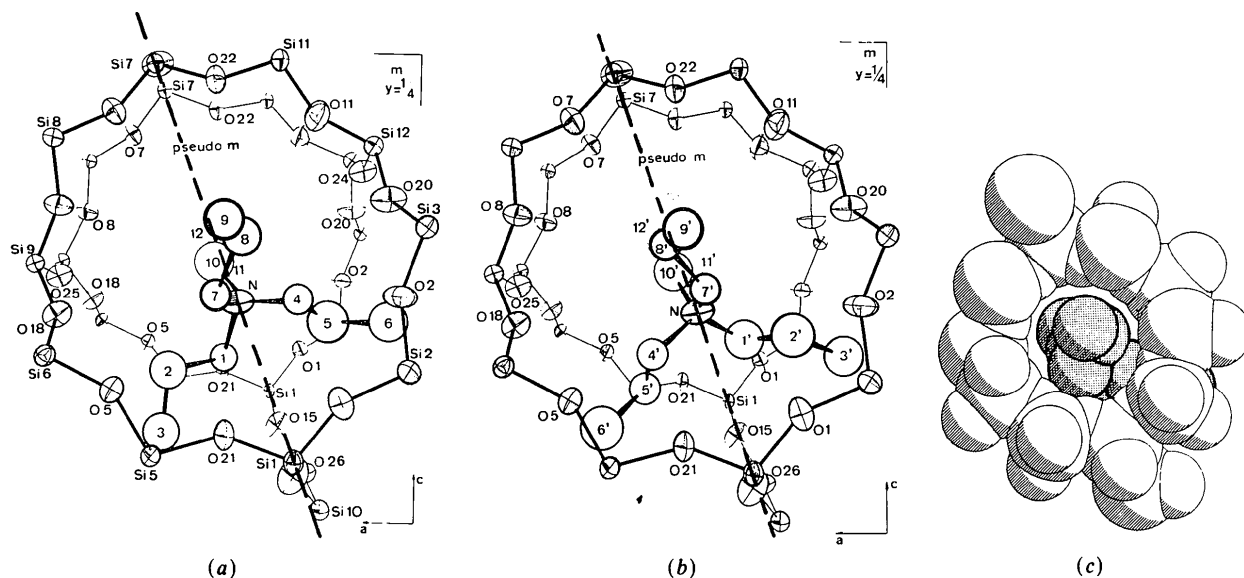

Fig. 3. TPA$^+$ at the intersection of channels seen along b. Pseudo-m is indicated. For reasons of clarity the mirror image of TPA$^+$ around m at $y = \frac{1}{4}$ is not drawn. (a) Orientation of the first TPA$^+$ ion. (b) Orientation of the second TPA$^+$ ion. (c) Space-filling drawing (Spek, 1982) of TPA$^+$ in first orientation showing the packing in the straight channel. van der Waals radii taken from Bondi (1964).
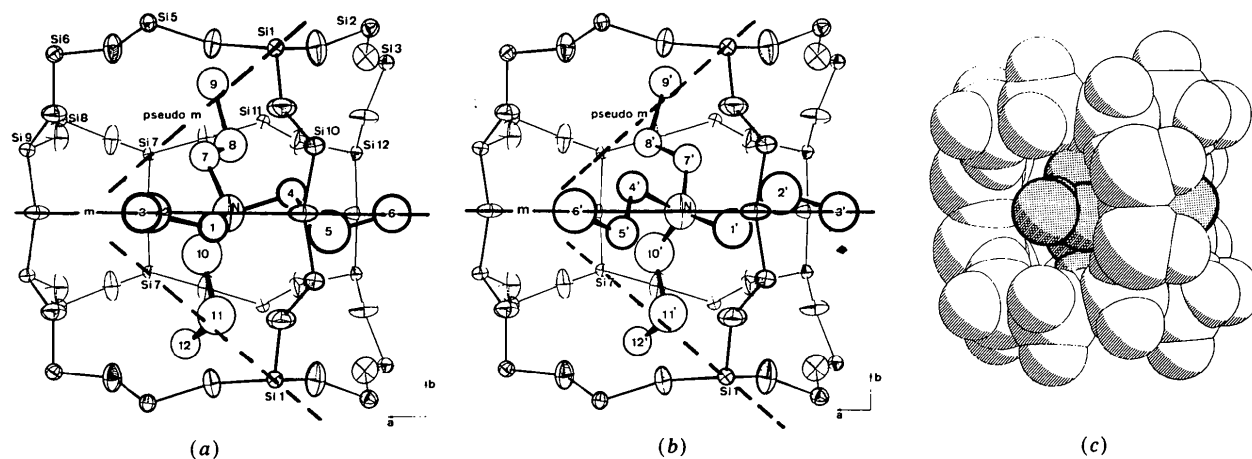

Fig. 4. As Fig. 3, seen along c. The packing of terminal C atoms of TPA$^+$ in the sinusoidal pores is shown.

References

AUROUX, A., DESEPERT, H., LECLERCQ, C. & VEDRINE, J. (1983). *Appl. Catal.* **6**, 95–119.

BAERLOCHER, C. (1984). Proc. 6th Int. Zeolite Conf., Reno, edited by D. OLSON & A. BISIO, pp. 823–833. Guildford: Butterworths.

BALLMOOS, R. VON (1981). Thesis, Zürich. Frankfurt am Main: Verlag GmbH.

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.

CHAO, K. J., LIN, J. C., WANG, Y. & LEE, G. H. (1986). *Zeolites*, **6**, 35–38.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

FLANIGEN, E. M., BENNETT, J. M., GROSE, R. W., COHEN, J. P., PATTON, R. L., KIRCHNER, R. L. & SMITH, J. V. (1978). *Nature (London)*, **271**, 512–516.

GILSON, J. P. & DEROUANE, E. G. (1984). *J. Catal.* **88**, 538–541.

HAAG, W. O., LAGO, R. M. & WEISZ, P. B. (1984). *Nature (London)*, **309**, 589–591.

JANSEN, J. C., VAN KONINGSVELD, H., SCHALKOORD, D. & VAN BEKKUM, H. (1987). *Zeolites.* To be submitted.

KEIJSPER, J., MACKAY, M., VAN DEN BERG, K., KORTBEEK, A. G. T. G. & POST, M. F. M. (1986). KNCV Katalyse Symposium (Catalysis Symp. of the Royal Dutch Chem. Soc.), 17–18 April, TH Twente, The Netherlands, p. 39.

LERMER, H., DRAEGER, M., STEFFEN, J. & UNGER, K. K. (1985). *Zeolites*, **5**, 131–134.

OLSON, D. H., HAAG, W. O. & LAGO, R. M. (1980). *J. Catal.* **61**, 390–396.

OLSON, D. H., KOKOTAILO, G. T., LAWTON, S. L. & MEIER, W. M. (1981). *J. Phys. Chem.* **85**, 2238–2243.

PRICE, G. D., PLUTH, J. J., SMITH, J. V., BENNETT, J. M. & PATTON, R. L. (1982). *J. Am. Chem. Soc.* **104**, 5971–5977.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

SPEK, A. L. (1982). The *EUCLID* package. In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The *XRAY72* system. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

ZALKIN, A. (1957). *Acta Cryst.* **10**, 557–560.

Conflicting Results for the Deformation Properties of Forsterite, Mg_2SiO_4

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Abstract

Deformation properties of forsterite have been deduced simultaneously from X-ray diffraction data affected by extinction in Bonn-Pittsburgh (B), and in Groningen (G). For the G crystals, GI and GII, extinction is anisotropic and considerably larger than for crystal B. Measurements were made with Mo radiation for B, and with Mo and Ag radiation for GI and GII. As the Becker & Coppens [*Acta Cryst.* (1974), A30, 129–147, 148–153; *Acta Cryst.* (1975), A31, 417–425] extinction model is not exact, the deformation properties had to be filtered from the data with refinement models. The flexible B model [α's and populations for single exponential functions (SEF's) refined for $l = 0$–4] and the more rigid G model (SEF populations refined for $l = 0$–3 and α for $l = 0$; further α's and n's fixed at standard values) yield different results. Refinement of α makes the majority of the SEF's notably diffuse, presumably due to correlation with incorrect extinction corrections. The order of the deformation potentials at the Mg(1) and Mg(2) sites is reversed for B and G. Maxima on the Si–O bonds, which are polarized towards O, are smaller for G ($0\cdot20$–$0\cdot25$ e Å^{-3}) than for B ($0\cdot25$–$0\cdot45$ e Å^{-3}). Although each of the two sets of deformation properties looks acceptable by itself, the present comparison shows that neither of them may be sufficiently close to the truth. The diffraction data are available on request from the Electron Density Data Bank (Professor H. Burzlaff, Institut für Angewandte Physik, Bismarckstrasse 10, D-8520 Erlangen, Federal Republic of Germany). Details of the measurements are described in the paper.

Introduction

The present paper describes two independent attempts, in Bonn-Pittsburgh (B) and in Groningen (G), to determine the deformation properties of forsterite by X-ray diffraction. The conflicting results obtained show that incorrect conclusions can be drawn from deformation densities and potentials which, judged by themselves, seem reliable.