transformations involving at least three modifications. The results are described separately (Sarma & Dunitz, 1990). Here we mention only one feature that seems important in the present context; in all three modifications, the structural units are head-to-tail chains, packed such that each zwitterion is surrounded by six neighbours with opposite polarity. By contrast, the starting structure is built from stacks, and the only strongly dipolar interactions are between neighbouring molecules in the same stack. The dipole moment of the zwitterion (2) is clearly much larger than that of the methyl ester (1); the values estimated with the *OPEC* program are 6·31 and 3·42 debye. This increase in the polarity of the molecule may be the determining factor that makes the alternating chain structure of (2) more stable than the stack structure of (1) and hence is responsible for the breakdown of the latter as the reaction proceeds.

This work was carried out with the financial support of the Swiss National Science Foundation. We are also indebted to Dr Bernd Schweizer and Paul Seiler for their help at several stages of the work.

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Structures of Three Crystalline Phases of *p*-(Trimethylammonio)benzenesulfonate and their Interconversions

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(*Received* 14 *March* 1990; *accepted* 27 *June* 1990)

Abstract

$C_9H_{13}NO_3S$, M_r = 215·29; at 193 K, α phase, orthorhombic, *Pnc*2, *a* = 10·121 (2), *b* = 9·421 (1), *c* = 20·891 (3) Å, *V* = 1992·0 (5) Å^3, *Z* = 8, D_x = 1·44 g cm^{-3}, Mo *Kα* radiation, λ = 0·71069 Å, μ = 3·04 cm^{-1}, *F*(000) = 912, *R* = 0·029 for 1787 observed reflections with $I \geq 3\sigma(I)$; at 298 K, coexistence of α and β phases; β phase, orthorhombic, *Pbma*, *a* = 10·183 (2), *b* = 9·568 (3), *c* = 10·444 (2) Å, *V* = 1017·6 (7) Å^3, *Z* = 4, D_x = 1·41 g cm^{-3}, Mo *Kα* radiation, λ = 0·71069 Å, μ = 2·97 cm^{-1}, *F*(000) = 456, *R* = 0·049 for 822 selected reflections with $I \geq 3\sigma(I)$; at 385 K, γ phase, tetragonal, *P*4/*nmm*, *a* =

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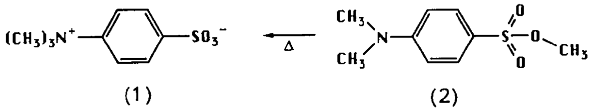
0108-7681/90/060784-11$03.00

7·21 (1), $c = 10{\cdot}45\,(1)$ Å from precession photographs, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}542$ Å. The structures of the α and β phases have been determined, a model structure has been proposed for the high-temperature γ phase, and the mechanisms of the phase transitions, which involve disorder in the stacking of layers with ionic outer surfaces and nonpolar interiors, are discussed.

Introduction

When we tried to determine the crystal structure of the zwitterionic product (1), formed from (2) in the solid-state methyl-transfer reaction studied by Sukenik, Bonapace, Mandel, Lau, Wood & Bergman (1977), we found that its diffraction pattern undergoes an interesting series of transformations as the temperature is changed. In their study, at room temperature, Sukinek *et al.* (1977) reported cell dimensions $a = 10{\cdot}15$, $b = 9{\cdot}69$, $c = 20{\cdot}55$ Å, $Z = 8$, and possible space groups *Pc*2*a* (No. 32) or *Pcma* (No. 55) for the crystalline product but did not attempt to determine the detailed structure. If they had done so, they would have run into difficulties.



(1) (2)

Crystals of (1) obtained by slow evaporation of water–methanol solutions are well formed cubes, mostly twinned across the (110) face, as can easily be recognized in the polarization microscope. Occasionally, untwinned specimens can be found. They are usually more plate-like than the twins. On cooling from room temperature, reflections with l odd (based on the 20 Å translation) increased in intensity, indicating that a slow phase change was taking place. This appeared to be complete by 255 K. A full data set was collected (α phase) at 193 K.

As the crystal was warmed towards room temperature, reflections with l odd gradually weakened and showed diffuse streaks or satellites along the $\mathbf{c}^*$ direction in reciprocal space. Moreover, $hk0$ reflections with h odd, as well as $0kl$ reflections with k odd, weaken and become nearly undetectable by about 335 K. With the c axis halved and the new glide plane present, the formal space group becomes *Pbma* (No. 57, β phase), and the structure must be closely related to that of the α phase. We obtained no indication of any gradual phase change between 193 and 335 K by differential scanning calorimetry (DSC) measurements. However, DSC measurements did show a small endotherm ($T = 385$ K, $\Delta H \simeq 2{\cdot}2$ kJ mol^{-1}, $\Delta S \simeq 5{\cdot}9$ J mol^{-1} K^{-1} $\simeq R\ln 2$) on warming and an exotherm of similar energy at 382 K on cooling. On warming crystals above 385 K, we found that they had transformed to a tetragonal structure (γ phase).

Experimental

The zwitterion (1) was prepared from ester (2) as described by Sukinek *et al.* (1977). Slow evaporation of methanol–water (1:1) solutions yielded mostly twinned crystals (see *Introduction*). Untwinned crystals, size $0{\cdot}45 \times 0{\cdot}30 \times 0{\cdot}20$ mm; Enraf–Nonius CAD-4 diffractometer with cooling device; graphite monochromator, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å), ω/θ scan. From the constancy of three standard reflections, no crystal deterioration during the diffractometer measurements at 193 and 298 K could be detected, in spite of several passages through the phase transition.

Low-temperature structure (*α phase*)

Cell dimensions at 193 K by least-squares fit to setting angles of 23 automatically centred reflections with $24 < 2\theta < 26°$. Maximum $\sin\theta/\lambda = 0{\cdot}64$ Å^{-1}; index range $h = 0/13$, $k = 0/12$, $l = 0/26$; 2496 reflections measured, 2234 unique. Space group *Pnc*2, two independent molecules. Structure solved by direct methods using *SHELX*86 (Sheldrick, 1986). All non-H atoms located in first E map, all H atoms in a subsequent difference map. Refinement of positional parameters, anisotropic displacement parameters of non-H atoms and isotropic parameters of H atoms by *SHELX*76 (Sheldrick, 1976). Final $R = 0{\cdot}029$, $wR = 0{\cdot}032$ for 1787 reflections with $I > 3\sigma(I)$, $w = 1{\cdot}0/[\sigma^2(F) + 0{\cdot}003828F^2]$, 356 parameters, max. $\Delta/\sigma = 0{\cdot}5$ for H(9*D*,*z*/*c*); $\Delta\rho$(max.) $+0{\cdot}28$, $\Delta\rho$(min.) $-0{\cdot}27$ e Å^{-3}. Final parameters are given in Table 1.*

Room-temperature structure (*β phase*)

A reasonable interpretation of the diffraction pattern at room temperature was possible only by neglecting weak $hk0$ reflections with h odd and $0kl$ reflections with l odd (arising from residual amounts of the α phase) as well as the diffuse streaks with half-integral l (arising from lack of periodicity in the $\mathbf{c}$ direction) that are visible on precession photographs. These $hk0$ and $0kl$ reflections become weaker as the temperature is raised above 280 K and are hardly detectable by about 335 K, although the

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* Lists of torsion angles, structure factors for low- and room-temperature structures and atomic point charges adopted in the energy calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53326 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positional and displacement parameters* (Å^2) *of the* α *phase of zwitterion* (1) *at* 193 K

E.s.d.'s are given in parentheses in units of the last significant digit.

	x	y	z	U^{11} (or U)	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Molecule *A*									
S(1*A*)	0·7025 (1)	0·2422 (1)	0·0000 (1)	0·0168 (3)	0·0242 (4)	0·0124 (3)	0·0003 (3)	−0·0005 (4)	0·0009 (3)
O(1*A*)	0·8392 (2)	0·2449 (3)	0·0213 (2)	0·019 (1)	0·056 (1)	0·019 (1)	0·0016 (9)	−0·0037 (8)	0·0014 (9)
O(2*A*)	0·6324 (2)	0·1154 (2)	0·0196 (1)	0·030 (1)	0·030 (1)	0·018 (1)	0·0054 (8)	0·0027 (8)	−0·0026 (8)
O(3*A*)	0·6334 (2)	0·3731 (2)	0·0150 (2)	0·029 (1)	0·029 (1)	0·022 (1)	−0·0033 (8)	0·0007 (8)	0·0067 (8)
N(1*A*)	0·7113 (3)	0·2459 (3)	−0·2897 (2)	0·013 (2)	0·021 (2)	0·015 (2)	0·0012 (8)	−0·0021 (9)	−0·0009 (8)
C(1*A*)	0·7087 (2)	0·2372 (3)	−0·0852 (2)	0·018 (1)	0·019 (1)	0·016 (2)	0·000 (9)	−0·0025 (8)	0·0039 (9)
C(2*A*)	0·6631 (3)	0·1215 (3)	−0·1187 (2)	0·029 (1)	0·021 (1)	0·017 (1)	0·0036 (9)	0·001 (1)	−0·0035 (9)
C(3*A*)	0·6622 (3)	0·1214 (3)	−0·1856 (2)	0·026 (2)	0·018 (1)	0·019 (1)	−0·001 (1)	−0·002 (1)	−0·004 (1)
C(4*A*)	0·7101 (4)	0·2383 (4)	−0·2177 (2)	0·024 (2)	0·023 (2)	0·007 (2)	0·001 (1)	−0·0020 (9)	0·003 (1)
C(5*A*)	0·7604 (3)	0·3550 (3)	−0·1844 (2)	0·039 (2)	0·021 (1)	0·017 (1)	0·003 (1)	−0·002 (1)	−0·009 (1)
C(6*A*)	0·7587 (3)	0·3526 (3)	−0·1179 (2)	0·041 (2)	0·021 (1)	0·016 (1)	−0·0005 (9)	−0·003 (1)	−0·009 (1)
C(7*A*)	0·8527 (3)	0·2486 (4)	−0·3121 (2)	0·013 (1)	0·052 (2)	0·023 (2)	0·002 (1)	0·003 (1)	−0·003 (1)
C(8*A*)	0·6395 (3)	0·3773 (3)	−0·3120 (2)	0·027 (2)	0·021 (1)	0·023 (2)	0·004 (1)	−0·004 (1)	0·002 (1)
C(9*A*)	0·6431 (3)	0·1213 (3)	−0·3203 (2)	0·034 (2)	0·021 (1)	0·017 (2)	−0·002 (1)	−0·002 (1)	−0·003 (1)
H(2*A*)	0·630 (3)	0·041 (3)	−0·099 (1)	0·026 (8)					
H(3*A*)	0·631 (3)	0·040 (3)	−0·208 (1)	0·031 (9)					
H(5*A*)	0·792 (3)	0·438 (3)	−0·206 (1)	0·024 (7)					
H(6*A*)	0·789 (4)	0·436 (4)	−0·099 (2)	0·04 (1)					
H(7*A*)	0·859 (6)	0·262 (5)	−0·359 (4)	0·09 (2)					
H(7*B*)	0·902 (5)	0·145 (6)	−0·297 (3)	0·08 (2)					
H(7*C*)	0·887 (5)	0·330 (5)	−0·296 (3)	0·05 (1)					
H(8*A*)	0·637 (3)	0·373 (3)	−0·363 (2)	0·023 (9)					
H(8*B*)	0·553 (4)	0·375 (3)	−0·293 (2)	0·031 (9)					
H(8*C*)	0·686 (3)	0·458 (4)	−0·295 (2)	0·026 (8)					
H(9*A*)	0·647 (3)	0·134 (3)	−0·369 (2)	0·011 (8)					
H(9*B*)	0·549 (4)	0·115 (4)	−0·300 (2)	0·05 (1)					
H(9*C*)	0·690 (3)	0·033 (3)	−0·308 (1)	0·015 (7)					
Molecule *B*									
S(1*B*)	0·2133 (1)	0·2616 (1)	0·2507 (1)	0·0201 (3)	0·0232 (3)	0·0119 (3)	0·0014 (4)	−0·0001 (4)	0·0010 (2)
O(1*B*)	0·3513 (2)	0·2661 (3)	0·2314 (2)	0·024 (1)	0·059 (2)	0·018 (1)	0·004 (1)	0·0053 (8)	0·0037 (9)
O(2*B*)	0·1405 (2)	0·3869 (2)	0·2319 (2)	0·031 (1)	0·023 (1)	0·023 (1)	0·0045 (8)	−0·0030 (7)	0·0014 (8)
O(3*B*)	0·1473 (2)	0·1310 (2)	0·2319 (2)	0·040 (1)	0·021 (1)	0·022 (1)	−0·0028 (8)	−0·0078 (8)	0·0020 (8)
N(1*B*)	0·2120 (3)	0·2491 (3)	0·5397 (2)	0·020 (2)	0·030 (2)	0·015 (2)	0·0019 (9)	−0·002 (1)	−0·003 (1)
C(1*B*)	0·2158 (3)	0·2607 (3)	0·3360 (2)	0·019 (1)	0·025 (1)	0·011 (1)	−0·0008 (9)	−0·0012 (9)	−0·001 (1)
C(2*B*)	0·1008 (3)	0·2933 (4)	0·3694 (2)	0·017 (1)	0·064 (2)	0·018 (1)	0·002 (1)	−0·002 (1)	0·007 (1)
C(3*B*)	0·1008 (3)	0·2882 (4)	0·4357 (2)	0·014 (1)	0·074 (2)	0·017 (1)	0·000 (1)	0·004 (1)	0·006 (1)
C(4*B*)	0·2151 (4)	0·2541 (3)	0·4682 (2)	0·014 (2)	0·024 (2)	0·018 (3)	0·002 (1)	−0·002 (1)	−0·002 (1)
C(5*B*)	0·3307 (3)	0·2205 (3)	0·4356 (2)	0·019 (1)	0·038 (1)	0·017 (1)	0·002 (1)	−0·000 (1)	0·005 (1)
C(6*B*)	0·3298 (3)	0·2242 (3)	0·3688 (2)	0·020 (1)	0·034 (1)	0·019 (1)	−0·000 (1)	0·003 (1)	0·004 (1)
C(7*B*)	0·3473 (4)	0·2431 (5)	0·5688 (2)	0·018 (2)	0·085 (3)	0·013 (2)	0·003 (1)	−0·003 (1)	−0·005 (2)
C(8*B*)	0·1367 (3)	0·1185 (3)	0·5602 (2)	0·028 (2)	0·024 (2)	0·020 (2)	0·003 (1)	0·002 (1)	−0·002 (1)
C(9*B*)	0·1425 (4)	0·3777 (3)	0·5662 (2)	0·037 (2)	0·022 (2)	0·017 (2)	−0·003 (1)	0·001 (1)	−0·003 (1)
H(2*B*)	0·015 (4)	0·325 (4)	0·349 (2)	0·05 (1)					
H(3*B*)	0·031 (4)	0·312 (4)	0·458 (2)	0·05 (1)					
H(5*B*)	0·405 (4)	0·192 (4)	0·457 (2)	0·033 (8)					
H(6*B*)	0·409 (4)	0·198 (4)	0·345 (2)	0·042 (9)					
H(7*D*)	0·324 (4)	0·248 (3)	0·615 (2)	0·03 (1)					
H(7*E*)	0·396 (4)	0·331 (4)	0·552 (2)	0·036 (9)					
H(7*F*)	0·398 (5)	0·149 (5)	0·554 (2)	0·06 (1)					
H(8*D*)	0·138 (4)	0·110 (4)	0·602 (2)	0·04 (1)					
H(8*E*)	0·192 (4)	0·046 (5)	0·546 (2)	0·06 (1)					
H(8*F*)	0·052 (4)	0·125 (3)	0·544 (2)	0·03 (1)					
H(9*D*)	0·142 (5)	0·364 (5)	0·611 (3)	0·05 (1)					
H(9*E*)	0·056 (3)	0·369 (3)	0·556 (1)	0·019 (7)					
H(9*F*)	0·192 (4)	0·457 (4)	0·554 (2)	0·04 (1)					

streaks persist to much higher temperatures. On cooling from room temperature, the reverse changes occur with appreciable hysteresis, the diffraction pattern of the α phase being regained by about 255 K. After cycling several times through these changes, we found no appreciable deterioration in crystal quality. Cell dimensions at 298 K (β phase) by least-squares fit to setting angles of 25 automatically centred reflections with $24 < 2\theta < 43°$. Maximum $(\sin\theta)/\lambda$ = 0·64 Å^{-1}; index range $h = 0/13$, $k = 0/12$, $l = 0/13$; 1452 reflections measured, 1190 unique. Space group *Pbma* (No. 57), $Z = 4$, molecular mirror symmetry imposed. Structure solved by direct methods using *SHELX*86 (Sheldrick, 1986). The structure (β phase) is statistically disordered over four orientations of the phenylene rings. All ordered non-H atoms and six of the eight quarter-weight disordered phenylene C atoms in the asymmetric unit were located in the

Table 2. *Atomic positional and displacement parameters* (Å^2) *of the* β *phase of zwitterion* (1) *at* 298 K

	x	*y*	*z*	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	S.o.f.*
S(1)	0·4595 (1)	0·2500 (0)	0·2499 (1)	0·0314 (9)	0·0483 (9)	0·0174 (9)	0·000 (0)	0·0006 (5)	0·000 (0)	0·5
O(1)	0·5955 (4)	0·2500 (0)	0·2104 (4)	0·026 (2)	0·130 (5)	0·026 (2)	0·000 (0)	0·005 (2)	0·000 (0)	0·5
O(2)	0·3906 (3)	0·1238 (3)	0·2129 (3)	0·052 (2)	0·047 (2)	0·033 (2)	−0·006 (1)	−0·008 (1)	−0·003 (1)	1·0
N(1)	0·4630 (4)	0·2500 (0)	0·8287 (4)	0·025 (2)	0·047 (3)	0·017 (2)	0·000 (0)	−0·001 (1)	0·000 (0)	0·5
C(1)	0·4625 (5)	0·250 (0)	0·4201 (5)	0·032 (3)	0·041 (3)	0·017 (2)	0·000 (0)	0·003 (2)	0·000 (0)	0·5
C(2*A*)	0·511 (2)	0·140 (2)	0·488 (1)	0·025 (7)	0·09 (1)	0·039 (9)	0·000 (8)	0·016 (6)	0·022 (9)	0·25
C(2*B*)	0·429 (3)	0·128 (1)	0·4855 (9)	0·07 (1)	0·026 (6)	0·014 (6)	−0·001 (5)	0·008 (7)	0·018 (8)	0·25
C(2*C*)	0·581 (1)	0·240 (1)	0·486 (1)	0·016 (8)	0·10 (3)	0·018 (6)	0·02 (4)	0·007 (5)	−0·02 (3)	0·25
C(2*D*)	0·353 (1)	0·232 (2)	0·488 (1)	0·023 (7)	0·15 (2)	0·023 (6)	−0·011 (7)	0·006 (5)	−0·028 (9)	0·25
C(3*A*)	0·507 (2)	0·136 (1)	0·619 (1)	0·023 (7)	0·07 (1)	0·04 (1)	0·018 (8)	0·014 (7)	0·020 (8)	0·25
C(3*B*)	0·422 (2)	0·130 (1)	0·6191 (9)	0·06 (1)	0·033 (7)	0·014 (6)	0·001 (5)	0·008 (6)	0·013 (9)	0·25
C(3*C*)	0·583 (1)	0·232 (9)	0·620 (1)	0·014 (6)	0·19 (4)	0·024 (8)	0·03 (3)	0·001 (5)	0·02 (3)	0·25
C(3*D*)	0·350 (1)	0·223 (3)	0·6188 (9)	0·030 (7)	0·10 (3)	0·024 (6)	−0·007 (7)	0·016 (5)	−0·010 (9)	0·25
C(4)	0·4630 (5)	0·250 (0)	0·6849 (5)	0·034 (3)	0·047 (3)	0·017 (3)	0·000 (0)	0·002 (2)	0·000 (0)	0·5
C(7)	0·5993 (6)	0·250 (0)	0·8797 (6)	0·020 (3)	0·129 (7)	0·028 (3)	0·000 (0)	−0·003 (2)	0·000 (0)	0·5
C(8)	0·3914 (5)	0·1224 (5)	0·8785 (4)	0·050 (3)	0·041 (2)	0·032 (2)	0·003 (2)	0·006 (2)	−0·003 (2)	1·0
H(7*A*)	0·5964 (6)	0·2500 (0)	0·9740 (6)	0·063 (9)						0·5
H(7*B*)	0·6509 (6)	0·3407 (0)	0·8443 (6)	0·10 (2)						1·0
H(8*A*)	0·3031 (5)	0·1284 (5)	0·8497 (4)	0·19 (3)						1·0
H(8*B*)	0·3759 (5)	0·1334 (5)	0·9803 (4)	0·07 (2)						1·0
H(8*C*)	0·4496 (5)	0·0303 (5)	0·8602 (4)	0·08 (2)						1·0

* Site-occupancy factor. Atoms lying on the mirror plane have half-weight and the phenylene C atoms C(2) and C(3) were fixed at quarter-weight.

first *E* map, the two remaining C atoms and methyl-H atoms in subsequent difference maps. Refinement of positional parameters, anisotropic displacement parameters of non-H atoms (including the disordered ones) and isotropic parameters of methyl-H atoms by *SHELX76* (Sheldrick, 1976). In spite of large correlations (up to 0·9), especially between *y* and U^{22} of C(2*B*), C(3*B*), C(5*B*) and C(7*B*), the quarter-atoms closest to the mirror plane, the parameters converged to reasonable values close to positions found in the α phase with allowance for the higher symmetry (Table 2). Phenylene H atoms were fixed at 1·08 Å from their respective C atoms. Final $R = 0{\cdot}048$, $wR = 0{\cdot}052$ for 822 reflections with $I > 3\sigma(I)$, $w = 1{\cdot}0/[\sigma^2(F) + 0{\cdot}036433F^2]$, 178 parameters, max. $\Delta/\sigma = 0{\cdot}56$ for C(3*A*,*x*/*a*); $\Delta\rho$(max.) + 0·23, $\Delta\rho$(min.) $-0{\cdot}49$ e Å^{-3}. Three data sets, measured from three different crystals, led to essentially identical results.

High-temperature structure (γ *phase*)

Cell dimensions at 385 K from 30° precession photographs (Cu $K\alpha$ radiation, $\lambda = 1{\cdot}542$ Å), again neglecting streaks with half-integral *l* in the **c*** direction; space group *P*4/*nmm*, $Z = 2$. No attempt was made to measure the intensities or to solve the structure, the main features of which can easily be deduced from the structures of the α and β phases. In addition to the disorder of the phenylene group, as in the β phase, both the trimethylammonium and sulfonate groups are also rotationally disordered about the long axis of the molecule.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Geometry calculations were made with *GEOM* (Gilmore, 1979) and *MOMO* (Dobler, 1989), motional analyses with *THMA*11 (Dunitz, Schomaker & Trueblood, 1988), and illustrations with *PLUTO*78 (Motherwell, 1978) and *ORTEP* (Johnson, 1965).

Molecular and crystal structures

α *phase*

The two crystallographically independent zwitterions in the α phase show similar bond lengths and angles (Table 3) but they differ slightly in conformation (Fig. 1). In both molecules, the trimethylammonium and sulfonate substituents are practically eclipsed, with relevant C—N—S—O torsion angles all less than 3°. However, there is a perceptible difference in the aromatic ring plane orientations, the smallest C—C—N—C torsion angle being 5·8 (5)° in molecule *A* [involving C(9*A*)] and 14·8 (5)° in molecule *B* [involving C(7*B*)]. This difference shows itself in the pattern of C(4)—N—C bond angles in the two molecules; the angles involving C(9*A*) and C(7*B*) are about 2° larger than the others, presumably due to H(methyl)···H(phenylene) repulsive interactions. Although the rings themselves are planar to within 0·01 Å, the N and S substituents deviate from the aromatic planes by significant amounts and in the same sense (Table 4). The methyl groups all show staggered conformations.

A stereoview of the crystal packing is provided in Fig. 2. Each of the two independent molecules forms a set of polar chains running in the **c** direction, successive molecules along the chains being related by the *c*/*b* glide. In fact, the ionic groups within a

Table 3. *Bond lengths* (Å) *and angles* (°) *of the α and β phases of zwitterion* (1)

	α phase		
	Mol. *A*	Mol. *B*	β phase
S(1)—O(1)	1·454 (3)	1·453 (3)	1·445 (4)
S(1)—O(2)	1·448 (2)	1·446 (2)	1·449 (3)
S(1)—O(3)	1·452 (2)	1·455 (2)	
S(1)—C(1)	1·782 (4)	1·782 (4)	1·778 (5)
N(1)—C(4)	1·506 (6)	1·495 (6)	1·502 (7)
N(1)—C(7*A*)	1·506 (5)	1·499 (5)	1·487 (7)
N(1)—C(8*A*)	1·508 (4)	1·509 (4)	1·515 (5)
N(1)—C(9*A*)	1·505 (4)	1·506 (5)	
C(1)—C(2)	1·376 (5)	1·391 (5)	
C(1)—C(6)	1·380 (5)	1·386 (5)	
C(2)—C(3)	1·398 (6)	1·386 (6)	
C(3)—C(4)	1·378 (5)	1·378 (5)	
C(4)—C(5)	1·397 (5)	1·388 (5)	
C(6)—C(6)	1·389 (6)	1·398 (6)	
O(1)—S(1)—O(2)	113·2 (2)	113·0 (2)	113·0 (1)
O(1)—S(1)—O(3)	112·2 (2)	113·1 (2)	
O(2)—S(1)—O(3)	113·8 (1)	112·5 (2)	112·8 (1)
O(1)—S(1)—C(1)	105·8 (2)	105·3 (2)	105·5 (2)
O(2)—S(1)—C(1)	106·1 (1)	106·4 (2)	106·0 (1)
O(3)—S(1)—C(1)	104·8 (2)	105·8 (2)	
S(1)—C(1)—C(2)	121·2 (3)	119·3 (3)	
S(1)—C(1)—C(6)	119·1 (3)	120·4 (3)	
C(4)—N(1)—C(7)	108·6 (3)	112·8 (3)	110·8 (3)
C(4)—N(1)—C(8)	110·1 (3)	108·7 (3)	110·3 (2)
C(4)—N(1)—C(9)	112·5 (3)	110·6 (3)	
C(7)—N(1)—C(8)	110·4 (3)	108·4 (3)	109·0 (2)
C(7)—N(1)—C(9)	108·5 (3)	107·9 (3)	
C(8)—N(1)—C(9)	106·7 (3)	108·4 (3)	107·3 (2)
N(1)—C(4)—C(3)	121·8 (3)	118·8 (3)	
N(1)—C(4)—C(5)	117·2 (3)	119·9 (3)	
C(2)—C(1)—C(6)	119·7 (4)	120·2 (4)	
C(1)—C(2)—C(3)	120·7 (3)	119·6 (3)	
C(2)—C(3)—C(4)	119·0 (4)	120·1 (3)	
C(3)—C(4)—C(5)	121·0 (4)	121·2 (4)	
C(4)—C(5)—C(6)	118·7 (3)	118·6 (3)	
C(5)—C(6)—C(1)	120·8 (3)	120·3 (3)	

chain are almost translationally equivalent as they straddle the planes $y = \pm\frac{1}{4}$. The two sets of chains have opposite polarity, and each chain of one polarity is surrounded by four chains of the opposite polarity to give a well defined layer structure perpendicular to **c** (Fig. 3). In this description, the surfaces of the layers consist of an array of ionic groups with alternating charges, while the inner part consists of the aromatic rings. The planes of the phenylene groups in a given layer lie at a steep angle to one another; the normals make angles of ± 25° to the **a** direction (molecules *A*) and ± 15° to the **b** direction (molecules *B*). Thus, each phenylene group in one orientation is surrounded by four in another in a herringbone-like pattern. The layer group (Dornberger-Schiff, 1956) is *P*11(2), but if only the ionic outer parts are considered it is *Pbm*(*a*), corresponding to the symmetry of the β phase. In this way, we have a virtually nonpolar structure in a polar space group. The two independent molecules are closely mirror-symmetric across the planes $y = \pm\frac{1}{4}$ and the ionic groups are also related by a pseudo-inversion centre.

Table 4. *Planes and angles between normals of the planes in two independent molecules of the α phase of the zwitterion*

Equations of planes are referred to the Cartesian crystal frame. Distances are in Å and angles are in °.

Plane 1: C(1*A*) C(2*A*) C(3*A*) C(4*A*) C(5*A*) C(6*A*)
$-0{\cdot}9126X + 0{\cdot}4089Y - 0{\cdot}0021Z = 5{\cdot}641$
Deviations S(1*A*) + 0·085 (1); N(1*A*) + 0·031 (3)
Plane 2: C(1*B*) C(2*B*) C(3*B*) C(4*B*) C(5*B*) C(6*B*)
$-0{\cdot}2675X - 0{\cdot}9633Y - 0{\cdot}0242Z = 3{\cdot}117$
S(1*B*) + 0·039 (1); N(1*A*) + 0·011 (3)
Plane 3: O(1*A*) S(1*A*) C(1*A*) C(4*A*) N(1*A*) C(7*A*)
$-0{\cdot}0390X + 0{\cdot}9992Y + 0{\cdot}0044Z = -1{\cdot}975$
O(2*A*) − 1·137 (2); O(2*A*) + 1·289 (2); C(8*A*) + 1·296 (3); C(9*A*) − 1·117 (3)
Plane 4: O(1*B*) S(1*B*) C(1*B*) C(4*B*) N(1*B*) C(7*B*)
$0{\cdot}0112X + 0{\cdot}9996Y + 0{\cdot}0257Z = -2{\cdot}652$
O(2*B*) + 1·137 (2); O(2*A*) − 1·278 (2); C(8*A*) − 1·220 (3); C(9*A*) + 1·225 (3)
Plane 5: $Y = 2{\cdot}35525$ ($y = b/4$)

Angles between normals to planes

	1	2	3	4	5
1	0	98·6	63·6	66·5	65·9
2		0	− 17·8	− 14·9	− 15·6
3			0	3·1	2·3
4				0	1·6
5					0

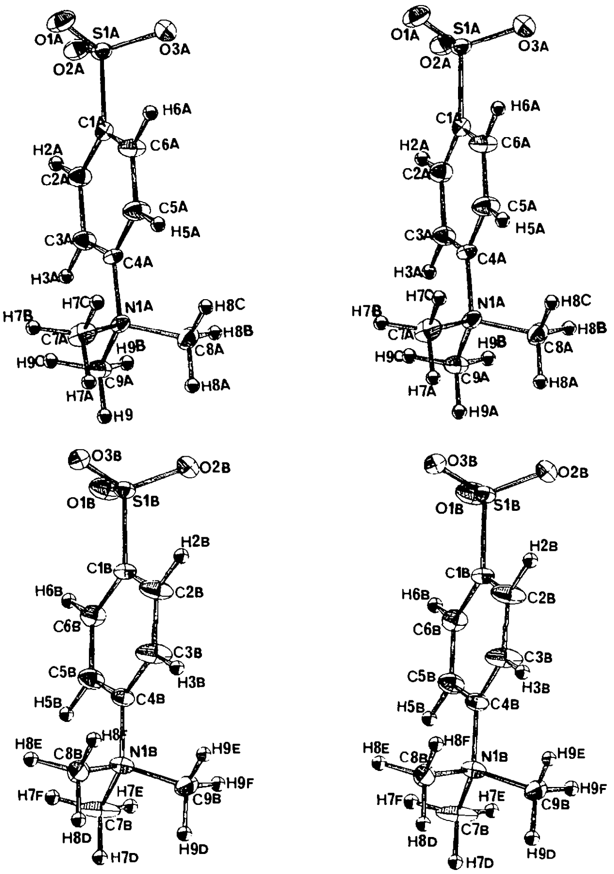

Fig. 1. α phase. *ORTEP* stereodrawings of the two independent molecules *A* (top) and *B* (bottom), showing atom numbering and displacement ellipsoids at 50% probability level.

The packing is dominated by ionic interactions between trimethylammonium and sulfonate groups of successive molecules along a given chain (between layers) and also between such groups in neighbouring chains within a layer (Fig. 3). Note that the eclipsed orientation of these ionic groups holds not only within individual molecules but also between such groups in different molecules along an entire chain (Fig. 2). Intermolecular $H_3C\cdots O$ distances are 3·4–3·5 Å between neighbouring molecules within a chain and somewhat shorter between chains (see Table 5; intermolecular distances and angles cited in this table and in the subsequent discussion have been derived by fixing the C—H bond lengths at 1·08 Å; they thus differ slightly from those based on the experimental coordinates of Table 1, which yield apparent C—H distances in the range 0·91 to 1·14 Å, average 1·01 Å). It can be no accident that every

Table 5. *Intermolecular contact distances* (Å) *and angles* (°) *for* O *atoms in the α phase*

These values are based on coordinates that differ slightly from those listed in Table 1, having been derived from a refinement in which the C—H distances were fixed at 1·08 Å. E.s.d.'s for O···C and O···H distances, and for angles are respectively 4, 4 and 9 units in the last significant digit.

O···C		O···H		O···H—C	
Intrachain					
O(1*A*)···C(7*A*)	3·484	O(1*A*)···H(7*A*)	2·41	O(1*A*)···H(7*A*)—C(7*A*)	171·9
O(2*A*)···C(8*A*)	3·522	O(2*A*)···H(8*A*)	2·45	O(2*A*)···H(8*A*)—C(8*A*)	171·8
O(3*A*)···C(9*A*)	3·443	O(3*A*)···H(9*A*)	2·37	O(3*A*)···H(9*A*)—C(9*A*)	169·6
O(1*B*)···C(7*B*)	3·400	O(1*B*)···H(7*D*)	2·32	O(1*B*)···H(7*D*)—C(7*B*)	174·8
O(2*B*)···C(8*B*)	3·588	O(2*B*)···H(8*D*)	2·51	O(1*B*)···H(8*D*)—C(8*B*)	174·4
O(3*B*)···C(9*B*)	3·463	O(3*B*)···H(9*D*)	2·39	O(3*B*)···H(9*D*)—C(9*B*)	175·8
Intralayer					
O(1*A*)···C(8*B*)	3·378	O(1*A*)···H(8*F*)	2·41	O(1*A*)···H(8*F*)—C(8*B*)	149·1
O(1*A*)···C(9*B*)	3·409	O(1*A*)···H(9*E*)	2·44	O(1*A*)···H(9*E*)—C(9*B*)	148·7
O(2*A*)···C(7*B*)	3·345	O(2*A*)···H(7*E*)	2·50	O(2*A*)···H(7*E*)—C(7*B*)	134·0
O(3*A*)···C(7*B*)	3·293	O(3*A*)···H(7*F*)	2·51	O(3*A*)···H(7*F*)—C(7*B*)	128·2
O(2*A*)···C(9*B*)	3·338	O(2*A*)···H(9*F*)	2·30*	O(2*A*)···H(9*F*)—C(9*B*)	160·1
O(3*A*)···C(8*B*)	3·413	O(3*A*)···H(8*E*)	2·38*	O(3*A*)···H(8*E*)—C(8*B*)	159·0
O(1*B*)···C(8*A*)	3·337	O(1*B*)···H(8*B*)	2·36	O(1*B*)···H(8*B*)—C(8*A*)	150·1
O(1*B*)···C(9*A*)	3·317	O(1*B*)···H(9*B*)	2·34	O(1*B*)···H(9*B*)—C(9*A*)	149·9
O(2*B*)···C(7*A*)	3·313	O(2*B*)···H(7*B*)	2·54	O(2*B*)···H(7*B*)—C(7*A*)	127·9
O(3*B*)···C(7*A*)	3·318	O(3*B*)···H(7*C*)	2·52	O(3*B*)···H(7*C*)—C(7*A*)	130·4
O(2*B*)···C(9*A*)	3·298	O(2*B*)···H(9*C*)	2·28*	O(2*B*)···H(9*C*)—C(9*A*)	156·0
O(3*B*)···C(8*B*)	3·345	O(3*B*)···H(8*C*)	2·33*	O(3*B*)···H(8*C*)—C(8*A*)	155·6
O(1*A*)···C(3*B*)	3·213	O(1*A*)···H(3*B*)	2·21	O(1*A*)···H(3*B*)—C(3*B*)	153·7
O(3*A*)···C(5*B*)	3·593	O(3*A*)···H(5*B*)	2·52	O(3*A*)···H(5*B*)—C(5*B*)	176·2
O(3*B*)···C(5*A*)	3·271	O(3*B*)···H(5*A*)	2·21	O(3*B*)···H(5*A*)—C(5*A*)	172·0

* These interactions are between molecules separated by **b**/2. Other interactions between ionic groups in a layer are between molecules separated by **a**/2 (Fig. 3). The longer the O···H distance, the greater the deviation from collinearity.

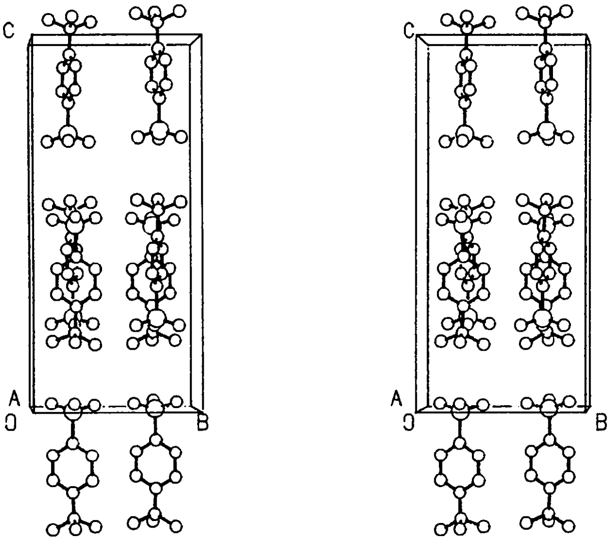

Fig. 2. α phase. Stereodrawing of crystal structure viewed along the **a** direction. Note the chains running along the *c* axis and the layers perpendicular to this direction. Successive molecules along the chains, related by the *c*/*b* glide, are almost translationally equivalent, apart from the orientations of their phenylene groups. These are different in the two sets of independent molecules.

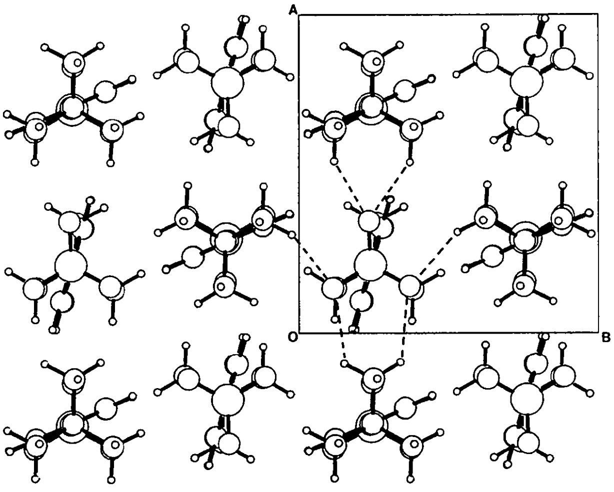

Fig. 3. α phase. Layer of molecules, viewed along the **c** direction. Each molecule is surrounded by four others of opposite polarity. The C—H···O interactions between ionic groups are marked with broken lines.

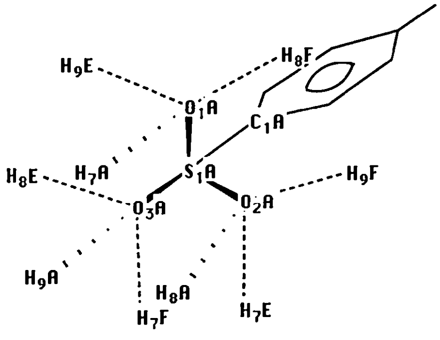

Fig. 4. α phase. Pattern of C—H···O interactions, showing that each O atom interacts with three H atoms from trimethylammonium groups. This pattern is almost the same for molecules *A* and *B*.

Table 6. *Results of motional analysis of the α phase of the zwitterion*

Eigenvalues of **T** and **L** are listed together with the direction cosines of the eigenvectors **L**1, **L**2 and **L**3 with respect to the crystal axes. The quantity R is defined as $[\Sigma(\Delta U^{ij})^2/\Sigma(U^{ij})^2]^{1/2}$. E.s.d.'s are given in parentheses in units of the last significant digit. In the non-rigid body model only the libration of the phenylene groups about the C(1)—C(4) axes is considered.

	Rigid body		Non-rigid body	
	Mol. *A*	Mol. *B*	Mol. *A*	Mol. *B*
T ($Å^2 \times 10^{-4}$)				
T1	205 (16)	156 (31)	165 (17)	149 (9)
T2	181 (14)	292 (36)	173 (12)	212 (16)
T3	171 (9)	170 (21)	167 (7)	164 (7)
L ($\deg^2$)				
L1	2·2 (5)	−0·8 (11)	2·6 (5)	2·3 (5)
L2	−1·0 (5)	0·9 (12)	0·3 (6)	1·9 (4)
L3	32 (3)	44 (7)	29 (3)	31 (2)
$\langle\varphi^2\rangle$*	–	–	20 (6)	42 (5)
*L*1/*a*	−0·999	0·998	−0·986	−0·799
*L*1/*b*	0·009	0·031	−0·168	0·601
*L*1/*c*	0·006	0·049	0·004	−0·018
*L*2/*a*	0·009	−0·033	−0·168	0·596
*L*2/*b*	1·000	0·998	0·985	0·796
*L*2/*c*	0·020	0·052	0·024	0·102
*L*3/*a*	−0·006	0·047	−0·008	0·076
*L*3/*b*	0·020	0·054	0·023	0·071
*L*3/*c*	−1·000	−0·997	−1·000	−0·995
R	0·166	0·303	0·125	0·091

* The determinate quantity is actually $\langle\varphi^2\rangle + 2\langle\varphi L^{\parallel}\rangle$ (Dunitz, Schomaker & Trueblood, 1988; Bürgi, 1989).

methyl C—H bond points more or less towards a sulfonate O atom of a neighbouring molecule. Within the individual chains, the C—H···O angles are close to 180°, between chains they deviate more from collinearity. The O···H distances vary between 2·2 and 2·5 Å and thus lie well in the range that has previously been regarded as evidence for C—H···O hydrogen bonding (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984; Sarma & Desiraju, 1986; Seiler, Weisman, Glendening, Weinhold, Johnson & Dunitz, 1987). As the number of H atoms in the structure greatly exceeds the number of O atoms, each O atom is the acceptor of several such hydrogen bonds, as indicated in Fig. 4.

Although the anisotropic displacement parameters (Table 1) have e.s.d.'s of up to about 25 pm² and are thus not of the best quality, their analysis with the program *THMA*11 (Dunitz, Schomaker & Trueblood, 1988) nevertheless yields interesting results for the atomic motions (Table 6). A model in which the phenylene groups are allowed to librate about the C(1)···C(4) axis (*i.e.*, about the chain direction) gives better agreement with the observed U^{ij} values than does the rigid-body model. For molecule *A*, the improvement is modest (*R* dropping from 0·166 to 0·125) for an internal* $\langle\varphi^2\rangle$ of 20 (6) deg², compared with L^{33} of 28 (3) deg²; for molecule *B*, it is impressive (*R* dropping from 0·303 to 0·091 for internal $\langle\varphi^2\rangle$ of 42 (5) deg², compared with L^{33} of 31 (2) deg². The other components of the molecular libration tensors are negligible. As we shall see, the structural changes that occur at higher temperatures can be understood in terms of these librations about the chain directions. For both molecules, the main translational component is in the direction nearly perpendicular to the plane of their respective phenylene groups, *i.e.* T^{11} for molecule *A* and T^{22} for molecule *B*.

β phase

The space group chosen to describe this structure requires the molecules to lie across the mirror planes at $y = \pm\frac{1}{4}$. This means that the atoms O(1), S(1), C(1), C(4), N(1), C(7) lie on this set of planes, which must bisect the ionic subtituents. In an ordered crystal the central aromatic ring would need to lie either in the mirror plane or perpendicular to it. We find, however, a disordered distribution over four orientations, two of them lying quite close (± 10°) to the mirror plane and two more nearly perpendicular (± 69°) to it, as shown in Fig. 5. Clearly, the structure of the β phase is related to that of the α phase by averaging over the four orientations of the phenylene planes in the latter.

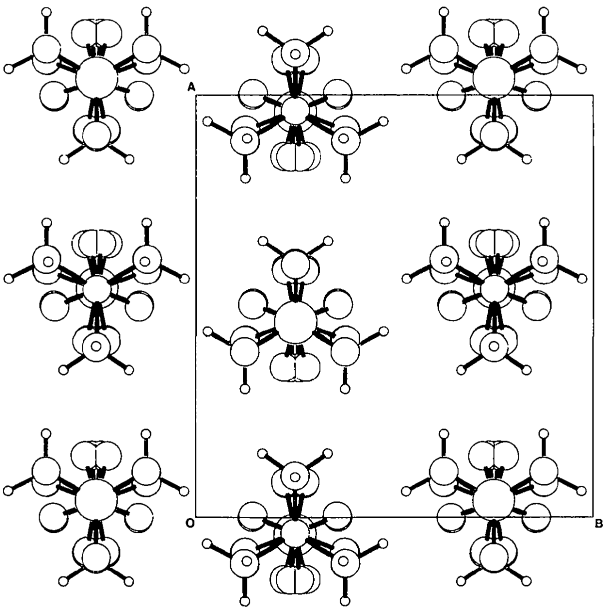

Fig. 5. β phase. As for Fig. 3, but showing disorder of the phenylene orientations owing to averaging over different layers.

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* The determinate quantity is actually $\langle\varphi^2\rangle + 2\langle\varphi L^{\parallel}\rangle$ (Dunitz, Schomaker & Trueblood, 1988; Bürgi, 1989).

γ phase

Just as the β phase is derived from the α by averaging over the four orientations of the phenylene groups, so the tetragonal γ phase is related to the β by averaging over the two orientations of the ionic substituents (Fig. 6). The chains along the c axis and the layers perpendicular to it both retain their identity.

Relationships between the phases

From the relationship between the ordered low-temperature α phase and the disordered β phase, and from the presence of the diffuse streaks along $\mathbf{c}^*$, we infer that the latter is derived from the former by introducing stacking faults in the sequence of the layers with associated loss of periodicity in the $\mathbf{c}$ direction. At low temperatures, stacking errors are infrequent so that the averaged structure is still predominantly that of the α phase;† at room temperature, domains of the ordered phase still co-exist with those of the disordered one, but by about 335 K they have more or less disappeared, judging by the weakness of the check reflections.

In the low-temperature structure, the ionic groups in a given chain are (very nearly) translationally equivalent, while the phenylene groups are related by the c/b glide reflection operation. From this ordered structure, a stacking fault consists of the flip of all phenylene planes in a layer into one of four symmetry-related arrangements with the same mutual orientations, leaving the arrangement of the ionic groups intact. These four ways of arranging the layer are illustrated in Fig. 7, together with the symmetry operations by which they are interrelated. In addition to the ordered double-layer arrangement of the α phase, many others can be imagined; for example, a single-layer repeating structure with the space group $P112$, ordered double-layer structures with space groups $P112/a$ and $P2_12_12$, various combinations of these, as well as disordered sequences. We do not know which of these corresponds best to the actual structure at intermediate temperatures, between the α phase and complete disorder in the layer sequence. (Refinement of the room-temperature data, including all reflections from the 20 Å cell, in space group $P2_12_12$ converged to an R factor of 10% but gave unacceptable U tensors and molecular dimensions.)

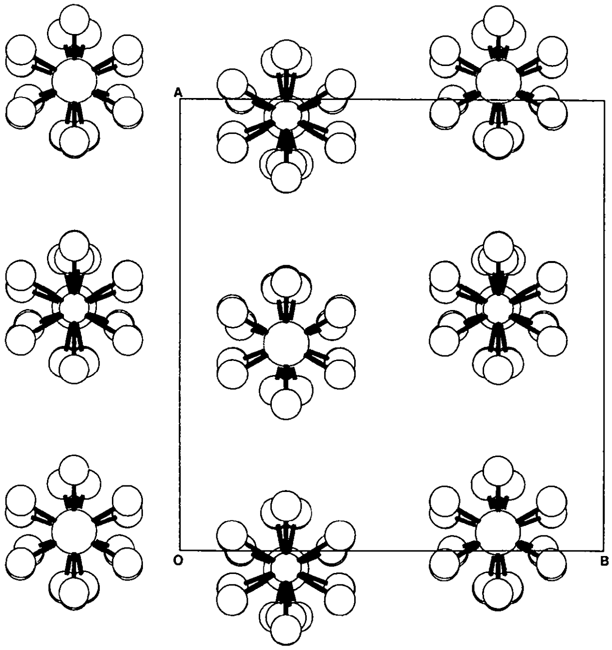
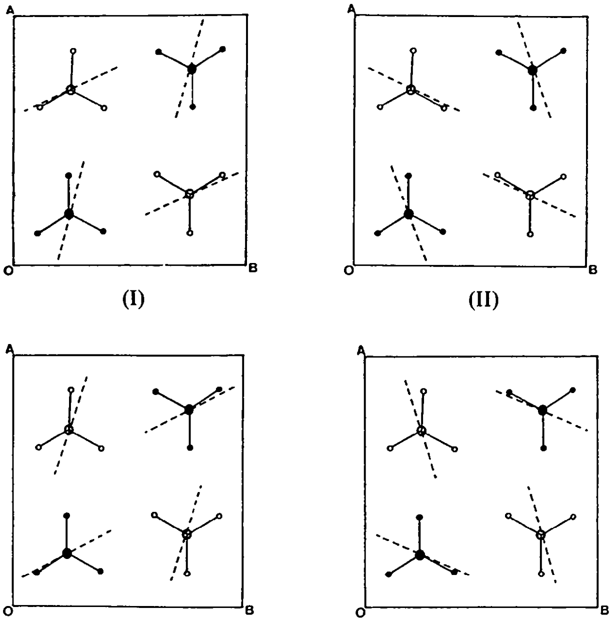


Fig. 6. Tetragonal γ phase. As for Figs. 3 and 5, but showing disorder of the ionic groups as well as the phenylenes.



(I) (II)

(III) (IV)

Fig. 7. Four symmetry-equivalent layers. A crystal consisting only of translationally equivalent single layers would have space group $P112$. Ordered double-layer structures can be constructed in space groups $Pnc2$ (I + II, α phase), $P112/a$ (I + III), and $P2_12_12$ (I + IV). Since the interactions between the ionic groups on the surfaces of the layers are the same for all sequences, stacking faults are to be expected. The β phase corresponds to a random sequence.

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† When the frequency of errors is small, the result of introducing them into the ordered double-layered α structure is not the same as introducing them by adding layers during crystal growth. In the former case, each 'incorrect' layer corresponds to two 'errors'; in the latter, each 'incorrect' layer inaugurates a portion of twinned or displaced structure.

Given that the ionic group arrangement is the same in these structures and has a higher symmetry (or, more correctly, a higher pseudosymmetry) than the structure as a whole, one might wonder why the sequence of phenylene orientations along a given chain should become ordered at all when the crystal is cooled. From the packing of the phenylene groups (Fig. 3), it is easy to see that their mutual orientations within a layer must be highly ordered, but how is the information about the orientation in one layer communicated to the next layer, insulated from it by the nearly symmetric ionic groups? We tentatively suggest that the signal from one molecule to its neighbour in the chain is communicated by a pattern of small bond-angle distortions induced by intramolecular nonbonded H(aromatic)···H(methyl) and H(aromatic)···O repulsions and transmitted along the chain by intermolecular C—H···O interactions, as indicated in Fig. 8.

For molecule *A*, the repulsion between the *ortho* H(3) and the methyl H(9*C*) widens the bond angles C(3)—C(4)—N and C(4)—N—C(9). These distortions lead to practically equal distances for H(3)···H(9*C*), 2·07 Å, and H(5)···H(8*C*), 2·06 Å, whereas with equal angles (C—C—N, 120; C—N—C, 110·6°) on the opposite sides of the molecule these distances would be 1·94 and 2·13 Å, respectively. They also lead to an asymmetry in the three C—H···O interactions along the chain. This imbalance of forces contracts the O(3)—S—C(1) angle in the next molecule at the expense of the opposite angle involving O(2). The pattern of bond angles at C(1) indicates that the interaction between *ortho* H and sulfonate O in this situation is repulsive, and the balance of forces is achieved when the phenylene group is oriented to bring its *ortho* H(2) closer to O(2) than to O(3). This orientation corresponds to glide reflection along the chain rather than translation. Similar arguments apply, *mutatis mutandis*, for molecule *B*.

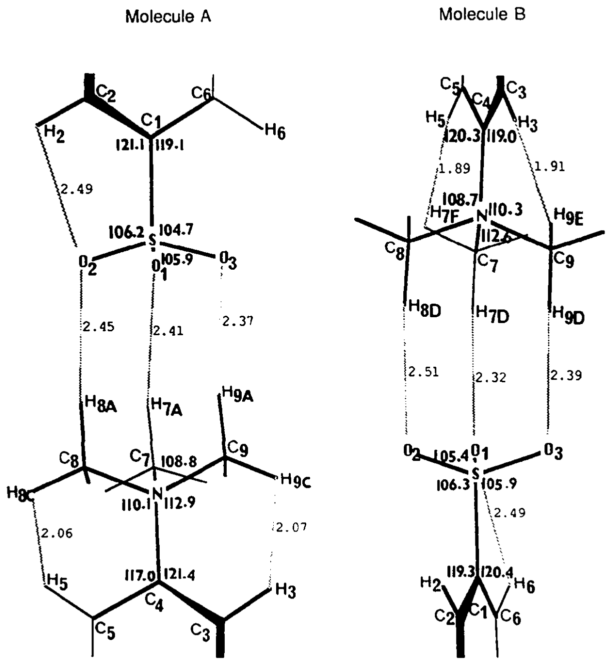

Fig. 8. Model for transmission of signal concerning phenylene orientation from one molecule to its neighbour along a chain in the α phase by small distortions from mirror symmetry of the ionic groups. Distances are given in Å and angles in °.

Given the smallness and subtlety of these effects, it comes as no surprise that the preferred orientational sequence along a chain is lost in the thermal noise as the temperature is raised. As stacking errors accumulate and periodicity is lost, the structure gradually approaches one in which the sequence of the layers is more or less random. The 'space group' of this disordered structure, averaged over all layers, is *Pbma* with each phenylene orientation represented at quarter-weight. In a sense, our choice of this space group can be considered to be somewhat arbitrary, as it is based on a disregard of the reflections in the room-temperature diffraction pattern that do not fit it. The structure thus obtained for the β phase in this space group represents the averaged superposition of the four types of layers, irrespective of the degree of order in their stacking.

As far as interactions between ionic groups within layers are concerned, it can be seen from Table 5 that C—H···O distances between molecules separated by **b**/2 are shorter than those separated by **a**/2. This difference is responsible for the difference in length between the *a* and *b* axes in the orthorhombic α and β phases.

In the high-temperature, tetragonal γ phase, the orientations of the ionic groups (Figs. 3 and 5) also become statistically disordered (Fig. 6) although presumably highly correlated. In contrast to the relatively slow development (or disappearance) of the disordered β structure over a considerable tempera-

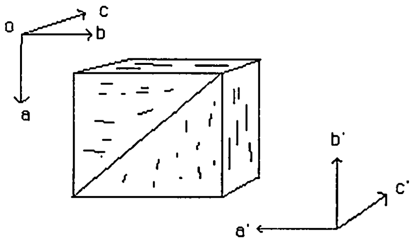

Fig. 9. Sketch of a twinned crystal before the orthorhombic β to tetragonal γ phase transition. On warming through the transition the twin boundary disappears, but it reappears, almost unchanged, on cooling. The squiggles represent the general directions of striations on the crystal surfaces.

ture range, the β to γ transition takes place quite sharply at 383 K and is accompanied by a measurable endotherm (see *Introduction*). Also in contrast to the α to β transition, where the expansion of the unit cell occurs continuously over a wide temperature range, the β to γ transition shows a discontinuous increase in the b translation by about 6% to bring it into equality with the a axis.

Cooling of the tetragonal γ phase below the transition temperature produces twinned crystals of the orthorhombic β phase, as can be seen in the polarization microscope (Fig. 9). The boundary between twinned specimens disappears on warming through the transition but reappears at the same place on cooling, even from temperatures as high as 10° above the transition, suggestive of some kind of memory mechanism (persistence of oriented domains of the orthorhombic structure?).

Table 7. *Packing potential-energy (PPE) calculations for the α phase of* (1)

Values in parentheses indicate Coulombic contributions. All energies are in negative kJ mol^{-1}

	Mol. A	Mol. B
Packing coefficient	0·74	
PPE/molecule	646·4 (491·9) [mol. A 651·9 (495·3) and mol. B 641·4 (488·2)]	
Contributions to PPE from nearest neighbours*		
I	58·32 (54·68) [x,0·5 − y, − 0·5 + z,A]	58·70 (54·89) [x,0·5 − y, − 0·5 + z,B]
II	58·32 (54·68) [x,0·5 − y,0·5 + z,A]	58·70 (54·89) [x,0·5 − y,0·5 + z,B]
III	102·91 (92·65) [x,0·5 − y, − 0·5 + z,B]	101·57 (93·16) [− 1 + x,0·5 − y,0·5 + z,A]
IV	101·57 (93·16) [1 + x,0·5 − y, − 0·5 + z,B]	102·91 (92·65) [x,0·5 − y,0·5 + z,A]
V	108·65 (96·63) [1 − x, − 0·5 + y, − 0·5 + z,B]	107·64 (97·72) [1 − x, − 0·5 + y,0·5 + z,A]
VI	107·64 (97·72) [1 − x,0·5 + y, − 0·5 + z,B]	108·65 (96·63) [1 − x,0·5 + y,0·5 + z,A]
Contribution from first coordination sphere	82·4%	83·9%
Estimated $\langle\varphi^2\rangle^{1/2}$ at 193 K†	6·0°	6·8°

* Note that for both sets of molecules the contributions from neighbours V and VI (separated by **b**/2 from the reference molecule) are slightly higher than those from III and IV (separated by **a**/2 from the reference molecule).

† Half-width at $RT/2$ of potential well for phenylene rotation in constant field of its neighbours (Shmueli & Kroon, 1974).

Energy aspects

The combination of the threefold ($3m$, C_{3v}) symmetry of the ionic substituents and the twofold rotational symmetry of the phenylene group about the long molecular axis enforces a high periodicity in the rotational potential energy function of the isolated molecule. With the outer substituents held mutually eclipsed, the *MM*2 force field (Still, 1987) with atomic charges set equal to zero gives an energy minimum at the eclipsed orientation of the phenylene plane and a barrier of 3·8 kJ mol^{-1} for a 30° rotation from this orientation. With the phenylene group constrained to be eclipsed with one of the ionic substituents, rotation of the other substituent is associated with even smaller barriers (*ca* 1·5 kJ mol^{-1} for the sulfonate and 2·3 kJ mol^{-1} for the trimethylammonium group at 30° rotations from their eclipsed orientations). Introduction of reasonable atomic point charges has very little effect on these values. Thus, neither the eclipsed conformation of the ionic substituents nor the orientations of the phenylene groups observed in the crystal can be ascribed to a dependency on the intramolecular potential alone.

Packing-energy-minimization calculations with *PCK*83 (Williams, 1983) in which the cell dimensions were varied along with the positions and orientations of the two independent molecules did not reproduce the observed crystal structure; both with and without atomic point charges [assigned using the *MOPAC* program package (Stewart, 1987) with the MNDO option] the molecules move from their observed positions and the a and b translations were about 15% too large. Calculations with cell dimensions fixed at their low-temperature values were made with *OPEC* (Gavezzotti, 1983) using Mirsky (1978) potentials. When the phenylene orientation of each molecule was varied in the constant field of its neighbours together with the above intramolecular potential, energy minima within 2° of the observed orientations were obtained for both independent molecules. When these calculations were repeated with allowance for relaxation of neighbouring molecules within the same layer, several other minima of comparable energy were found in the phenylene orientation circuit.

All calculations agree that the overwhelming part of the packing energy (≃93%) is attributable to Coulombic attractions between the ionic groups (Table 7). According to *OPEC* calculations similar to those described above, rotation of any of these groups from its observed, nearly mirror-symmetric, eclipsed orientation in the crystal is associated with a sharp loss of packing energy (about 55 kJ mol^{-1} for a 10° rotation). Each of the two independent molecules has six nearest neighbours, four in its layer and two in its chain. Table 7 shows the contributions from these to the PPE (packing potential energy) of a central reference molecule. These contributions amount to about 420 kJ mol^{-1} in the layer and about 115 kJ mol^{-1} in the chain. Non-Coulombic contributions show the same pattern as the total. The interaction energy between phenylene groups within a chain is negligible. Hence, the orientational relationship of these groups along a chain can be altered very easily, in contrast to a change in their mutual arrangement in a layer. This difference is the crucial factor in the transformation of ordered α to disordered β phase by introduction of stacking faults as the temperature is raised.* In the γ phase, the

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* Similar calculations in space group $P2_12_12_1$ resulted in a structure which is less stable by about 63 kJ mol^{-1} than the observed $Pnc2$ space group at low temperature.

eclipsed conformation of the ionic substituents within individual molecules can be lost at a low energy cost. Provided that the arrangement of ionic groups on the outer surfaces of the layers and the eclipsing between such groups at the interlayer contacts are maintained the PPE can retain much of its high calculated value. This may explain the absence of a melting point. When the crystals are heated to 600 K they begin to decompose with development of a colour change.

Concluding remarks

It is not obvious how the phase transitions occuring in this system are to be categorized in terms of the traditional classification. The $\beta \rightarrow \gamma$ transition apparently involves only an increase in the orientational disorder of the ionic groups. It is, however, accompanied by a discontinous change in the length of the *b* axis, and the endotherm observed by DSC measurements appears to be quite sharp. Thus, this transition shares some features generally asociated with a second-order transition and others associated with a first-order transition.

Although the transformation from the $\alpha \rightarrow \beta$ phase involves the introduction of stacking faults in the sequence of well defined layers, this process is not to be confused with the stacking faults characteristic of polytypism (Rao & Rao, 1978) or OD (order–disorder) families (Dornberger-Schiff, 1964; Dornberger-Schiff & Dunitz, 1965). In the latter, there are two or more structurally equivalent (and hence energetically equivalent) ways of stacking neighbouring layers. The particular stacking arrangement adopted in any given case then depends on interactions not between nearest neighbouring layers but between next neighbouring and more distant layers. This is not the case in our system. Here, all the layers are translationally equivalent as far as the arrangement of oppositely charged trimethylammonium and sulfonate groups is concerned. This stays invariant throughout the temperature range. The layers differ only with respect to the sequence of their phenylene group orientations. While the interactions among these groups within a layer are fairly strong, favouring a definite mutual arrangement, those between such groups in different layers are much weaker. The signal communicating the information about phenylene orientation in one layer to the next thus tends to be lost in the thermal noise as the temperature is raised. The structure can be pictured as a sequence of almost liquid-like nonpolar regions sandwiched between the layers of a rigid ionic framework. In the *α* phase the liquid freezes.

This work was carried out with the financial support of the Swiss National Science Foundation. We are also indebted to Dr Bernd Schweizer and Paul Seiler for their help at several stages of the work.

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