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Redetermination of the Structure of Methyl *p*-Dimethylaminobenzenesulfonate at Two Temperatures

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Abstract

$C_9H_{13}NO_3S$, $M_r = 215·29$, monoclinic, $P2_1/c$; $a = 8·855\,(2)$, $b = 10·426\,(5)$, $c = 11·082\,(3)$ Å, $\beta = 91·13\,(2)^\circ$, $V = 1022·9\,(5)$ Å^3 at 193 K; $a = 8·913\,(1)$, $b = 10·487\,(4)$, $c = 11·166\,(2)$ Å, $\beta = 90·95\,(1)^\circ$, $V = 1043·5\,(4)$ Å^3 at 255 K; $Z = 4$, $D_x = 1·40$ g cm^{-3} at 193 K (1·37 g cm^{-3} at 255 K), Mo $K\alpha$ radiation, $\lambda = 0·7107$ Å, $\mu = 2·84$ (2·78) cm^{-1}, $F(000) = 456$, $R = 0·054$ (0·044) for 963 (876) observed reflections with $I \geq 3\sigma(I)$. The crystal structure of methyl *p*-dimethylaminobenzenesulfonate has been redetermined at 193 and 255 K. Motional analysis and packing potential-energy calculations support the view [Sukenik, Bonapace, Mandel, Lau, Wood & Bergman (1977). *J. Am. Chem. Soc.* **99**, 851–858] that the thermally induced methyl transfer reaction which takes place in this crystal is assisted by cooperative motions of the molecules in stacks running along the **b** direction.

Introduction

One of the most interesting thermal solid-state reactions is the conversion (see scheme below) of methyl *p*-dimethylaminobenzenesulfonate (1) to the zwitterionic product *p*-trimethylammoniobenzenesulfonate (2) (Kuhn & Ruelius, 1950). Later Sukenik, Bonapace, Mandel, Lau, Wood & Bergman (1977) showed that the reaction is intermolecular and proceeds much faster in the crystal than it does either in the melt or in solution. They determined the crystal structure of (1), which contains stacks of molecules nearly ideally oriented for the intermolecular methyl transfer. From EHT (extended Hückel theory) calculations, Gavezzotti & Simonetta (1977) proposed a two-step mechanism, involving a molecular ion-pair intermediate, but they did not discuss the possibility of correlated motions of molecules within the stacks. Menger, Kaiserman & Scotchie (1984) showed that the reaction proceeds faster in the bulk crystal than on the surface, where an unidentified reaction intermediate accumulates; however, no such intermediate was detectable in the bulk. From Raman phonon spectroscopic measurements, Dwarakanath & Prasad (1980) suggested that softening of a lattice vibration mode (27 cm^{-1} at 163 K) plays an important role in the reaction. In support of this, Prasad (1987) made a motional analysis of the crystal structure results of Sukenik *et al.* (1977) and found the major rigid-body motion to be libration about the long molecular axis. Since the accuracy of the room-temperature crystal structure suffers from several factors [use of Cu radiation; slow crystal decomposition (~22% in three days); intensity standards reduced by 60%], we thought it worthwhile to make new structure analyses at lower temperatures. We report these results here, together with results of packing-energy calculations.

(1) (2)

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Experimental

Crystals of (1) obtained by slow evaporation of a methanol soluton at 263 K were thin plates bounded by {001}. To prevent solid-state reaction they were stored at this temperature. The melting point of a single crystal, as measured with the Mettler Thermosystem FP800, was 363–363·8 K, in good agreement with the value recorded by Sukenik *et al.* (1977). Enraf–Nonius CAD-4 diffractometer with cooling device; graphite monochromator, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å), ω/θ scan; crystal size 0·35 × 0·21 × 0·05 mm. Cell dimensions by least-squares fit to setting angles of 23 automatically centred reflections with $14 < 2\theta < 35°$. No absorption correction. Two data sets measured at 193 ± 1 (and 255 ± 1) K, to $\sin\theta/\lambda \leq 0{\cdot}595$ (0·64) Å^{-1}; index range h 0/10 (−11/11), k 0/12 (0/13), l −13/13 (0/14); 1915 (2418) reflections measured, 1785 (2025) unique, 963 (876) with $I \geq 3\sigma(I)$ used in refinements. Poor crystal quality (wide mosaic spread) was the main hindrance to more extensive and accurate intensity measurements, but three standard reflections indicated inappreciable crystal deterioration during the measurement period. Since the crystal structure was known at room temperature (Sukenik *et al.*, 1977), we proceeded directly to refine it (positional coordinates of all atoms, anisotropic displacement parameters of non-H atoms and isotropic parameters for H atoms) with *SHELX*76 (Sheldrick, 1976). Final $R = 0{\cdot}054$ (0·044), $wR = 0{\cdot}061$ (0·054), $w = 0{\cdot}5653/[\sigma^2(F) + 0{\cdot}0385F^2]$ $\{3{\cdot}4/[\sigma^2(F) + 0{\cdot}00004F^2]\}$, 179 parameters, maximum $\Delta/\sigma = 0{\cdot}3$ and 0·2 for H9*A* (x coordinate) and H7*A* (y coordinate), $\Delta\rho$(max.) + 0·3 (0·2), $\Delta\rho$(min.) −0·2 (−0·1) e Å^{-3} close to N(1). Final parameters are listed in Table 1.* Atomic scattering factors were those incorporated in *SHELX*76.

Geometric calculations were carried with *GEOM* (Gilmore, 1979). Illustrations were prepared using *PLUTO*78 (Motherwell, 1978) and *ORTEP* (Johnson, 1965). Motional analyses were carried out with *THMA*11 (Dunitz, Schomaker & Trueblood, 1988).

Table 1. *Fractional coordinates and equivalent isotropic displacement parameters for all atoms at* 193 (*upper rows*) *and* 255 K (*lower rows*)

E.s.d.'s are given in parentheses in units of the last significant digit. $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$. $\sigma U_{eq} = [\sigma^2U_{11}(U_{22}U_{33})^{1/3}(1/3)U_{11}^{-2/3} + \sigma^2U_{22}(U_{11}U_{33})^{1/3}(1/3) \times U_{22}{}^{2/3} + \sigma^2U_{33}(U_{22}U_{11})^{1/3}(1/3)U_{33}^{-2/3}]^{1/2}$.

	x	y	z	U_{eq}
S1	0·8135 (1)	0·3923 (2)	0·1141 (1)	0·0550 (8)
S1	0·8115 (1)	0·3917 (1)	0·1150 (1)	0·0714 (8)
O1	0·9327 (4)	0·4844 (5)	0·1717 (3)	0·070 (2)
O1	0·9300 (4)	0·4827 (5)	0·1721 (3)	0·092 (3)
O2	0·7637 (4)	0·4439 (4)	0·0017 (3)	0·060 (2)
O2	0·7615 (3)	0·4423 (3)	0·0032 (2)	0·078 (2)
O3	0·8888 (4)	0·2715 (4)	0·1165 (3)	0·086 (3)
O3	0·8856 (4)	0·2720 (4)	0·1176 (3)	0·112 (3)
N1	0·3047 (5)	0·3744 (5)	0·4481 (4)	0·065 (3)
N1	0·3055 (4)	0·3750 (4)	0·4471 (4)	0·083 (3)
C1	0·6650 (5)	0·3919 (5)	0·2134 (4)	0·049 (2)
C1	0·6639 (4)	0·3905 (4)	0·2126 (3)	0·056 (3)
C2	0·6740 (5)	0·3204 (6)	0·3180 (4)	0·053 (3)
C2	0·6713 (6)	0·3210 (5)	0·3180 (4)	0·069 (3)
C3	0·5578 (5)	0·3175 (5)	0·3973 (4)	0·055 (3)
C3	0·5564 (5)	0·3178 (5)	0·3947 (5)	0·069 (4)
C4	0·4230 (5)	0·3844 (5)	0·3718 (4)	0·049 (3)
C4	0·4226 (5)	0·3841 (5)	0·3710 (4)	0·063 (3)
C5	0·4164 (6)	0·4577 (5)	0·2655 (4)	0·056 (3)
C5	0·4154 (6)	0·4564 (5)	0·2652 (5)	0·073 (3)
C6	0·5334 (5)	0·4630 (5)	0·1878 (4)	0·054 (3)
C6	0·5333 (6)	0·4599 (5)	0·1891 (4)	0·067 (4)
C7	0·1690 (8)	0·4474 (9)	0·4269 (9)	0·092 (6)
C7	0·1699 (9)	0·4460 (9)	0·426 (1)	0·112 (7)
C8	0·3189 (7)	0·2999 (9)	0·5586 (5)	0·072 (6)
C8	0·3171 (8)	0·3022 (9)	0·5575 (5)	0·092 (6)
C9	0·9068 (8)	0·6177 (8)	0·1607 (6)	0·076 (5)
C9	0·907 (1)	0·6183 (9)	0·1597 (8)	0·104 (6)
H2	0·757 (6)	0·273 (5)	0·335 (4)	0·06 (1)
H2	0·755 (5)	0·278 (4)	0·333 (3)	0·06 (1)
H3	0·578 (7)	0·258 (5)	0·469 (5)	0·08 (2)
H3	0·565 (4)	0·268 (4)	0·465 (4)	0·07 (1)
H5	0·327 (5)	0·504 (4)	0·245 (4)	0·04 (1)
H5	0·330 (5)	0·505 (4)	0·251 (4)	0·08 (1)
H6	0·526 (6)	0·516 (5)	0·119 (5)	0·06 (1)
H6	0·529 (4)	0·509 (4)	0·122 (3)	0·06 (1)
H7*A*	0·097 (8)	0·411 (7)	0·482 (6)	0·10 (2)
H7*A*	0·098 (7)	0·425 (7)	0·476 (6)	0·15 (3)
H7*B*	0·123 (9)	0·414 (7)	0·352 (7)	0·11 (3)
H7*B*	0·131 (8)	0·426 (8)	0·347 (7)	0·18 (4)
H7*C*	0·190 (5)	0·559 (6)	0·428 (4)	0·06 (1)
H7*C*	0·190 (5)	0·545 (5)	0·426 (4)	0·09 (2)
H8*A*	0·236 (9)	0·294 (7)	0·588 (6)	0·10 (2)
H8*A*	0·218 (6)	0·292 (5)	0·591 (5)	0·13 (2)
H8*B*	0·38 (1)	0·364 (8)	0·621 (8)	0·14 (3)
H8*B*	0·389 (7)	0·337 (5)	0·610 (5)	0·12 (2)
H8*C*	0·318 (9)	0·203 (9)	0·534 (7)	0·13 (3)
H8*C*	0·35 (1)	0·203 (9)	0·536 (7)	0·24 (4)
H9*A*	0·96 (1)	0·666 (8)	0·209 (7)	0·13 (3)
H9*A*	0·964 (9)	0·677 (7)	0·210 (6)	0·18 (3)
H9*B*	0·809 (6)	0·640 (4)	0·184 (4)	0·04 (1)
H9*B*	0·816 (7)	0·630 (6)	0·181 (6)	0·13 (3)
H9*C*	0·925 (8)	0·646 (6)	0·083 (7)	0·10 (2)
H9*C*	0·924 (8)	0·649 (7)	0·084 (7)	0·17 (3)

Discussion

Molecular and crystal structure

Molecule (1), with its atom-numbering scheme, is shown in Fig. 1. Molecules related by the 2_1 symmetry operation of the space group are linked in stacks running parallel to **b**, and are shown with their respective displacement ellipsoids in Fig. 2. Although our results represent an improvement on the earlier room-temperature study, they are not as accurate as we would have liked. Since e.s.d.'s in some of the C positions are of the order of 0·01 Å, there is not much new information in the molecular geometry. However, we do detect a small but significant pyramidality of the amino N atom; the deviation of N1 from the C4, C7, C8 plane is 0·044 (5), 0·054 (4) and 0·07 (1) Å at 193, 255 and 298 K respectively. All three deviations are in the same sense, such that the developing lone pair is directed towards the methyl group of the neighbouring molecule in the stack (see Fig. 2). There appear to be parallel changes in bond lengths and bond angles: S1—O1, 1·555 (5),

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* Lists of anisotropic displacement parameters, bond lengths, bond angles, torsion angles, structure factors and atomic point charges have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53266 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1·553 (4), 1·50 (1) Å; O1—C9, 1·414 (9), 1·443 (9), 1·49 (2) Å; O1—S1—O2 108·8 (2), 109·4 (2), 113 (1)°; C7—N1—C8, 118·6 (6), 117·3 (6), 114 (1)°. All these changes are only on the verge of significance but they are consistent with an incipient movement along the reaction coordinate as the temperature is increased.

Each molecule of (1) is surrounded by seven others (Fig. 3). Molecules related by the screw axis form a stack with alternating dimethylamino and sulfonate groups and with the aromatic rings inclined steeply (76°) to each other (Fig. 2). The N1 atom of one molecule is nearly aligned with the H_3C—O bond of its neighbour in the stack. At the three temperatures the intermolecular C9···N1 distance is 3·469 (9), 3·492 (9), 3·54 (3) Å and the O1—C9···N1 angle is 150·9 (9), 150·4 (9), 147 (2)°. In addition, one of the sulfonate O atoms, O3, is involved in two O···H—C interactions that might be weakly bonding (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984; Sarma & Desiraju, 1986; Seiler, Weisman, Glendening, Weinhold, Johnson & Dunitz, 1987); the relevant interatomic distances and angles (at 255 K) are O3···H7*C*—C7 $(1-x,\ -0{\cdot}5+y,\ 0{\cdot}5-z)$ 2·51 (2) Å, 150 (3)°; O3···H9*A*—C9 $(2-x,\ -0{\cdot}5+y,\ 0{\cdot}5-z)$ 2·48 (2) Å, 163 (6)°.

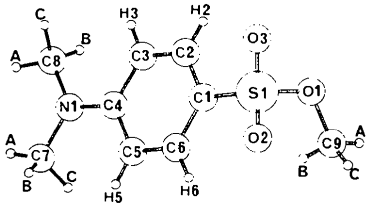

Fig. 1. *PLUTO* diagram of molecule (1) showing the atom-numbering scheme.

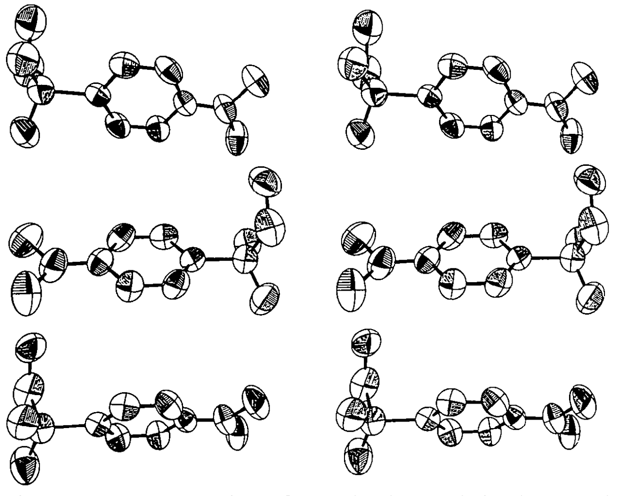

Fig. 2. *ORTEP* stereoview of a molecular stack in the crystal structure of (1) at 255 K showing displacement ellipsoids (at 50% probability level).

Motional analysis

The anisotropic displacement parameters (ADP's) have been analyzed with the program *THMA*11 (Dunitz, Schomaker & Trueblood, 1988). For comparison with the low-temperature results, the room-temperature data of Sukenik *et al.* were also analyzed with the new program. The ADP's used as the basis for our analyses are not of the highest quality, as can be seen from the respective e.s.d.'s of $U_{\rm eq}$'s in Table 1. Nevertheless, some inferences could be made by examining the quantities $\Delta_{A,B} = z^2_{A,B} - z^2_{B,A}$ for all pairs of heavy atoms (*i.e.*, excluding hydrogen) where $z^2_{A,B}$ is the mean-square displacement amplitude (MSDA) of atom *A* in the direction of atom *B* (Hirshfeld, 1976). At all three temperatures the MSDA's of C9 and to a lesser extent those of the O and C atoms of the dimethylamino group are much larger than would be expected for a rigid molecule.

Results of the motional analysis are summarized in Table 2. In the rigid-body model both the translational and librational motions are quite anisotropic. The largest component of **L** (L_1) is about an axis parallel to the long direction of the molecule and the largest component of **T** (T_1) makes an angle of about 30° with the **b** direction. Several models for the internal molecular motion were considered, but none of them was successful in improving the agreement between observed and calculated ADP's to any significant extent.

Packing potential energy and molecular motions

Packing potential-energy (PPE) calculations were made with the programs *PCK*83 (Williams, 1983) and *OPEC* (Gavezzotti, 1983) with H atoms relocated at 1·08 Å. Atomic point charges are called for in these calculations and were assigned using the *MOPAC* program package (Stewart, 1987) with the MNDO option. Model dependence was tested by

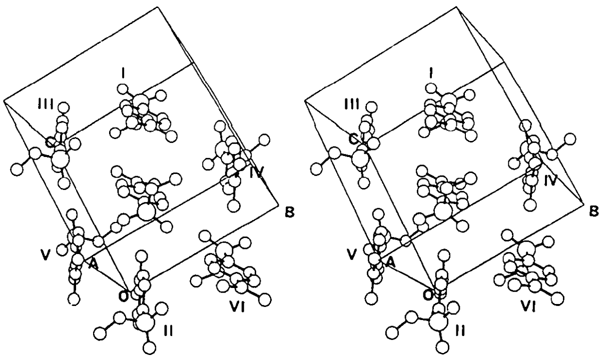

Fig. 3. *PLUTO* stereoview of the 'first coordination sphere' surrounding a central molecule in the crystal structure of (1). For clarity, molecule VII (Table 3), related to VI by the **a** translation is not shown.

Table 2. *Summary of results of rigid-body motional analysis at three temperatures*

Eigenvalues of **T** and **L** are listed together with the direction cosines of the eigenvectors $\mathbf{n}(L_1)$, $\mathbf{n}(L_2)$ and $\mathbf{n}(L_3)$ with respect to the inertial molecular axes. The quantity R is defined here as $[\sum(\Delta U_{ij})^2/\sum(U_{ij})^2]^{1/2}$. E.s.d.'s are given in parentheses in units of the last significant digit.

	193 K	255 K	298 K
T (Å^2 × 10^{-4})			
T_1	642 (22)	781 (32)	1232 (75)
T_2	442 (17)	553 (21)	846 (36)
T_3	303 (17)	387 (20)	552 (34)
L (deg^2)			
L_1	50 (5)	75 (5)	89 (14)
L_2	9·1 (0·9)	11·2 (1·0)	12·2 (2·2)
L_3	5·9 (0·4)	7·4 (0·5)	9·6 (1·9)
$\mathbf{n}(L_1)$	0·969, 0·242, 0·045	0·980, 0·168, 0·103	0·987, 0·154, −0·055
$\mathbf{n}(L_2)$	−0·071, 0·450, −0·891	−0·041, 0·684, −0·728	−0·099, 0·829, 0·550
$\mathbf{n}(L_3)$	−0·236, 0·860, 0·454	−0·193, 0·710, 0·677	0·130, −0·537, 0·833
R	0·067	0·077	0·094

Table 3. *Lattice-energy calculations on* (1) *at* 255 *and* 354 K

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

	255 K	354 K
Initial sublimation energy	104·3 (22·1)	99·6 (20·1)
Final sublimation energy	110·2 (22·0)	106·9 (19·8)
Packing coefficient	0·701	0·685
Total PPE	220·4 (44·0)	213·9 (39·6)
Contributions for PPE from nearest neighbours		
I $(1-x, 1-y, 1-z)$	31·0 (0·4)	31·6 (0·63)
II $(x, 0{\cdot}5-y, 0{\cdot}5+z)$	18·8 (1·3)	18·6 (1·47)
III $(x, 0{\cdot}5-y, 1{\cdot}5+z)$	18·8 (1·3)	18·6 (1·47)
IV $(1-x, 0{\cdot}5+y, 0{\cdot}5-z)$	33·8 (12·9)	32·9 (11·5)
V $(1-x, -0{\cdot}5+y, 0{\cdot}5-z)$	33·8 (12·9)	32·9 (11·5)
VI $(1-x, 1-y, -z)$	11·7 (0·4*)	10·8 (0·50*)
VII $(2-x, 1-y, -z)$	27·5 (13·2)	26·5 (11·9)
Percentage contribution by first coordination sphere	79·7 (94·5)	80·4 (95·7)
R.m.s. value of φ (about long axis) at $RT/2$ (°)	8·5	9·8

* Repulsive electrostatic contribution.

comparing results obtained with Williams & Cox (1984) and Mirsky (1978) potentials, including electrostatic contributions; the same trends were observed. In subsequent calculations the Mirsky potentials were used. The *OPEC* program also yields the energy as a sum of interactions between a central standard molecule and its neighbours. Calculations were made for the observed crystal structures at three temperatures and also for a hypothetical model structure at 354 K, derived by extrapolating the cell parameters and minimizing the PPE with respect to the position and orientation of the standard molecule. Sublimation energies (*PPE*/2; Gavezzotti & Simonetta, 1982) at 193, 255 and 354 K respectively are 110·9 (21·3), 110·5 (21·8) and 109·5 (22·2) kJ mol^{-1} (numbers in parentheses are Coulombic contributions). Energy profiles were then obtained for rotations of the central molecule about its inertial axes, and mean-square libration amplitudes estimated from the half-widths of the curves at energy values $RT/2$, as described by Shmueli & Kroon (1974). Table 3 gives these results for the structures at 255 and 354 K; the estimated root-mean-square librational amplitude L_1 is 8·5° at 255 K, in good agreement with the value from the motional analysis (Table 2), and the same is true at the other temperatures. Table 3 also gives interaction energies between the central molecule and the seven molecules in its 'first coordination sphere' (Fig. 3). The interactions with the two neighbours in the same stack (IV, V) clearly dominate.

From the motional analysis, phase relationships among the different types of motion are indeterminate. To make any further progress, some assumptions about the relative motions of neighbouring molecules in a stack are needed. One of the simplest models is to assume that molecules in a given stack rotate about their long axes in the same sense (*i.e.*, preserving the space-group symmetry). Fig. 4 shows how the N···C—O angle and the N···C distance vary with the rotation angle φ. The S_N2 type of nucleophilic displacement that is presumably involved requires a collinear arrangement of the incoming atom with the bond to be broken, and the optimal N···C—O angle attainable by the rotation described is close to this, 169° at $\varphi \simeq 9°$. The corresponding intermolecular N···C distance is 2·96 Å. From the PPE calculations, the r.m.s. libration amplitude at 354 K is 10°; extrapolation of L_1 derived from motional analyses to this temperature gives nearly the same value. Thus, this optimal orientation of the reacting centres can be achieved at an energy cost well within the available thermal energy of the crystal.

As already pointed out by Sukenik *et al.*, the zwitterionic product (2) formed in the thermal reaction has quite a different crystal structure from (1). We have recently succeeded in determining the crystal structure of (2), or rather the crystal structures, because the compound undergoes a series of phase

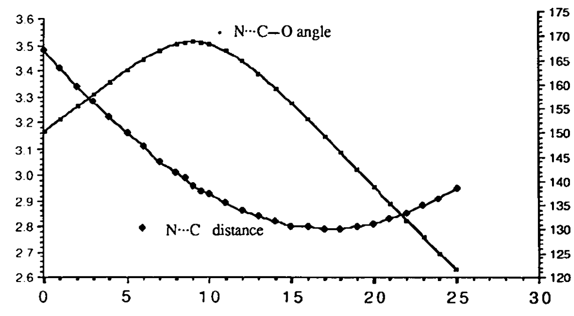

Fig. 4. Variations in intermolecular N1···C9 distance and N1···C9—O1 angle as a function of cooperative rotation (φ) of adjacent molecules in the stack of (1) at 255 K. The left and right ordinates indicate distance (Å) and angle (°) respectively.

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.

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

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Abstract

$C_9H_{13}NO_3S$, $M_r = 215{\cdot}29$; at 193 K, α phase, orthorhombic, $Pnc2$, $a = 10{\cdot}121\,(2)$, $b = 9{\cdot}421\,(1)$, $c = 20{\cdot}891\,(3)$ Å, $V = 1992{\cdot}0\,(5)$ Å^3, $Z = 8$, $D_x = 1{\cdot}44$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}04$ cm^{-1}, $F(000) = 912$, $R = 0{\cdot}029$ for 1787 observed reflections with $I \geq 3\sigma(I)$; at 298 K, coexistence of α and β phases; β phase, orthorhombic, $Pbma$, $a = 10{\cdot}183\,(2)$, $b = 9{\cdot}568\,(3)$, $c = 10{\cdot}444\,(2)$ Å, $V = 1017{\cdot}6\,(7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}41$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 2{\cdot}97$ cm^{-1}, $F(000) = 456$, $R = 0{\cdot}049$ for 822 selected reflections with $I \geq 3\sigma(I)$; at 385 K, γ phase, tetragonal, $P4/nmm$, $a =$

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