Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Liquid Crystalline Catalysis. Crystal Structure of Allyl Sulfonate Ester (ASE) and its Solid State Reactivity

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Version of record first published: 19 Dec 2006.

To cite this article: Elisabetta Foresti , Bruno Samori & Paolo Zani (1988): Liquid Crystalline Catalysis. Crystal Structure of Allyl Sulfonate Ester (ASE) and its Solid State Reactivity, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 154:1, 107-118

To link to this article: http://dx.doi.org/10.1080/00268948808078726

Mol. Cryst. Liq. Cryst., 1988, Vol. 154, pp. 107–118
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Printed in the United States of America

Liquid Crystalline Catalysis. Crystal Structure of Allyl Sulfonate Ester (ASE) and its Solid State Reactivity

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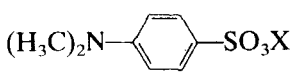
(*Received October 20, 1986; in final form June 16, 1987*)

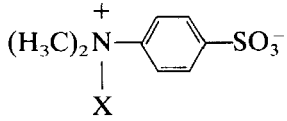
Allyl (*p*-dimethylamino)benzenesulfonate (ASE) is indefinitely stable in its crystalline state, but is converted to a quaternary ammonium zwitterion when dissolved in Smectic solvents. On the contrary, the corresponding methyl sulfonate rearranges to the quaternary zwitterion both in the solid state and in Smectic solutions. The X-rays analysis of ASE-d_2 crystals presented in this paper can explain this different reactivity. ASE-d_2 crystals belong to the triclinic space group $P\bar{1}$. The unit cell contains two independent, centrosymmetric pairs of molecules, stacked in a head-to-tail-like orientation. Intermolecular quaternization of ASE in the solid state is prevented by the distances between the reactive dimethylamino and allyl groups, which are considerably longer than those found in methyl(*p*-dimethylamino) benzene sulfonate.

Keywords: liquid crystalline catalysis, solid state reactivity

At room-temperature crystalline methyl *p*-(dimethylamino)benzenesulfonate (methyl sulfonate ester (MSE)) rearranges to a zwitterionic product, *p*-(trimethylammonium)benzenesulfonate (MZWI).[2]

On the other hand, anhydrous solutions of MSE in various isotropic organic solvents are indefinitely stable. This rearrangement at room temperature is due to an intermolecular methyl migration which is controlled not by the normal reactivity of the functional groups but by stacking of the MSE reactant molecules.[2]





X: CH_3:	MSE;	MZWI
CH_2—CH=CH_2:	ASE;	AZWI
CD_2—CH=CH_2:	ASE-d_2,	AZW-d_2

The crystal structure consists in fact of MSE sheets in a perfect orientation for chain intermolecular methyl migrations to take place.[2] This reaction was recently studied also by Gavezzotti.[3] His computations of molecular volumes within the MSE crystalline packing found pockets of empty space which are able to assist, during the quaternization process, both the methyl displacements and the ongoing pyramidalization at nitrogen.

This approach, which focuses attention also on the role of the dynamic nature of the lattice in the solid-state reactivity, is strongly supported by the Raman phonon studies of Prasad and coll.[4] They show that the soft (with low-activation energy) phonon mode at 18 cm^{-1} which is expected to assist the MSE rearrangement corresponds to a cooperative lattice vibration that is able to force the two reactive groups closer to each other.

As our interest is in the reactivity within mesomorphic solvent, we used MSE quaternization to probe liquid crystalline catalysis effects. We found that Smectic B (SmB) solvents are able to reproduce this reaction in solution.[5]

A better probe is the analogous reaction of the related ester, allyl (*p*-dimethylamino)benzenesulfonate (allyl sulfonate ester (ASE)), because it is indefinitely stable at room temperature in both isotropic solutions and its crystalline state.[6] A very sluggish ASE quaternization may be achieved by melting the ASE crystals. In this way the total conversion requires 26 days at 44°C.[7]

Higher ASE reaction rates may be achieved by using SmB liquid crystalline solvents.[7]

This paper reports an X-ray diffraction study of the molecular packing within the ASE-d_2 single crystals. This compound which we synthesized for a DNMR study of its preferred orientation within SmB solvents, provided better crystals than the non-deuteriated ASE.

The crystallographic data thus obtained clearly show the reasons why ASE may rearrange only in the melt. By contrast the MSE conversion collapses on passing from the crystal phase to the melt.[2]

RESULTS AND DISCUSSION

The reactivity within crystalline solids is, in the first instance, "topochemically" controlled,[8] i.e. it is the separations of the reactive centers of the properly oriented molecules which determine if the reaction takes place or not. The distance of 3.5 Å found in the MSE single crystals between each nitrogen and the closest sulfonate ester methyl group[2] is the necessary condition for the soft and cooperative local displacements to be effective in the ongoing reaction.

Figure 1 shows the molecular arrangement in the unit cell. The asymmetric unit contains two independent molecules (A and B). Molecules related by centre of symmetry form a pair with head-to-tail arrangement (A_i–A_i, B_i–B_i). Within each pair the two allyl chains are extended perpendicularly to the stacked aromatic rings, thus forcing the nearest pairs to stay far apart (see Figure 2).

The chains' thermal mobility is displayed by the ORTEP drawing in Figure 3.

The distance of the allyl terminal (C_{13}) carbons to the closest nitrogens (N_{14}) are ranging from 4.75 to 5.02 Å as displayed in Figure 2. Another distance of 4.74 Å cannot be shown both in Figure 1 and 2. *These distances are more than 35% longer than that (3.5 Å) which makes the MSE quaternization possible. The migrations of the allyl moieties from the sulfonate to the amino groups are therefore prevented in the crystal phase by the distance between the reactive parts of the molecules.*

By raising temperature on passing from the crystal phase to the melt, and thus softening the tight crystal packing, the ASE molecules may be allowed to undergo the displacements expressly required for quaternization.

EXPERIMENTAL

Crystal data: $C_{11}H_{13}D_2O_3SN$, M = 243.33, triclinic, space group $P\bar{1}$, a = 7.332 (3), b = 10.812 (3), c = 16.105 (4) Å, α = 80.60 (3), β = 81.33 (3), γ = 81.43 (4)°, Z = 4, Dc = 1.31 g cm^{-3}, V = 1235.0 A^3, μ = 2.10 cm^{-1}, MoK_α radiation, λ = 0.71069 Å.

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer, in the range $2.5° < \vartheta < 25°$ by the $\omega/2\vartheta$ scan method.

A total of 2293 reflections was measured, 1290 of which $|Io > 2\sigma(Io)|$ were used in the analysis.

The structure was solved by direct methods and refined by block-

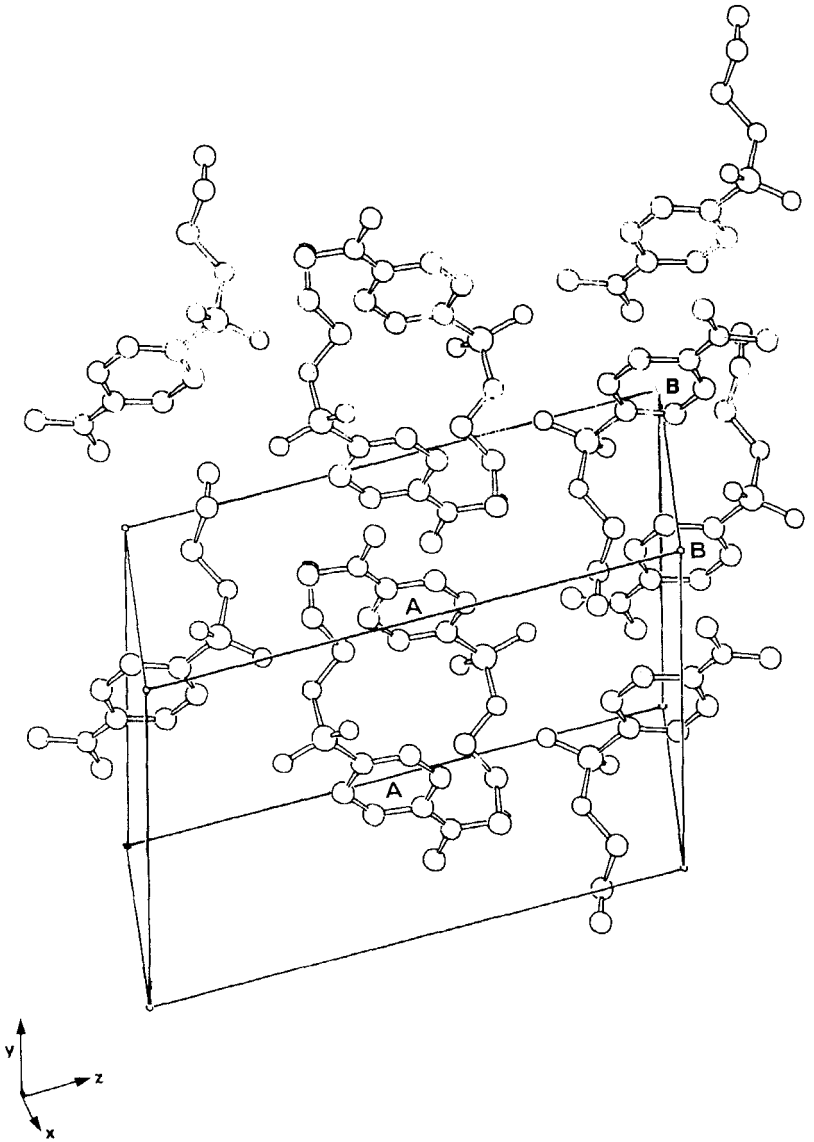


FIGURE 1 A view of the molecular stacking within ASE-d_2 crystals as seen along the X axis.

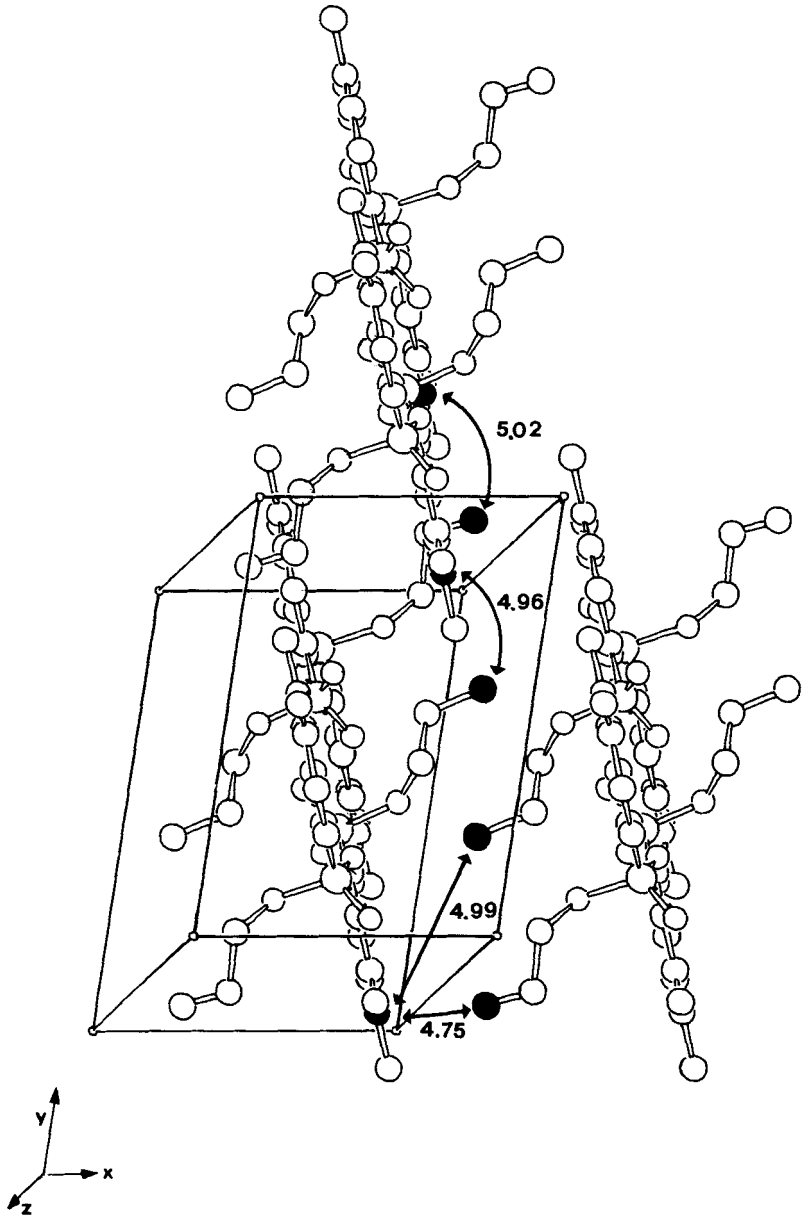


FIGURE 2 Molecular stacking within ASE-d_2 crystals (view along Z axis). Distances (in Å) of the allyl terminal (C_{13}) carbons to the closest nitrogens (N_{14}) are reported.

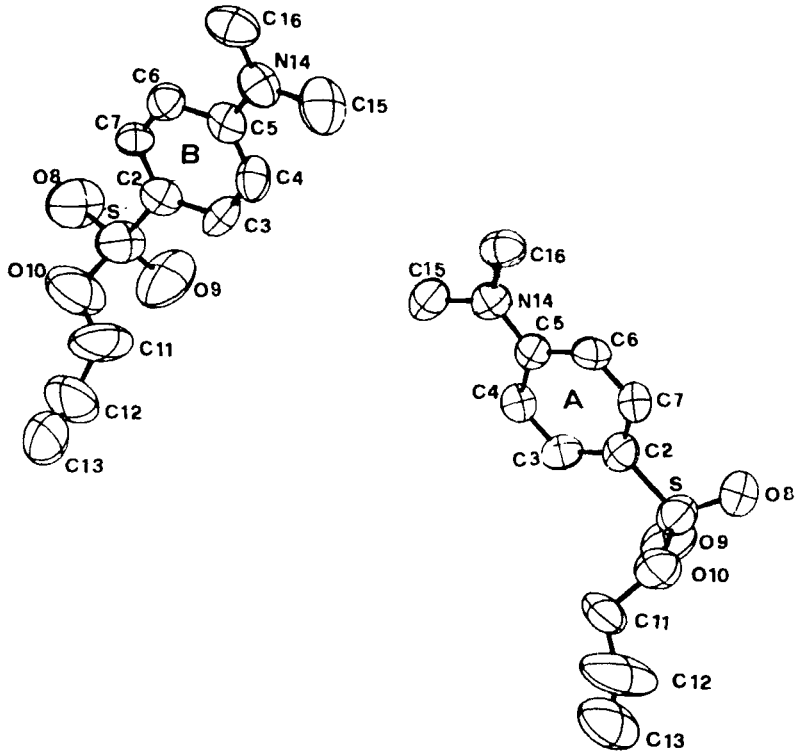


FIGURE 3 ORTEP drawing of an A and B molecular couple.

diagonal least squares techniques, using anisotropic temperature factors for the non-H atoms.

Hydrogen atoms were placed geometrically (C—H = 1.08 Å). The final R index was 0.044.

For all computation the SHELX package[9] of crystallographic programs was used.

(d_2) Allyl (p-dimethylamino)benzenesulphonate ester (ASE-d_2)

An ethereal solution of allyl alcohol $1d_2$ (prepared according to the method of Schuetz)[10] (1.92 g, 32 mmol) was allowed to react with powdered NaOD (1.0 g, 24 mmol), then stirred with *p*-(dimethylamino)benzenesulphonyl chloride (2.06 g, 9.4 mmol). After 12 h in refrigerator, the resulting mixture was evaporated in vacuo and the solid residue taken up with ethyl ether (200 mL). The salts were filtered off and the filtrate was dried (Na_2SO_4) and evaporated in

vacuo again. The crude product was crystallized from petroleum ether (b.p. 40–60°C) (500 mL) giving ASE-d_2 (1.68 g, 73% yield on sulphonyl chloride): m.p. 40–41°C; IR spectrum was obtained on a Perkin Elmer 177 spectrophotometer: ν_{max} (KBr) 1260 and 1345 cm^{-1}. Proton nuclear magnetic resonance spectrum was recorded on a Varian EM360L, employing $CDCl_3$ as solvent and tetramethyl silane as internal reference: δ 3.1 (s, 6H), 5–6 (m, 3H), 6.6 and 7.6 (q, AB system, j 10 Hz, 4H). Mass spectrum was taken at 70 eV on a Jeol JMS d-100 spectrometer: m/z 243 (M^+), 200 ($M^+-C_3H_3D_2$), 184 ($M^+-C_3H_3D_2O$), 168 ($M^+-C_3H_3D_2O_2$), 163 (M^+-SO_3), 132, 121, 105, 91, 77.

Both from ^1H NMR and MS spectra, deuteriation grade was determined to be more than 95%.

TABLE I

Fractional atomic coordinates and thermal parameters (A)

Atom	X	Y	Z	UISO or UEQ
S1A	.6086(4)	.3803(3)	.3540(2)	.083(2)
C2A	.6578(11)	.2430(8)	.4246(6)	.064(7)
C3A	.6236(11)	.2473(8)	.5117(6)	.064(7)
C4A	.6583(11)	.1398(9)	.5678(5)	.063(6)
C5A	.7262(11)	.0231(9)	.5384(6)	.060(7)
C6A	.7600(11)	.0226(8)	.4506(6)	.065(7)
C7A	.7267(11)	.1300(9)	.3948(5)	.064(6)
D8A	.5917(10)	.3456(6)	.2742(4)	.114(6)
D9A	.4621(9)	.4639(6)	.3941(4)	.098(5)
D10A	.7939(9)	.4442(6)	.3362(4)	.092(5)
C11A	.8307(16)	.5192(11)	.3978(7)	.119(10)
C12A	.9014(39)	.6227(20)	.3614(11)	.250(22)
C13A	1.0096(22)	.6950(15)	.3429(8)	.164(14)
N14A	.7559(10)	−.0853(7)	.5946(5)	.069(6)
C15A	.7228(14)	−.0842(8)	.6846(6)	.097(8)
C16A	.8313(11)	−.2035(8)	.5647(6)	.080(7)
S1B	.5128(5)	−.1649(3)	1.1547(2)	.098(2)
C2B	.5991(11)	−.2709(9)	1.0841(6)	.069(7)
C3B	.6142(11)	−.2336(9)	.9968(6)	.068(7)
C4B	.6788(12)	−.3208(10)	.9427(6)	.076(7)
C5B	.7332(11)	−.4461(9)	.9728(6)	.063(7)
C6B	.7183(12)	−.4829(9)	1.0609(6)	.069(7)
C7B	.6507(11)	−.3967(9)	1.1151(6)	.069(7)
D8B	.4498(11)	−.2287(7)	1.2341(4)	.135(7)
D9B	.3965(13)	−.0647(7)	1.1151(5)	.145(7)
D10B	.6945(14)	−.1143(9)	1.1760(5)	.146(9)
C11B	.7969(25)	−.0400(13)	1.1094(8)	.170(14)
C12B	.8333(39)	.0585(24)	1.1409(11)	.253(26)
C13B	.9352(26)	.1264(17)	1.1522(9)	.162(15)
N14B	.7951(10)	−.5296(8)	.9170(5)	.084(6)
C15B	.8153(15)	−.4884(10)	.8257(6)	.120(10)
C16B	.8567(13)	−.6591(9)	.9465(7)	.103(9)

TABLE II

Fractional atomic coordinates for the hydrogen atoms

Atom	X	Y	Z	
H3A	.570(1)	.336(1)	.535(1)	.09(1)
H4A	.633(1)	.144(1)	.635(1)	.09(1)
H6A	.814(1)	−.065(1)	.427(1)	.09(1)
H7A	.754(1)	.127(1)	.327(1)	.09(1)
H111A	.929(2)	.463(1)	.437(1)	.64(12)
H112A	.702(2)	.545(1)	.437(1)	.64(12)
H12A	.789(4)	.671(2)	.327(1)	.18(8)
H131A	1.110(2)	.699(1)	.287(1)	.64(12)
H132A	1.013(2)	.774(1)	.375(1)	.64(12)
H151A	.754(1)	−.179(1)	.717(1)	.15(2)
H152A	.579(1)	−.050(1)	.703(1)	.15(2)
H153A	.810(1)	−.023(1)	.702(1)	.15(2)
H161A	.844(1)	−.277(1)	.618(1)	.15(2)
H162A	.967(1)	−.195(1)	.529(1)	.15(2)
H163A	.740(1)	−.227(1)	.525(1)	.15(2)
H3B	.575(1)	−.136(1)	.971(1)	.09(1)
H4B	.688(1)	−.291(1)	.875(1)	.09(1)
H6B	.761(1)	−.580(1)	1.086(1)	.09(1)
H7B	.638(1)	−.427(1)	1.183(1)	.09(1)
H12B	.701(4)	.094(2)	1.173(1)	.18(10)
H131B	.955(3)	.216(2)	1.114(1)	.64(12)
H132B	1.006(3)	.116(2)	1.208(1)	.64(12)
H151B	.866(1)	−.569(1)	.793(1)	.15(2)
H152B	.913(1)	−.420(1)	.809(1)	.15(2)
H153B	.682(1)	−.446(1)	.807(1)	.15(2)
H161B	.900(1)	−.710(1)	.893(1)	.15(2)
H162B	.744(1)	−.701(1)	.987(1)	.15(2)
H163B	.972(1)	−.664(1)	.982(1)	.15(2)

TABLE III

Anisotropic thermal parameters (A)

Atom	U11	U22	U33	U23	U13	U12
S1A	.088(2)	.076(2)	.085(2)	.007(2)	−.022(2)	−.011(2)
C2A	.046(6)	.068(7)	.077(7)	−.006(5)	−.018(5)	−.005(5)
C3A	.058(6)	.057(7)	.076(7)	−.016(6)	−.003(5)	0.000(5)
C4A	.061(6)	.072(7)	.056(5)	−.011(6)	−.004(5)	−.006(5)
C5A	.051(6)	.063(7)	.065(7)	−.007(6)	−.007(5)	−.012(5)
C6A	.072(7)	.051(6)	.072(7)	−.012(5)	−.008(5)	−.010(5)
C7A	.066(7)	.070(7)	.057(6)	−.015(6)	−.009(5)	−.011(5)
O8A	.154(7)	.095(5)	.092(5)	.007(4)	−.056(5)	−.025(5)
O9A	.082(5)	.080(5)	.133(6)	.001(4)	−.006(4)	−.013(4)
O10A	.099(5)	.088(5)	.088(5)	−.001(4)	.005(4)	−.034(4)
C11A	.158(11)	.099(9)	.100(9)	−.034(7)	−.017(8)	−.066(8)
C12A	.413(32)	.221(20)	.116(13)	−.107(13)	.099(19)	−.219(23)
C13A	.226(16)	.155(14)	.112(10)	−.078(10)	.025(10)	−.095(11)
N14A	.077(6)	.061(6)	.070(5)	−.003(5)	−.015(5)	−.004(4)
C15A	.129(10)	.084(8)	.076(8)	.009(6)	−.025(7)	−.008(6)
C16A	.062(6)	.064(7)	.113(8)	−.005(6)	−.013(6)	−.001(5)
S1B	.124(3)	.086(2)	.085(2)	−.022(2)	.019(2)	−.016(2)
C2B	.059(7)	.068(7)	.081(8)	−.014(6)	−.001(6)	−.011(5)
C3B	.066(7)	.078(7)	.059(6)	.022(6)	−.012(5)	−.003(5)
C4B	.079(7)	.096(9)	.053(6)	−.020(6)	−.006(5)	−.006(6)
C5B	.031(5)	.071(8)	.088(8)	−.013(6)	−.014(5)	−.003(5)
C6B	.072(7)	.068(7)	.069(7)	−.005(6)	−.015(6)	−.009(5)
C7B	.064(7)	.081(8)	.062(6)	−.002(6)	−.003(5)	−.027(6)
O8B	.187(8)	.132(7)	.086(5)	−.030(5)	.051(5)	−.035(6)
O9B	.203(9)	.101(6)	.131(7)	−.015(5)	.000(6)	.052(6)
O10B	.179(10)	.132(9)	.127(9)	−.052(6)	.008(7)	−.067(8)
C11B	.232(18)	.139(13)	.140(13)	−.035(10)	.044(12)	−.128(12)
C12B	.335(31)	.311(33)	.114(14)	.040(15)	−.026(17)	−.243(25)
C13B	.231(20)	.159(15)	.097(11)	.024(10)	−.022(12)	−.075(13)
N14B	.071(6)	.090(7)	.090(7)	.037(6)	−.008(5)	.003(5)
C15B	.129(10)	.150(11)	.080(8)	−.047(7)	−.008(7)	.011(8)
C16B	.084(8)	.088(9)	.138(10)	−.044(7)	−.005(7)	−.002(6)

TABLE IV

Bond distances (A) with E.S.D.S. in parenthesis

S1A	—C2A	1.744(8)
S1A	—O8A	1.423(8)
S1A	—O9A	1.442(6)
S1A	—O10A	1.582(7)
C2A	—C3A	1.39(1)
C2A	—C7A	1.38(1)
C3A	—C4A	1.37(1)
C4A	—C5A	1.41(1)
C5A	—C6A	1.40(1)
C5A	—N14A	1.37(1)
C6A	—C7A	1.36(1)
O10A	—C11A	1.46(1)
C11A	—C12A	1.32(2)
C12A	—C13A	1.17(3)
N14A	—C15A	1.44(1)
N14A	—C16A	1.44(1)
S1B	—C2B	1.73(1)
S1B	—O8B	1.398(7)
S1B	—O9B	1.406(8)
S1B	—O10B	1.62(1)
C2B	—C3B	1.39(1)
C2B	—C7B	1.39(1)
C3B	—C4B	1.37(1)
C4B	—C5B	1.38(1)
C5B	—C6B	1.40(1)
C5B	—N14B	1.36(1)
C6B	—C7B	1.37(1)
D10B	—C11B	1.42(1)
C11B	—C12B	1.33(3)
C12B	—C13B	1.18(3)
N14B	—C15B	1.46(1)
N14B	—C16B	1.43(1)

TABLE V

Bond angles( ) with E.S.D.S. in parentheses

O9A	—S1A	—O10A	108.9(4)
O8A	—S1A	—O10A	103.7(4)
O8A	—S1A	—O9A	120.0(4)
C2A	—S1A	—O10A	104.9(4)
C2A	—S1A	—O9A	109.7(4)
C2A	—S1A	—O8A	108.6(4)
S1A	—C2A	—C7A	120(1)
S1A	—C2A	—C3A	119(1)
C3A	—C2A	—C7A	120(1)
C2A	—C3A	—C4A	120(1)
C3A	—C4A	—C5A	120(1)
C4A	—C5A	—N14A	120(1)
C4A	—C5A	—C6A	117(1)
C6A	—C5A	—N14A	121(1)
C5A	—C6A	—C7A	121(1)
C2A	—C7A	—C6A	119(1)
S1A	—O10A	—C11A	118(1)
O10A	—C11A	—C12A	112(1)
C11A	—C12A	—C13A	158(2)
C5A	—N14A	—C16A	120(1)
C5A	—N14A	—C15A	121(1)
C15A	—N14A	—C16A	117(1)
O9B	—S1B	—O10B	110(1)
O8B	—S1B	—O10B	100(1)
O8B	—S1B	—O9B	119(1)
C2B	—S1B	—O10B	104(1)
C2B	—S1B	—O9B	109.3(5)
C2B	—S1B	—O8B	110.6(5)
S1B	—C2B	—C7B	119(1)
S1B	—C2B	—C3B	121(1)
C3B	—C2B	—C7B	118(1)
C2B	—C3B	—C4B	120(1)
C3B	—C4B	—C5B	121(1)
C4B	—C5B	—N14B	119(1)
C4B	—C5B	—C6B	118(1)
C6B	—C5B	—N14B	122(1)
C5B	—C6B	—C7B	120(1)
C2B	—C7B	—C6B	120(1)
S1B	—O10B	—C11B	117(1)
O10B	—C11B	—C12B	106(1)
C11B	—C12B	—C13B	151(2)
C5B	—N14B	—C16B	120(1)
C5B	—N14B	—C15B	121(1)
C15B	—N14B	—C16B	117(1)

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