fixed, $R = 0.055$, $wR = 0.074$, $w = 1/[\sigma^2(F_o) + 0.00047F_o^2]$, $(\Delta\rho)_{\max} = 0.2$, $(\Delta\rho)_{\min} = -0.3$ e Å^{-3}, $\Delta/\sigma_{\max} = 0.04$, $S = 0.91$; H atoms located on difference Fourier maps were given the equivalent isotropic thermal factor of the bonded atom. The H-atom positions were generated geometrically (C—H = 1.08 Å), except for H7 which was refined. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters and equivalent isotropic thermal factors are given in Table 1.* Bond distances, bond angles and selected torsion angles are listed in Table 2. Numbering scheme and absolute configuration are depicted in Fig. 1.

The *o*-nitrobenzamide group is not planar. The aromatic ring is almost perpendicular to the amido group, the dihedral angle between these planes being 94 (1)°. The signs of the CD bands can be ascribed to the sign of the dihedral angle N1—C7′—C1′—C2′ [+90.9 (3)°] which characterizes the chirality of the *o*-nitrobenzamide group. It is anticipated that the sign of the torsion angle N1—C7′—C1′—C2′ would be negative in (2). The amido group (C1′, C7′, N1, O8′) is planar [maximum deviation 0.027 (3) Å], the C2 and C5 atoms deviating from that plane by 0.332 (4) and 0.131 (4) Å, respectively. The sum of the bond angles around the N1 atom is 356.2 (6)°, near the expected value (360°) for sp^2 hybridization. Torsional angles show the five-membered ring in a near-envelope conformation with atom C4 out of the plane of the four others by 0.593 (6) Å [C6 −1.279 (5) and O8 −1.340 (3) Å]. The hydroxyl group is engaged in an intramolecular hydrogen bond with the carbonyl O atom of the amido group [O7···O8′ = 2.772 (4), O7—H = 1.05 (7), H···O8′ = 1.73 (7) Å, ∠O7—H···O8′ = 171 (4)°].

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A Substrate for the Asymmetric Nazarov Cyclization

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Abstract. [1*R*-(2-*exo*,3-*exo*)]-3-{[*N*-(3,5-Dimethylphenyl)]benzenesulfonylamino}-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl [2*R*-(2α,3β,5β,6α)]-tetrahydro-2,5,6-trimethyl-4-oxo-2*H*-pyran-3-carboxylate, $C_{33}H_{43}NO_6S$, $M_r = 581.7$, orthorhombic, $P2_12_12_1$, $a = 11.945$ (2), $b = 22.240$ (6), $c = 24.407$ (5) Å, $V = 6483.9$ Å^3, $Z = 8$, $D_x = 1.19$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.3$ cm^{-1}, $F(000) = 2496$, $T = 293$ K, $R = 0.050$ for 1992 observed reflections. The two unique molecules have similar conformations and orientations in the crystal lattice. The N atoms of the tertiary sulfonamides have pyramidal bonding geometries [sum of angles at N: 349 (2) and 347 (2)°] and the N and S aromatic rings lie close to one another with angles of only 24.1 (4) and 28.4 (5)° between their least-squares planes.

Introduction. The Nazarov cyclization reaction is a very useful method of preparing substituted cyclopentenones (Santelli-Rouvier & Santelli, 1983). With a view to modifying this reaction to produce enantiomerically pure products, the racemic ester (1) was prepared [by the reaction of ethyl acetoacetate and

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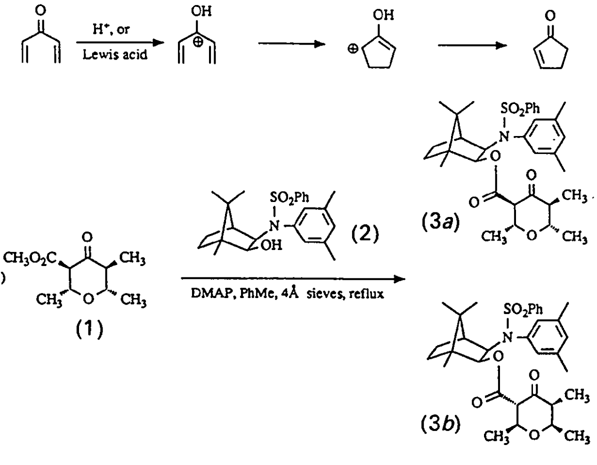
(*E*)-2-methyl-2-butenoyl chloride followed by catalytic hydrogenation] and transesterified with the enantiomerically pure alcohol (2) to produce two diastereoisomers (3*a*) and (3*b*). Treatment of either of these substances with suitable Lewis acids will lead to dehydration to a divinylketone structure suitable for Nazarov cyclization. The determination of the X-ray crystal structure of the major diastereoisomer was undertaken to establish its absolute stereochemical configuration and also to examine the conformation of the chiral auxiliary group. The alcohol (2) was introduced as a chiral auxiliary by Helmchen and has been used for highly enantioselective alkylations of propionates and glycolates (Schmierer, Grotemeier, Helmchen & Selim, 1981; Helmchen & Wierzchowski, 1984). No structures of the alcohol (2) or its esters have been reported.



Experimental. Ester (1) (250 mg, 1.23 mmol) and alcohol (2) (509 mg, 1.23 mmol) were reacted together in refluxing toluene containing 4-dimethylaminopyridine (151 mg) and powdered 4 Å molecular sieves, for 3 d under a nitrogen atmosphere. The two diastereoisomeric products (1.7:1, 32%) were separated by preparative high-performance liquid chromatography. For the major diastereoisomer, ^{1}H NMR (270 MHz, $CDCl_3$, δ): 0.59 (*s*), 0.86 (*s*), 1.06 (*d*), 1.12 (*s*), 1.37 (*d*), 1.49 (*d*), 6 × CH_3; 1.96–2.43 (*br s*), 2 × CH_3; 1.14–1.79 (*dd*), CH and (*m*) 2 × CH_2; 2.39 (*dq*), 3.47 (*dq*), 3.70 (*dd*), 3.88 (*d*), 4.15 (*dq*), 5.28 (*d*), 6 × CH; 6.83–7.50 (*m*), Ar-H_8. Analysis found C 68.0, H 7.5, N 2.9%; $C_{33}H_{43}NO_6S$ requires C 68.1, H 7.5, N 2.4%. Colourless plates of the major diastereoisomer were grown from ethyl acetate/hexane (5:95); m.p. 458–459 K. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator, ω–2θ scans; crystal dimensions 0.52 × 0.27 × 0.15 mm; unit-cell dimensions by least-squares fit to setting angles of 25 automatically centred reflections with $7.5 < \theta < 12°$. Room-temperature measurement; no absorption correction; max. $(\sin\theta/\lambda)$ in intensity measurements 0.53 Å^{-1}; one standard reflection monitored (2% loss in intensity during data collection); 4434 reflections measured, 3475 unique ($R_{\rm int} = 0.03$), 1992 counted as observed [$I > 3\sigma(I)$]; index range *h* 0 to 12, *k* 0 to 23, *l* 0 to 25; *h*00 reflections absent for *h* = odd, 0*k*0 absent for *k* = odd, 00*l* absent for *l* = odd. Structure solved in $P2_12_12_1$ using *SHELXS*86 (Sheldrick, 1986) and refined on *F* by full-matrix least-squares analyses including all non-H atoms with isotropic displacement parameters (*SHELX*76; Sheldrick, 1976). Refinement continued by blocked-matrix methods including anisotropic displacement parameters for non-H atoms; 739 parameters. H-atom positions calculated and assigned fixed isotropic displacement factors (0.05–0.20 Å^2, depending on $U_{\rm eq}$ of attached C atom). The absolute configuration was assigned from that of the enantiomerically pure alcohol (2). The structure is (3*a*) not (3*b*). With weights $w = (\sigma^2F + 0.0007F^2)^{-1}$, the model converged to $R = 0.05$, $wR = 0.05$. Max. (Δ/σ) in final cycle for positional parameters 0.6, for displacement parameters 0.5. Max. and min. residual electron density in final difference Fourier synthesis 0.17 and −0.19 e Å^{-3}, respectively. Molecular illustrations produced with *PLUTON*91 (Spek, 1991); geometry calculations made with *PARST*91 (Nardelli, 1991). Atomic scattering factors for O, N, C atoms from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965).

Discussion. The structure of the major diastereoisomer is (3*a*). The two crystallographically unique molecules (*A* and *B*) have similar conformations and orientations in the crystal lattice (Figs. 1 and 2). Fractional atomic coordinates and equivalent isotropic displacement parameters for all non-H atoms are presented in Table 1,* with bond lengths and angles in Table 2.

The N atoms of the tertiary sulfonamides have pyramidal bonding geometries [sum of angles at N: *A* 349 (2), *B* 347 (2)°], whereas earlier publications on the use of similar compounds in asymmetric synthesis have implied planar bonding geometry at the N atoms. The conformations about the N—S bonds are near to staggered [C(31)—S(1)—N(1)—C(21): *A* −64 (1), *B* −56 (1)° and C(31)—S(1)—N(1)—C(1): *A* 80 (1), *B* 84 (1)°] such that the two aromatic substituents lie adjacent to each other. Indeed, there

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* Lists of structure factors, anisotropic displacement parameters and H-atom coordinates and isotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55424 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1000]

are some short contacts between them [C(22)···C(31): *A* 3.19 (2), *B* 3.10 (2) Å and C(22)···C(36): *A* 3.12 (2), *B* 3.09 (2) Å] and the angles between their best planes are 24.1 (4) and 28.4 (5)°. The electron-rich O(2) atoms of the sulfonamide side chains are directed towards the electron-deficient C(2) and C(11) atoms with which they make close contacts [O(2)···C(2): *A* 2.90 (1), *B* 2.90 (1) Å and O(2)···C(11): *A* 2.96 (2), *B* 3.01 (1) Å]. The tetrahydropyranone rings adopt chair conformations with all substituents in equatorial positions.

The 18 tertiary sulfonamides with *R* factors less than 0.08 listed in the Cambridge Structural Database display various bonding geometries about the N atom, ranging from almost planar in an *N*,*N*-dicyclohexylsulfonamide derivative in which all bonded neighbours are at least disubstituted with non-H atoms [N atom only 0.04 (2) Å out of the

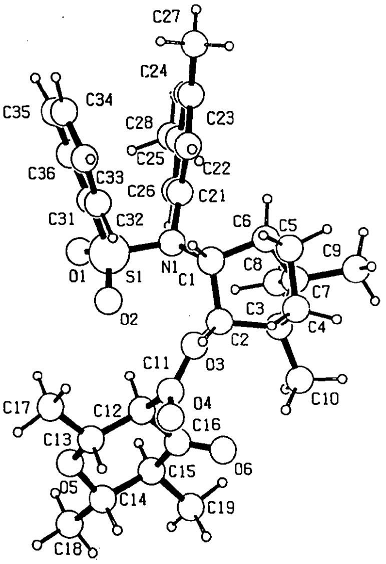

Fig. 1. Structure of molecule *B* of the (3*a*) diastereoisomer showing the atomic labelling scheme.

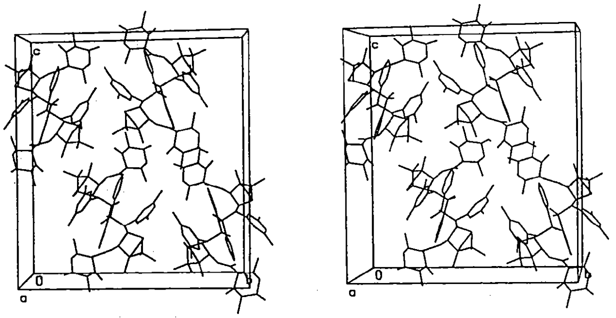

Fig. 2. Stereoscopic view of the crystal packing of (3*a*) viewed down the *a* axis, illustrating the similar orientations of the two independent molecules.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for molecules A and B of diastereoisomer* (3*a*) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Molecule *A*				
C(1)	0.6467 (8)	0.7985 (6)	0.1573 (4)	0.052 (8)
C(2)	0.588 (1)	0.8321 (6)	0.1091 (5)	0.062 (9)
C(3)	0.5366 (9)	0.7842 (6)	0.0716 (6)	0.07 (1)
C(4)	0.447 (1)	0.7554 (7)	0.1112 (7)	0.09 (1)
C(5)	0.508 (1)	0.7178 (7)	0.1524 (6)	0.09 (1)
C(6)	0.6317 (9)	0.7327 (5)	0.1387 (5)	0.062 (9)
C(7)	0.6252 (9)	0.7339 (5)	0.0743 (5)	0.061 (9)
C(8)	0.7412 (9)	0.7491 (5)	0.0485 (4)	0.064 (8)
C(9)	0.592 (1)	0.6723 (6)	0.0501 (5)	0.08 (1)
C(10)	0.497 (1)	0.8037 (7)	0.0162 (6)	0.10 (1)
C(11)	0.644 (1)	0.9241 (7)	0.0645 (6)	0.07 (1)
C(12)	0.750 (1)	0.9547 (6)	0.0420 (6)	0.07 (1)
C(13)	0.746 (1)	1.0226 (7)	0.0442 (7)	0.10 (1)
C(14)	0.867 (1)	1.031 (1)	−0.0321 (9)	0.12 (2)
C(15)	0.870 (1)	0.9649 (8)	−0.0410 (7)	0.10 (1)
C(16)	0.771 (1)	0.9347 (8)	−0.0164 (7)	0.09 (1)
C(17)	0.738 (2)	1.0448 (7)	0.1007 (8)	0.15 (2)
C(18)	0.979 (1)	1.0628 (9)	−0.0465 (8)	0.15 (2)
C(19)	0.880 (1)	0.9481 (9)	−0.1046 (7)	0.14 (2)
C(21)	0.8507 (9)	0.7780 (5)	0.1813 (5)	0.052 (8)
C(22)	0.848 (1)	0.7405 (5)	0.2264 (5)	0.059 (9)
C(23)	0.941 (1)	0.7069 (5)	0.2412 (6)	0.059 (9)
C(24)	1.035 (1)	0.7120 (5)	0.2083 (6)	0.055 (9)
C(25)	1.038 (1)	0.7463 (6)	0.1627 (6)	0.07 (1)
C(26)	0.944 (1)	0.7818 (5)	0.1477 (5)	0.055 (8)
C(27)	0.941 (1)	0.6715 (6)	0.2922 (6)	0.10 (1)
C(28)	1.141 (1)	0.7481 (7)	0.1264 (7)	0.11 (1)
C(31)	0.747 (1)	0.8640 (5)	0.2711 (5)	0.068 (9)
C(32)	0.635 (1)	0.8605 (7)	0.2910 (6)	0.09 (1)
C(33)	0.621 (1)	0.8403 (8)	0.3436 (7)	0.11 (1)
C(34)	0.712 (2)	0.8254 (8)	0.3780 (6)	0.11 (1)
C(35)	0.816 (1)	0.8297 (8)	0.3567 (8)	0.10 (1)
C(36)	0.832 (1)	0.8499 (6)	0.3060 (7)	0.07 (1)
N(1)	0.7601 (7)	0.8208 (4)	0.1685 (4)	0.055 (6)
O(1)	0.8789 (7)	0.9071 (4)	0.1983 (4)	0.100 (7)
O(2)	0.6740 (7)	0.9213 (3)	0.1849 (4)	0.086 (6)
O(3)	0.6683 (6)	0.8678 (4)	0.0788 (3)	0.061 (6)
O(4)	0.5552 (8)	0.9463 (5)	0.0655 (5)	0.110 (8)
O(5)	0.851 (1)	1.0458 (5)	0.0243 (6)	0.12 (1)
O(6)	0.708 (1)	0.9025 (6)	−0.0409 (5)	0.12 (1)
S(1)	0.7661 (3)	0.8843 (2)	0.2034 (2)	0.071 (2)
Molecule *B*				
C(1)	0.6416 (8)	0.5270 (5)	0.7121 (5)	0.054 (9)
C(2)	0.6065 (9)	0.5654 (5)	0.6613 (5)	0.045 (7)
C(3)	0.5630 (9)	0.5178 (5)	0.6212 (5)	0.047 (8)
C(4)	0.4526 (9)	0.4957 (5)	0.6473 (6)	0.073 (9)
C(5)	0.492 (1)	0.4563 (5)	0.6947 (6)	0.07 (1)
C(6)	0.6213 (9)	0.4631 (5)	0.6932 (5)	0.053 (9)
C(7)	0.643 (1)	0.4651 (5)	0.6319 (5)	0.056 (9)
C(8)	0.7671 (9)	0.4762 (6)	0.6166 (5)	0.070 (9)
C(9)	0.609 (1)	0.4051 (5)	0.6022 (5)	0.08 (1)
C(10)	0.552 (1)	0.5383 (6)	0.5627 (6)	0.09 (1)
C(11)	0.675 (1)	0.6565 (5)	0.6244 (5)	0.056 (9)
C(12)	0.7814 (9)	0.6893 (5)	0.6079 (5)	0.055 (9)
C(13)	0.776 (1)	0.7556 (6)	0.6229 (6)	0.07 (1)
C(14)	0.880 (1)	0.7817 (7)	0.5417 (7)	0.09 (1)
C(15)	0.897 (1)	0.7170 (7)	0.5245 (6)	0.08 (1)
C(16)	0.805 (1)	0.6784 (6)	0.5491 (6)	0.07 (1)
C(17)	0.772 (1)	0.7694 (6)	0.6818 (6)	0.10 (1)
C(18)	0.975 (1)	0.8242 (7)	0.5254 (7)	0.12 (1)
C(19)	0.908 (1)	0.7066 (8)	0.4625 (6)	0.12 (1)
C(21)	0.825 (1)	0.4950 (5)	0.7546 (5)	0.07 (1)
C(22)	0.784 (1)	0.4567 (7)	0.7960 (6)	0.09 (1)
C(23)	0.852 (2)	0.4142 (8)	0.8215 (8)	0.12 (2)
C(24)	0.963 (2)	0.4105 (9)	0.8013 (9)	0.13 (2)
C(25)	1.005 (2)	0.4478 (9)	0.7610 (8)	0.11 (2)
C(26)	0.935 (1)	0.4917 (6)	0.7360 (6)	0.08 (1)
C(27)	0.811 (2)	0.377 (1)	0.870 (1)	0.25 (2)
C(28)	1.128 (1)	0.4459 (8)	0.7435 (7)	0.15 (2)
C(31)	0.731 (1)	0.5859 (5)	0.8360 (5)	0.060 (9)
C(32)	0.620 (1)	0.5880 (8)	0.8514 (6)	0.10 (1)
C(33)	0.599 (1)	0.5688 (9)	0.9038 (7)	0.13 (1)
C(34)	0.678 (1)	0.550 (1)	0.9409 (6)	0.14 (2)
C(35)	0.787 (1)	0.5515 (9)	0.9247 (7)	0.12 (1)
C(36)	0.814 (1)	0.5664 (7)	0.8723 (6)	0.08 (1)
N(1)	0.7562 (7)	0.5427 (4)	0.7325 (3)	0.046 (6)

Table 1 (*cont.*)

	x	y	z	U_{eq}
Molecule *B*				
O(1)	0.8810 (6)	0.6245 (3)	0.7680 (4)	0.087 (6)
O(2)	0.6816 (7)	0.6453 (3)	0.7474 (3)	0.068 (6)
O(3)	0.6975 (5)	0.6006 (3)	0.6403 (3)	0.047 (5)
O(4)	0.5851 (7)	0.6798 (3)	0.6224 (4)	0.077 (6)
O(5)	0.8692 (7)	0.7860 (4)	0.5987 (4)	0.082 (7)
O(6)	0.7490 (8)	0.6459 (5)	0.5197 (4)	0.106 (8)
S(1)	0.7666 (3)	0.6056 (2)	0.7688 (1)	0.058 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *for molecules A and B of diastereoisomer* (3*a*) *with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
C(1)—C(2)	1.56 (2)	1.56 (2)	C(15)—C(16)	1.49 (2)	1.53 (2)
C(1)—C(6)	1.54 (2)	1.52 (2)	C(15)—C(19)	1.60 (2)	1.53 (2)
C(1)—N(1)	1.47 (1)	1.50 (1)	C(16)—O(6)	1.19 (2)	1.21 (2)
C(2)—C(3)	1.53 (2)	1.53 (2)	C(21)—C(22)	1.38 (2)	1.41 (2)
C(2)—O(3)	1.44 (1)	1.43 (1)	C(21)—C(26)	1.39 (2)	1.40 (2)
C(3)—C(10)	1.50 (2)	1.50 (2)	C(21)—N(1)	1.48 (1)	1.45 (1)
C(3)—C(4)	1.58 (2)	1.54 (2)	C(22)—C(23)	1.39 (2)	1.39 (2)
C(3)—C(7)	1.54 (2)	1.53 (2)	C(23)—C(24)	1.38 (2)	1.42 (3)
C(4)—C(5)	1.50 (2)	1.53 (2)	C(23)—C(27)	1.47 (2)	1.53 (2)
C(5)—C(6)	1.55 (2)	1.55 (2)	C(24)—C(25)	1.35 (2)	1.38 (3)
C(6)—C(7)	1.57 (2)	1.52 (2)	C(25)—C(26)	1.42 (2)	1.42 (2)
C(7)—C(8)	1.56 (2)	1.55 (2)	C(25)—C(28)	1.52 (2)	1.53 (2)
C(7)—C(9)	1.54 (2)	1.57 (2)	C(31)—C(32)	1.42 (2)	1.38 (2)
C(11)—C(12)	1.53 (2)	1.52 (2)	C(31)—C(36)	1.36 (2)	1.40 (2)
C(11)—O(3)	1.33 (1)	1.33 (2)	C(31)—S(1)	1.73 (1)	1.75 (1)
C(11)—O(4)	1.17 (1)	1.20 (1)	C(32)—C(33)	1.37 (2)	1.37 (2)
C(12)—C(13)	1.51 (2)	1.52 (2)	C(33)—C(34)	1.41 (2)	1.38 (2)
C(12)—C(16)	1.51 (2)	1.48 (2)	C(34)—C(35)	1.35 (2)	1.37 (2)
C(13)—C(17)	1.47 (2)	1.47 (2)	C(35)—C(36)	1.33 (2)	1.36 (2)
C(13)—O(5)	1.44 (2)	1.43 (1)	N(1)—S(1)	1.651 (9)	1.659 (9)
C(14)—C(15)	1.49 (2)	1.51 (2)	O(1)—S(1)	1.445 (9)	1.430 (8)
C(14)—C(18)	1.54 (2)	1.53 (2)	O(2)—S(1)	1.446 (9)	1.444 (8)
C(14)—O(5)	1.42 (2)	1.40 (2)			

	Molecule *A*	Molecule *B*
C(2)—C(1)—C(6)	100.4 (9)	103.1 (9)
C(2)—C(1)—N(1)	113.0 (9)	112.5 (8)
C(6)—C(1)—N(1)	118.9 (9)	117.8 (9)
C(1)—C(2)—C(3)	107 (1)	102.8 (8)
C(1)—C(2)—O(3)	110.8 (9)	112.2 (8)
C(3)—C(2)—O(3)	110 (1)	113.9 (9)
C(2)—C(3)—C(4)	101 (1)	104.2 (9)
C(2)—C(3)—C(7)	101.6 (9)	102.0 (9)
C(2)—C(3)—C(10)	118 (1)	115.3 (9)
C(4)—C(3)—C(7)	98 (1)	102.5 (9)
C(4)—C(3)—C(10)	117 (1)	114 (1)
C(7)—C(3)—C(10)	118 (1)	117 (1)
C(3)—C(4)—C(5)	108 (1)	103.6 (9)
C(4)—C(5)—C(6)	101 (1)	103 (1)
C(1)—C(6)—C(5)	104.4 (9)	104.1 (9)
C(1)—C(6)—C(7)	106.5 (9)	104.2 (9)
C(5)—C(6)—C(7)	99.9 (9)	101.2 (9)
C(3)—C(7)—C(6)	95.1 (9)	94.9 (9)
C(3)—C(7)—C(8)	116 (1)	115.6 (9)
C(3)—C(7)—C(9)	117 (1)	114 (1)
C(6)—C(7)—C(8)	111.4 (9)	113.8 (9)
C(6)—C(7)—C(9)	112 (1)	112.8 (9)
C(8)—C(7)—C(9)	105.5 (9)	105.5 (9)
C(12)—C(11)—O(3)	110 (1)	111 (1)
C(12)—C(11)—O(4)	124 (1)	122 (1)
O(3)—C(11)—O(4)	126 (1)	127 (1)
C(11)—C(12)—C(13)	114 (1)	111.3 (9)
C(11)—C(12)—C(16)	110 (1)	110 (1)
C(13)—C(12)—C(16)	109 (1)	114 (1)
C(12)—C(13)—C(17)	112 (1)	116 (1)
C(12)—C(13)—O(5)	109 (1)	109 (1)
C(17)—C(13)—O(5)	105 (1)	109 (1)
C(15)—C(14)—C(18)	113 (2)	114 (1)
C(15)—C(14)—O(5)	111 (2)	111 (1)
C(18)—C(14)—O(5)	104 (2)	106 (1)
C(14)—C(15)—C(16)	112 (1)	109 (1)
C(14)—C(15)—C(19)	112 (2)	115 (1)
C(16)—C(15)—C(19)	110 (1)	111 (1)
C(12)—C(16)—C(15)	112 (1)	115 (1)
C(12)—C(16)—O(6)	123 (1)	125 (1)
C(15)—C(16)—O(6)	124 (2)	120 (1)
C(22)—C(21)—C(26)	122 (1)	122 (1)

Table 2 (*cont.*)

	Molecule *A*	Molecule *B*
C(22)—C(21)—N(1)	123 (1)	121 (1)
C(26)—C(21)—N(1)	115 (1)	117 (1)
C(21)—C(22)—C(23)	121 (1)	122 (1)
C(22)—C(23)—C(24)	117 (1)	115 (2)
C(22)—C(23)—C(27)	121 (1)	122 (2)
C(24)—C(23)—C(27)	122 (1)	123 (2)
C(23)—C(24)—C(25)	123 (1)	124 (2)
C(24)—C(25)—C(26)	120 (1)	120 (2)
C(24)—C(25)—C(28)	121 (1)	122 (2)
C(26)—C(25)—C(28)	119 (1)	118 (2)
C(21)—C(26)—C(25)	117 (1)	117 (1)
C(32)—C(31)—C(36)	118 (1)	121 (1)
C(32)—C(31)—S(1)	118 (1)	119 (1)
C(36)—C(31)—S(1)	124 (1)	120 (1)
C(31)—C(32)—C(33)	117 (1)	115 (1)
C(32)—C(33)—C(34)	123 (1)	125 (1)
C(33)—C(34)—C(35)	118 (2)	117 (2)
C(34)—C(35)—C(36)	121 (2)	120 (2)
C(31)—C(36)—C(35)	124 (1)	121 (1)
C(1)—N(1)—C(21)	119.8 (9)	118.2 (9)
C(1)—N(1)—S(1)	115.1 (7)	116.2 (7)
C(21)—N(1)—S(1)	114.3 (7)	112.1 (7)
C(2)—O(3)—C(11)	120 (1)	117.6 (8)
C(13)—O(5)—C(14)	112 (1)	117 (1)
C(31)—S(1)—N(1)	105.4 (5)	105.7 (5)
C(31)—S(1)—O(1)	107.4 (6)	108.6 (6)
C(31)—S(1)—O(2)	110.1 (6)	108.7 (5)
N(1)—S(1)—O(1)	107.3 (5)	108.2 (5)
N(1)—S(1)—O(2)	107.0 (5)	105.7 (4)
O(1)—S(1)—O(2)	118.9 (5)	119.2 (5)

plane defined by its three bonded atoms] (Oppolzer, Chapuis & Bernardinelli, 1984), to quite pyramidal in *N*,*N*-dimethyltoluene-4-sulfonamide [N atom 0.29 (2) Å out of the corresponding plane] (Hakkinin, Ruostesuo & Kivekas, 1988). Tertiary amines show a similar trend in their molecular structures (Bock, Göbel, Havlas, Liedle & Oberhammer, 1991).

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