Structure analyses of menthone- and isomenthonetosylhydrazones, $C_{17}H_{26}N_2O_2S^1$

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The crystal and molecular structures of two configurational isomers of the title compound have been determined by three-dimensional, single-crystal X-ray diffractometry. Both (2S,5R)- and (2R,5R)-4-methylbenzenesulfonic acid-[5-methyl-2-(1-methylethyl)cyclohexylidene] hydrazide (hereafter referred to as menthone- and isomenthone-tosylhydrazone, or I and II, respectively) crystallize in the orthorhombic space group $P2_12_12_1$ (No. 19, D_2^4) with four formula units per cell and a = 5.209(1), b = 17.501(1), c = 20.154(1)Å and a = 5.281(1), b = 17.300(1), c = 17.300(1)20.422(1)Å, respectively. The phase problems were solved by direct methods and the respective final full-matrix least-squares refinements of 1767 and 3010 unique reflections converged to R =0.046 and 0.052. In both structures, the toluenesulfonamide group occupies a position anti to the more substituted side of the cyclohexyl ring, the C(16)-C(11)-N(2) angles are significantly wider than 120°, and each sulfonamide nitrogen (1) atom appears to exhibit a distorted trigonal pyramidal geometry. The structures differ in the positioning of the isopropyl and methyl substituents on the cyclohexane ring, with the *trans* isomer I having both groups equatorial, while the cis isomer II exhibits an axial isopropyl group. The molecules in the crystal lattice are held together by van der Waals forces. X-ray powder diffraction, conoscopic, infrared, and ¹H and ¹³C NMR analyses have been performed.

Introduction

Tosylhydrazones are versatile intermediates in organic synthesis which allow the fairly direct conversion of ketones to alkenes and functionalized alkenes via the Shapiro reaction. Naturally occurring enantomerically pure and enriched ketones can provide, by means of the corresponding tosylhydrazones, high optical purity vinyllithium reagents and products derived thereof. Such chiral, nonracemic materials are of value in the synthesis of pharmaceuticals, natural products, and many other organic materials. However, α -chiral ketones can potentially undergo epimerization of that stereocenter during and/or after hydrazone formation. This would seriously limit the applicability hydrazone

related conversions in the case of (-)-menthone, perhaps the most common epimerizable naturally derived α -chiral ketone. (-)-Menthone is commercially available and is also easily prepared by the oxidation of (-)menthol (Brown *et al.*, 1971). In the course of studying the application of the Shapiro reaction to (-)-menthone, we had occasion to synthesize both menthoneand isomenthone-tosylhydrazones and determine the structural features by single-crystal X-ray analysis.

Experimental

Materials were obtained from commercial sources and used as received unless otherwise noted. Melting points were calibrated. The NMR spectra were obtained on a Bruker AMX-360 spectrometer. Chemical shifts were assigned relative to TMS internal standard (0 ppm) for ¹H, and CDCl₃ (77.0 ppm) or CD₂Cl₂ (53.8 ppm) for ¹³C. Coupling constants are given in Hertz. Infrared

¹(2S,5R)- and (2R,5R)-4-Methylbenzenesulfonic acid-[5-methyl-2-(1-methylethyl)cyclohexylidene]hydrazide.

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spectra were obtained on a Mattson Cygnus 100 FT IR using the KBr pellet technique.

The preparation of menthonetosylhydrazone (I) in high isomeric purity has not been previously described. Menthonetosylhydrazone (I) was prepared by suspending tosylhydrazine (2.001 g, 10.7 mmole) in acid-free dichloromethane (12 ml) and then cooled to 0°C. To this stirred suspension was added (-)menthone (2.05 ml, 10.7 mmole; trans: cis = 97:3) and the mixture was allowed to stir for 2.5 h, at which time an additional 0.5 ml (4.0 mmole) of menthone was added. After one additional hour of stirring at 0°C, the mixture was nearly homogeneous and was then quickly passed through a 3-cm layer of silica gel on a coarse porosity fritted funnel, rinsing with two 10-ml portions of dichloromethane. The resultant clear, colorless solution was immediately concentrated by rotary evaporation at approximately 0°C. A colorless oil resulted. Treatment of this product with hexanes (5 ml) caused crystallization of the hydrazone, which was transferred to a fritted glass funnel and washed well with hexanes. Drying under vacuum (0.1 mm Hg) yielded the hydrazone (2.498 g, 72.4% yield) as a white powder (m.p. = 121-122°C). Isomeric purity was 97 \pm 1% by reversed-phase (C-18) HPLC. ¹H NMR (CDCl₃): 0.75 (d, 3H, J = 6.8); 0.78 (d, 3H, J = 6.7); 0.90 (d, 3H, J = 6.5); 1.04-1.15 (m, 3H)1H); 1.18-1.30 (m, 1H); 1.51 (dd, 1H, J = 13.5, 10.7); 1.57-1.68 (m, 1H); 1.72-1.88 (m, 3H); 2.10 (octet, 1H, J = 6.7; 2.42 (s, 3H); 2.53 (ddd, 1H, J = 13.5, 3.9, 1.4); 7.29 (d, 2H, J = 8); 7.68 (br. s, 1H), 7.85 (d, 2H, J = 8). ¹³C NMR (CDCl₃): 18.7, 21.3, 21.41, 21.47, 26.4, 27.1, 32.86, 32.93, 34.6, 50.4, 128.2, 129.3, 135.6, 143.6, 162.2. IR: 3221 cm⁻¹ (NH), 1642 cm^{-1} (C=N), 1328, 1160 cm^{-1} (SO₂).

A portion of the product (99.6 mg) in a vial was dissolved in toluene (2.0 ml) at 0°C. While taking care not to agitate the solution, hexanes (5 ml) were carefully layered above the toluene, and the vial was allowed to stand in a freezer (-20° C) undisturbed for 48 h. The supernatant was removed by pipette after which the crystals were washed once with hexanes. After drying under vacuum, the hydrazone (87.9 mg) was obtained as clear colorless crystals suitable for single crystal X-ray diffraction.

A mixture of I and II (29:71 ratio by HPLC) was obtained as previously described (Hutchens *et al.*, 1973). A crystal of II suitable for X-ray analysis was chosen from material obtained by crystallization of this mixture from hot ethanol; after analysis, this crystal exhibited a melting point of $118-120^{\circ}$ C. Furthermore, we found that the flotation technique described below would allow a degree of separation of the isomers based on slight differences in densities. In this way, we obtained a small amount (13 mg) of material enriched in **II** (\approx 90%) for ¹H and ¹³C NMR analyses. ¹H NMR (CDCl₃): 0.45 (d, 3H, J = 6.6); 0.85 (d, 3H, J = 6.4); 0.93 (d, 3H, J = 6.1); 1.2–1.3 (m, 1H); 1.43–1.6 (m, 4H); 1.72–1.84 (m, 1H); 1.84–1.96 (m, 2H); 2.41 (s, 3H); 2.50 (br. d, 1H, J = 11.2) 7.28 (d, 2H, J = 8); 7.61 (v. br. s, 1H); 7.83 (d, 2H, J = 8). ¹³C NMR (CDCl₃, 25°C): 20.3, 20.6, 21.5, 22.1, 26.9, 27.7, 29.4, 32.3, 33.3, 50.3, 128.1, 129.4, 135.6, 143.7, 165.8 (v. br., \approx 110 Hz wide). ¹³C (CD₂Cl₂, -60°C): 20.00, 20.04, 21.3, 21.9, 26.2, 27.7, 28.7, 31.6, 33.4, 49.9, 127.4, 129.3, 134.1, 144.0, 164.2 (5 Hz wide).

The flotation technique (sat'd ZnCl₂ and H₂O) was used to determine the experimental densities of I and II [1.17(1) and 1.15(1) Mg m⁻³, respectively]. A conoscopic study of single crystals of both hydrazones provided evidence that the isomeric system was biaxial (anisotropic in nature, optically birefringent). Crystal rotation between two crossed polarizers on a Ziess Photomicroscope II was employed for the optical examination.

The reported X-ray powder diffraction data were obtained using a Siemens Debye-Scherrer cylindrical camera (114.6 mm) under vacuum at 293 K. Copper $K\alpha$ $(\lambda_{mean} = 1.54184 \text{ Å})$ radiation filtered with a nickel foil was used. Finely ground crystals of compound I were placed into a 0.2-mm glass capillary. Characterization was based on 40 measured lines which were employed to refine the lattice parameters by placing the corresponding S values into a least-squares X-ray powder diffraction program designed by Roof (1968). The refined powder lattice constants (orthorhombic) are a =5.210(2), b = 17.510(4), and c = 20.159(5)Å, see Table 1. The "figures-of-merit" used as the measuring test for assessment of reliability and quality of the powder pattern indexing are F_N (Smith and Synder, 1979) and M_{20} (Dewolff, 1968). In this report, F(30) =52(0.010, 57) and $M_{20} = 25.5$. Table 2 presents experimental 2θ values, visual estimated relative intensities, and observed d-spacing values with associated Miller indices. The average percentage deviation between observed and calculated 2θ values and d-spacing values are 0.049 and 0.25, respectively.

Single crystals of **I** and **II** ($0.40 \times 0.49 \times 0.85$ mm and $0.69 \times 0.69 \times 0.81$ mm) were chosen on the basis of optical homogeneity and were mounted on an Enraf-Nonius CAD4-F autodiffractometer (Mo $K\alpha$, $\lambda = 0.71073$ Å, 292 K) that is equipped with a dense graphite monochromator (take-off angle, 5.8°). The orienta-

Table 1. Experimental and statistical summaries

		I	
	Powder	Single Crystal	Single Crystal
Molecular formula		C ₁₇ H ₂₆ N ₂ O ₂ S	$C_{17}H_{26}N_2O_2S$
Crystal system		Orthorhombic	Orthorhombic
Space group		$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$
Radiation	Cu Ka	Μο Κα	Μο Κα
λ _{mean} (Å)	1.54184	0.71073	0.71073
a (Å)	5.210(2)	5.209(1)	5.281(1)
b (Å)	17.510(4)	17.501(1)	17.300(1)
c (Å)	20.159(5)	20.154(1)	20.422(1)
$V(Å^3)$	1839.0(16)	1837.3(6)	1865.8(6)
$D_m ({\rm Mg}{\rm m}^{-3})$	1.17(1)	1.17(1)	1.15(1)
$D_{\rm x} ({\rm Mg}{\rm m}^{-3})$	1.165	1.166	1.148
M _r	322.5	322.5	322.5
Z	4	4	4
μ (Mo K α) (mm)		0.176	0.173
$\Delta \theta$ (°)		1.5-25.0	1.5-25.0
R _{int}		0.010	0.036
R		0.046	0.054
$R_{\rm w} (R_{\rm all})$		0.057(0.056)	0.065(0.062)
$g (e^{-2}) (\times 10^{-5})$		1.3(5)	1.0(7)
Gnft (Σ_2)		1.85	1.59

tion matrices and initial unit cell parameters were determined from the least-squares refinement of twentyfive accurately centered reflections (low θ angles, 2.0-10.0°). Final lattice constants were obtained at high θ angles, $>20^{\circ}$. Both intensity data sets were collected over the ranges of $3.0 < 2\theta < 50.0^{\circ}$ employing the ω -2θ scan technique at a varied scan rate (0.46 to 3.44° \min^{-1}) determined by a fast prescan of 3.44° \min^{-1} . The scan range (ω) was $1.20^{\circ} + 0.344 \tan \theta$. Reflections having less than 75 counts above background during the prescan were deemed unobserved. Periodic intensity measurements of two control reflections for I and II, monitored at 2-hr intervals of collection time, revealed no signs of deterioration. Hence, electronic hardware reliability and crystal stability were confirmed. Of the 2322 measured reflections (h: $0 \rightarrow 6$, k: $-8 \rightarrow 20$, $l:-9 \rightarrow 23$) for I and 4164 reflections (h: 0) \rightarrow 6, k: -20 \rightarrow 20, l: -9 \rightarrow 24) for **II**, 1767 and 3010 were respectively independent fitting $F > 6.0\sigma(F)$. All intensities were corrected for Lorentz and polarization effects. After applying the zero-moment test (NZ-test) proposed by Howell et al. (1950) to the observed data, a noncentrosymmetric system was indicated consistent with the presence of chiral carbons [C(12) and C(15)]in both molecules. Nonextinction in hkl and the conditions $h00 \ (h = 2n), \ 0k0 \ (k = 2n), \ and \ 00l \ (l = 2n)$

Table 2. X-ray powder diffraction data

2θ obs (°)	I/I _o	d_o (Å)	h	k	l
6.70	20	13.19	0	1	1
10.11	100 + a	8.75	0	2	0
11.02	5	8.03	0	2	1
13.40	15	6.61	0	2	2
15.83	35	5.60	0	3	1
16.63	15	5.332	0	2	3
17.58	50	5.046	1	0	1
17.77	100	4.990	1	1	0
18.33	90	4.841	0	1	- 4
19.17	55	4.629	1	0	2
19.85	30	4.473	1	1	2
20.15	45	4.407	0	3	3
20.33	45	4.369	1	2	1
20.77	45	4.276	0	4	1
21.60	40	4.114	1	0	3
22.17	95	4.009	1	1	3
22.65	10	3.926	0	1	5
23.32	25	3.8137	0	3	4
23.90	10	3.7232	1	2	3
24.28	30	3.6665	0	4	3
24.57	20	3.6225	1	0	4
25.12	3	3.5444	1	1	4
25.82	45	3.4499	0	5	1
26.65	25	3.3449	1	2	4
27.02	30	3.2994	0	1	6
28.00	55	3.1867	1	0	5
28.47	25	3.1346	0	2	6
28.75	10	3.1052	0	5	3
29.80	20	2.9981	1	4	3
30.65	10	2.9169	0	6	0
30.98	3	2.8870	0	6	1
31.70	10	2.8226	1	0	6
32.07	10	2.7905	1	4	4
32.75	3	2.7345	0	2	7
33.50	15	2.6750	0	6	3
34.45	15	2.6034	2	0	0
34.75	25	2.5816	0	3	7
35.63	45	2.5201	1	0	7
36.20	10	2.4814	0	7	1
37.05	15	2.4264	0	7	2

^{*a*} The observed d-space value of 8.75 Å is closer to the calculated value of 0 2 0 (8.775 Å) than that of 0 1 2 (8.736 Å). Using Cu $K\alpha$ radiation, one can not resolve these lines. Therefore, the intensity values of 100+ is listed.

implied space group $P2_12_12_1$. Table 1 presents experimental and statistical summaries of the title compounds.

A crystallographic analysis (direct methods) of the reduced and averaged data using Siemens SHELXTL-PC (1989) and electron density calculations revealed the locations of all nonhydrogen atoms. The hydrogen atoms in both I and II were generated with idealized geometry and were constrained (at 0.96 Å from carbon atoms and

at 0.90 Å from nitrogen atoms) to ride on their connected atoms with isotropic temperature factors fixed arbitrarily at U = 0.08 Å². After several cycles of fullmatrix least-squares anisotropic refinements of all nonhydrogens and including secondary extinction corrections (g, see Table 1), final residual index values were obtained (R = 0.046, $R_w = 0.057$ and $R_{all data} = 0.056$ for **I** and R = 0.054, $R_w = 0.065$, and $R_{\text{all data}} = 0.062$ for II). The respective "goodness-of-fit" values (Σ_2) are 1.85 and 1.59. The absolute configuration for II was tested based on the parameter η proposed by Rogers (1981). The value of η refined to 0.9(2) which indicates the correctness of the configuration. A value of η close to +1 signifies correct assignment whereas, a value close to -1 implies an incorrect configuration. A final electron density map of **II** revealed a maximum peak of $0.69 e^{-1} Å^{-3}$ in the vicinity of the sulfur atom which is plausible. Elsewhere, the difference Fourier map of II and that of I were virtually featureless disclosing only random fluctuating backgrounds in the ranges of -0.37to 0.32 and -0.26 to 0.25 e⁻ Å⁻³, respectively. The weighting scheme for I and II was based on counting statistics minimizing $\Sigma w \Delta F^2$ where respective values of $w = 1/(\sigma^2 |F_o| + 0.0017 F_o^2)$ and $1/(\sigma^2 |F_o| +$ $0.0028F_o^2$). Atomic scattering factors and associated anomalous dispersion correction factors were taken from the usual source (Ibers and Hamilton, 1974).

Results and discussion

Final fractional atomic coordinates according to the number scheme in Fig. 1 and isotropic equivalent thermal parameters are presented in Table 3. Interatomic bond distances and angles with their standard deviations are listed in Tables 4 and 5. The stereoscopic views of I and II displaying perpendicular layer formation (*z*-axis) are shown in Fig. 2. This layering is oriented in such a manner that hydrogen bonding cannot occur. The IR study confirmed the lack of hydrogen bonding in I (NH at 3221 cm⁻¹, sharp). Consequently, the molecules within the crystal lattices are held together by van der Waals forces (m.p. = $121-122^{\circ}$ C, I; m.p. = $118-120^{\circ}$ C, II), since no intermolecular contact distances are shorter than the sum of the respective van der Waals radii of the atoms (Pauling, 1960).

The bond distances and angles associated with the phenyl [C(1)-C(6)] and cyclohexyl [C(11)-C(16)] rings in both compounds are within the range of expected values; see Table 4 for averaged C-C lengths and Table



Fig. 1. Perspective views of I and II showing the atomic numbering scheme.

5 for averaged C-C-C angles. The remaining $C(sp^3)-C(sp^3)$ and $C(sp^3)-C(sp^2)$ distances are in direct agreement with published values found in BID-ICS (1969-1981). The S=O, S-N, S-C, N-N, and N=C lengths are internally consistent and are also in accord with values found in BIDICS (1969-1981). Specifically, the experimental values for these bond lengths are in line with values obtained from the summation of the involved radii found in the work of Pauling (1960) and Demitras et al. (1972). The polyhedral arrangement about the sulfur atoms in I and II is a distorted tetrahedral which is evidenced by the O(1)-S-O(2) angles of 119.4(2) and 119.8(2)°, respectively. However, the respective mean angles about the sulfur atom in both compounds are 109.4(48) and 109.4(50)°.

Comparison of I and II show interesting differences in the positioning of the isopropyl and methyl groups on the cyclohexane ring. In I, both the isopropyl and methyl groups occupy sterically favorable equatorial positions with the cyclohexane ring essentially in a chair conformation. However, in order to maintain a chair conformation in II, the *cis* relationship forces one of these groups into a sterically crowded axial position. Interestingly, it is the isopropyl group which adopts the axial orientation, while the methyl group occupies the equatorial position. This is somewhat surprising, since

Table 3.	Fractional atomic	coord	inate	s ($\times 10^4$) and e	quivalent
isotropic th	ermal parameters	$(Å^2 \times$	10^{3}) with esd's in	parentheses

	Atom	x	у	z	$U_{ m eq}{}^a$
I trans isomer					
	S	1368(2)	5562(1)	3289(1)	45(1)
	O(1)	2138(6)	6021(2)	2750(1)	62(1)
	O(2)	-1183(5)	5636(2)	3550(2)	64(1)
	N(1)	3402(6)	5776(2)	3886(1)	47(1)
	N(2)	3251(6)	5226(2)	4414(2)	44(1)
	C(1)	1835(7)	4591(2)	3096(2)	43(1)
	C(2)	3919(8)	4388(2)	2700(2)	56(1)
	C(3)	4299(9)	3636(3)	2542(2)	64(1)
	C(4)	2649(10)	3089(2)	2774(2)	64(1)
	C(5)	602(1)	3291(2)	3160(3)	72(1)
	C(6)	188(8)	4040(2)	3326(2)	59(1)
	C(7)	3015(15)	2244(3)	2598(3)	106(2)
	C(11)	4777(7)	5333(2)	4900(2)	46(1)
	C(12)	4711(9)	4746(2)	5451(2)	59(1)
	C(13)	3913(11)	5181(3)	6092(2)	69(1)
	C(14)	5560(9)	5868(3)	6220(2)	64(1)
	C(15)	5683(8)	6425(3)	5644(2)	61(1)
	C(16)	6491(8)	6008(2)	5009(2)	56(1)
	C(17)	3113(14)	4024(3)	5295(2)	82(2)
	C(18)	2527(21)	3554(4)	5913(3)	157(2)
	C(19)	4457(17)	3543(3)	4789(3)	111(2)
	C(20)	7371(12)	7114(3)	5789(2)	87(2)
II cis isomer					
	S	825(1)	5458(1)	3184(1)	54(1)
	O(1)	1478(5)	5980(1)	2673(1)	69(1)
	O(2)	-1691(4)	5447(2)	3432(1)	74(1)
	N(1)	2743(5)	5702(2)	3792(1)	57(1)
	N(2)	2510(5)	5152(2)	4316(1)	59(1)
	C(1)	1651(5)	4510(2)	2951(1)	49(1)
	C(2)	3784(5)	4410(2)	2567(2)	56(1)
	C(3)	4450(6)	3681(2)	2371(2)	68(1)
	C(4)	3035(7)	3043(2)	2554(2)	72(1)
	C(5)	895(8)	3164(2)	2929(2)	78(1)
	C(6)	207(6)	3893(2)	3130(2)	64(1)
	C(7)	3789(11)	2250(3)	2344(4)	118(1)
	C(11)	3993(6)	2554(2)	4791(2)	60(1)
	C(12)	3763(7)	4666(2)	5341(2)	70(1)
	C(13)	3420(8)	5097(3)	5983(2)	75(1)
	C(14)	5333(6)	5742(3)	6094(2)	73(1)
	C(15)	5340(6)	6324(2)	5543(2)	68(1)
	C(16)	5851(7)	5905(2)	4887(2)	64(1)
	C(17)	5990(10)	4095(3)	5349(3)	103(1)
	C(18)	5583(18)	3494(4)	5870(4)	164(2)
	C(19)	6357(16)	3696(4)	4708(3)	150(1)
	C(20)	7212(9)	6975(3)	5654(3)	94(1)

"Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ii} tensor.

cyclohexanes usually place the smaller group (here methyl) in an axial position. Axial orientations have been observed in cyclohexanes where an equatorial

Table 4. Interatomic bond lengths (Å) with esd's in parenthesis

I trans isomer				
	S-O(1)	1.408(3)	C(4) - C(7)	1.532(7)
	S-O(2)	1.434(3)	C(11) - C(12)) 1.513(5)
	S-N(1)	1.644(3)	C(12) - C(13)) 1.555(6)
	S-C(1)	1.760(3)	C(13) - C(14)) 1.497(7)
	N(1) - N(2)	1.436(4)	C(14) - C(15)) 1.517(6)
	N(2) - C(11)	1.274(5)	C(15) - C(16)) 1.530(6)
	C(1) - C(2)	1.393(5)	C(16) - C(11)) 1.497(6)
	C(2) - C(3)	1.369(6)	C(12) - C(17)) 1.546(7)
	C(3) - C(4)	1.367(6)	C(17) - C(18)) 1.521(8)
	C(4) - C(5)	1.365(7)	C(17) - C(19)) 1.495(8)
	C(5) - C(6)	1.370(6)	C(15) - C(20)) 1.520(7)
	C(6) - C(1)	1.371(5)		
			Mean	Range
Phenyl ring	C(1) - C(1) - C(1)	C(6)	1.373(9)	1.365-1.393
Cyclohexyl Rin	C(11) - C(11)	C(16)	1.52(2)	1.495-1.555
II cis isomer				
	S-O(1)	1.422(3)	C(4)—C(7)	1.491(6)
	S-O(2)	1.423(2)	C(11) - C(12)) 1.519(5)
	S-N(1)	1.657(3)	C(12) - C(13)) 1.519(5)
	S-C(1)	1.762(3)	C(13)-C(14)) 1.522(6)
	N(1) - N(2)	1.438(4)	C(14) - C(15)) 1.511(6)
	N(2) - C(11)	1.259(4)	C(15)-C(16)) 1.546(5)
	C(1) - C(2)	1.383(4)	C(16)-C(11)) 1.508(5)
	C(2) - C(3)	1.369(5)	C(12)-C(17)) 1.536(7)
	C(3) - C(4)	1.385(5)	C(17)-C(18)) 1.505(10)
	C(4)-C(5)	1.381(6)	C(17)-C(19)) 1.492(9)
	C(5)-C(6)	1.377(5)	C(15) - C(20)) 1.516(6)
	C(6) - C(1)	1.362(4)		
			Mean	Range
Phenyl ring	C(1) = C	C(6)	1.376(8)	1.362-1.385
Cyclohexyl Rin	ng C(11)—	C(16)	1.52(1)	1.508-1.546

group would interact sterically with an *syn* exocyclic substituent (Johnson and Dix, 1971), but in both I and II the sulfonamide group is *anti* to the isopropyl group, and so the cause of this conformation is unclear. In solution, the proton NMR of I strongly supports an all-equatorial arrangement on the cyclohexane ring, since the axial hydrogen on C(16) (1.51 ppm) exhibits a large axial-axial coupling (10.7 Hz) to the C(15) proton. For II, the couplings are less well resolved, and at this point we are unable to assign the solution conformation by NMR with any certainty. Interestingly, the C=N carbon in II is very broad at room temperature (ca. 110 Hz and half-height, CDCl₃), while that of I shows no unusual broadening. Upon cooling II (in CD₂Cl₂ solution), the C=N carbon resonance sharpens (19 Hz at 0°C, 5

I trans isomer				
	O(1) - S - O(2)	119.6(2)	N(2) = C(11) = C(16)	126.9(3)
	C(1) = S = N(1)	107.0(2)	C(11) - C(12) - C(17)	114.7(3)
	C(1) = S = O(1)	109.9(2)	C(13) - C(12) - C(17)	115.2(4)
	C(1) - S - O(2)	107.2(2)	C(12) = C(17) = C(18)	112.5(5)
	N(1) = S = O(1)	104.5(2)	C(12) - C(17) - C(19)	110.3(5)
	N(1) = S = O(2)	108.0(2)	C(18) - C(17) - C(19)	110.3(5)
	S = C(1) = C(2)	118.7(3)	C(16) - C(15) - C(20)	112.3(4)
	S = C(1) = C(6)	121.2(3)	C(14) = C(15) = C(20)	112.8(4)
	S = N(1) = N(2)	110.7(2)	C(3) = C(4) = C(7)	121.2(5)
	N(1) = N(2) = C(11)	115.9(3)	C(5) = C(4) = C(7)	118.6(4)
	N(2) = C(11) = C(12)	116.7(3)		
			Mean	Range
Phenyl ring	C(1) - C(6)		120.0(4)	119.4-120.6
Cyclohexyl Ring	C(11) - C(10)	5)	111.5(32)	106.4-116.2
II cis isomer				
	O(1) = S = O(2)	119.8(2)	N(2) = C(11) = C(16)	127.6(3)
	C(1) = S = N(1)	106.7(1)	C(11) - C(12) - C(17)	112.1(3)
	C(1) = S = O(1)	109.5(1)	C(13) = C(12) = C(17)	113.5(4)
	C(1) = S = O(2)	108.4(1)	C(12) = C(17) = C(18)	110.0(5)
	N(1) - S - O(1)	103.9(1)	C(12)-C(17)-C(19)	112.9(5)
	N(1) = S = O(2)	107.9(1)	C(18) - C(17) - C(19)	108.6(5)
	S - C(1) - C(2)	118.1(2)	C(14) - C(15) - C(20)	112.6(3)
	S = C(1) = C(6)	121.1(2)	C(16) - C(15) - C(20)	111.4(3)
	S = N(1) = N(2)	109.7(2)	C(3) - C(4) - C(7)	120.8(4)
	N(1) - N(2) - C(11)	115.3(3)	C(5) - C(4) - C(7)	121.1(4)
	N(2) - C(11) - C(12)	115.2(3)		
			Mean	Range
Phenyl ring	C(1) - C(6)		120.0(11)	118.1-121.3
Cyclohexyl Ring	C(11)-C(16	ó)	112.0(30)	108.6-117.2

 Table 5. Selective bond angles (°) with esd's in parentheses

Hz at -60° C) without the remainder of the spectrum showing any dramatic changes. This dynamic behavior is probably related to conformational equilibria of the cyclohexane ring, in which either the isopropyl group or the methyl group can be equatorial, but not both.

The experimental angles S-N(1)-N(2) of 110.7(2) and 109.7(2)° in **I** and **II** dictate the ideal placement of H(1) in a position that develops a pyramidal molecular shape with a lone pair of electrons in the apical position above the sulfonamide nitrogen atom. However, because only two atoms attached to N(1) could be located [S and N(2)], two H(1) positions consistent with the pyramidal geometry are possible in each structure. In light of the enlarged C(16)-C(11)=N(2) angles (discussed below), H(1) was assigned to the posi-

tion which would maximize its interaction with H(16a). This assignment also provides an antiperiplanar (rather than gauche) relationship between H(1) and C(1) of the phenyl ring. Thus, the torsion angle C(1)-S-N(1)—H(1) is 169 and 177° in I and II, respectively. The N(2)=C(11)-C(16) angles are much greater than the 120° ideally expected, being 126.9(3)° in I and 127.6(3)° in II. This angle distortion is thought to be due to repulsions between H(1) and H(16a) [the equatorial proton on C(16)], based on other studies of various hydrazones. Similar expansions have been observed in the structural analysis of benzophenone (2-nitrophenyl) hydrazone by Drew and Willey (1986), N=C-C, 125.2 and 126.1°, respectively, and in studies dealing

Fig. 2. Stereoscopic views of the molecular packing arrangement in the unit cells of I and II. Note, the hydrogen atoms dealing with *trans* and *cis* orientations and the idealized H(1) atoms are included. All other H-atoms have been eliminated for clarity.

with sulfone structures (Cameron *et al.*, 1971), and with reactions of 3-acylpyridinium hydrazones (Street *et al.*, 1987).

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Hydrogen atom coordinates, anisotropic thermal parameters, complete bond distances and angles, and structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication No. 67085 (47 pages).