# X-ray and NMR structural investigations of $(\pm)$ (*u*) N-(1-phenylethyl)-1-*t*-butylsulfinyl-1-propenyl-2-amine, C<sub>15</sub>H<sub>23</sub>NOS

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The structure of the title compound has been investigated in the solid state and in solution by Xray and NMR-NOE methods, respectively. The crystals are monoclinic:  $P2_1/c$ , a = 9.828(1), b = 12.326(2), c = 13.976(2) Å,  $\beta = 107.36(1)^\circ$ . The structure was solved by direct methods, and refined against 2495 unique reflections by a full-matrix, least-squares procedure giving R = 0.046. In the solid state the compound exists as the *E* isomer with unlike relative configurations on asymmetric atoms. In solution the compound is found as a mixture of a single enamine and two imine forms. The MM calculations suggest that of the two possible geometrical isomers of both diastereoisomers *u* and *l* of the enamine, the *Z* forms should be of lower energy. The total recognition of the homonuclear <sup>1</sup>H NMR-NOE data interpreted in terms of their distance dependence in the two geometrical forms also favors the *Z* isomer in both diastereomers.

# Introduction

The configuration assignment of di- and trisubstituted ethylenes can pose a challenging problem (Emsley *et al.*, 1987) if the compound exists as a single isomer in solution. Even any predictions based on substituent's electronegativity dependent parameters such as vicinal  ${}^{3}J(H, H)$  (Koole *et al.*, 1984) or geminal  ${}^{2}J(Csp^{2}, H)$ (Marshall, 1983) coupling constants can be ambiguous, owing to overlap of values for Z and E isomers.

In previous papers of this series (Urbańczyk-Lipkowska *et al.*, 1988a, b), we have based our predictions of a configuration in solution of substituted  $\beta$ -sulfinylenamines on the <sup>1</sup>H and <sup>13</sup>C NMR chemical shift correlations (Kozerski *et al.*, 1987) in a series of di- and trisubstituted derivatives.

In this paper we present the crystal structure of the title diastereoisomer (1) and compare it with the molecular structure in solution as judged from the NMR spectral parameters of both u and l diastereoisomers, force field calculation on the level of MM approach and total



recognition of interactions in  ${}^{1}H - {}^{1}H$  NMR double res-

onance experiment leading to NOE.

### Experimental

Preparation of  $(\pm)$  N-(1-phenylethyl)-1-t-butylsulfinyl-1-propenyl-2-amine (1)

A mixture of 2.1 g (13 mmol) of 1-t-butylsulfinyl-2-propanone [obtained from 1-t-butylsulfenyl-2-propanone (Bradsher *et al.*, 1954) by oxidation with hydrogen

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peroxide (30%) in acetone (yield 62%)] and 1.6 g (13) mmol) of  $(\pm)$ 1-phenylethylamine in 50 ml of benzene was heated under reflux for 5 hr with azeotropic removal of water. The solvent was evaporated and crude crystals of 1 were washed twice with diethyl ether. Crystallization from benzene gave 2.54 g (74%) of colorless crystals (ratio of diastereoisomers u: l = 2:3). Recrystallization from benzene-ether-methanol (84:15:1 v/v) gave 0.81 g of pure *u* diastereoisomer. The same procedure applied to optically pure (S)-1-phenylethylamine failed. Crystals for X-ray analysis were obtained from benzenedi-ethyl ether (5:1) crystallization: m.p. 176°- $178^{\circ}$  (dec., uncorr.) IR (CHCl<sub>3</sub>) (cm<sup>-1</sup>): 1610,(C=C); 1000,(S=O). MS ( $M-C_4H_8^+$ ): calcd. for  $C_{11}H_{15}NOS$ : 209.0874. Found: 209.0874. <sup>1</sup>H NMR (AM 500-Bruker)  $\delta$  (ppm) CDCl<sub>3</sub>, -40°C; *u*: 1.22 (s, 9H, *t*-C<sub>4</sub>H<sub>9</sub>), 1.50 [d, J 7.0 Hz, 3H, CH<sub>3</sub>(12)], 2.12 [s, 3H, CH<sub>3</sub>(9)], 4.44 [qv,  $J^1$  6.5,  $J^2$  6.5 Hz, 1H, CH(11)], 4.54 [d, J 6.5 Hz, 1H, NH(10)], 4.63 [s, 1H, CH(7)], 7.2-7.5 (m, 5H,  $H_{ar}$ ); *l*: 0.79 (s, 9H,  $t - C_4 H_9$ ), 1.48 [d, *J* 7.0 Hz, 3H, CH<sub>3</sub>(12)], 2.10 [s, 3H, CH<sub>3</sub>(9)], 4.37 [s, 1H, CH(7)], 4.44 [qv,  $J^{1}$  6.5,  $J^{2}$  6.5 Hz, 1H, CH(11)], 4.72 [d, J 6.5 Hz, 1H, NH(10)], 7.2–7.5 (m, 5H, H<sub>ar</sub>).

### X-ray structural investigations

A colorless crystal of **1** (0.22, 0.19, 0.19 mm) was obtained as above. The reflection intensities were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu K $\alpha$  radiation (1.54178 Å). The cell constants were obtained from a least-squares refinement on the setting angles of 25 reflections. The data were collected with the  $\omega/2\theta$  scan technique up to  $2\theta_{max} = 140^{\circ}$ .

Crystal data:  $C_{15}H_{23}NOS$ ,  $M_r = 265.42$ , monoclinic, space group  $P2_1/c$ , a = 9.828(1), b = 12.326(2), c = 13.976(2) Å,  $\beta = 107.36(1)^\circ$ , V = 1615.9(3) Å<sup>3</sup>, Z = 4, F(000) = 572,  $D_x = 1.09$  g cm<sup>-3</sup>,  $\mu$ (Cu K $\alpha$ ) = 1.65 mm<sup>-1</sup>.

A total of 3653 reflections was collected, of which 2695 were unique and 2495 reflections were found to have  $I > 2\sigma_I$ . Lorentz and polarization corrections were applied to the data. No absorption correction was applied at measurement stage.

The phase problem was solved by direct methods (program SHELXS-86, Sheldrick, 1985). A total of 18 atoms was found in an *E*-map. Initially, the positional parameters and individual isotropic temperature factors of all non-hydrogen atoms were refined to R = 0.115 (program SHELX-76, Sheldrick, 1976). At this stage an

empirical, spherical absorption correction (program DIFABS, Walker and Stuart, 1983) was performed. For 2495 reflections, the minimum, maximum, and average corrections were 0.700, 1.240, and 0.987, respectively.

The positions of the hydrogen atoms bonded to carbon atoms were generated from assumed geometries and those of the amino hydrogen atom were found from a difference Fourier map and added with isotropic temperature factors to the set of atomic parameters. The refinement of atomic positional and thermal anisotropic parameters (isotropic for H) was performed by the leastsquares, full matrix procedure using SHELX-76. The final R was 0.0460,  $R_w = 0.0526$ ,  $w = 2.37/(\sigma_F^2 + 0.000464F^2)$ . The highest peak in the final difference map was 0.27 e/Å<sup>3</sup>.

The refined positional parameters for the non-H atoms of 1, together with their  $B_{eq}$  values are given in Table 1.

### NOE measurements

The measurements were performed on a Bruker AM 500 MHz NMR spectrometer and the spectra were recorded in CDCl<sub>3</sub> solutions at  $-40^{\circ}$  to avoid exchange of NH proton and freeze the rotation along C8–N10 bond. A standard program for irradiation of multiplets was used (Kinns and Sanders, 1984). It enables the same irradiation time (1.6 s) over several stereochemical sites in one experiment, using frequency lists for each multiplet. A total time of acquisition and delay between the pulses was set to 6 s, and the irradiation power was adjusted so that a selective irradiation of closely lying multiplets and almost full saturation of a desired signal were achieved. Averaging within three hours was applied to achieve good *S/N* ratio in difference spectra which were used for analysis.

### **Results and discussion**

Compound 1 in the crystalline state exists as an enamine derivative in the *E* configuration (see Fig. 1) with unlike configurations on asymmetric centers, i.e., on S5 and C11. The same configuration was found in the previously studied *N*-benzyl-1-phenylsulfinyl-1-propenyl-2-amine monohydrate (2) (Urbańczyk-Lipkowska *et. al.*, 1988a). A comparison of the geometrical data (Table 2) shows that both compounds exist in solid state in approximately the same conformations along C1-S5, N10-C11, and C8-N10 bonds.

	<i>x</i>	у	z	B <sub>eq</sub>
C1	3917(3)	2580(2)	-77(2)	4.82(6)
C2	5091(4)	3465(3)	164(2)	6.8(1)
C3	2584(4)	2964(3)	-865(2)	7.4(1)
C4	4458(4)	1531(3)	-387(2)	7.6(1)
S5	3352.2(5)	2308.3(4)	1043.1(4)	3.93(1)
06	2978(2)	3391(1)	1383(1)	5.09(5)
C7	4925(2)	1890(2)	1886(2)	4.04(5)
C8	5082(2)	906(2)	2342(1)	3.69(5)
C9	3904(2)	78(2)	2140(2)	4.86(6)
N10	6292(2)	600(1)	3031(1)	4.34(4)
C11	7559(2)	1262(2)	3335(2)	4.69(6)
C12	8579(3)	789(2)	4282(2)	5.91(7)
C13	8288(2)	1373(2)	2522(2)	5.30(7)
C14	8887(3)	2330(3)	2354(3)	7.4(1)
C15	9631(5)	2412(6)	1641(5)	9.0(2)
C16	9690(6)	1516(8)	1086(5)	11.2(3)
C17	9094(5)	595(6)	1219(4)	11.5(3)
C18	8414(4)	487(4)	1962(3)	8.2(1)

Table 1. Fractional coordinates (×10<sup>4</sup>) and  $B_{eq}^{\ a}$  values for non-hydrogen atoms<sup>b</sup>

Refined anisotropic thermal parameters (×10<sup>4</sup>) for 1. The exponential form is  $\exp \left[-2\pi^2 (U_{11}a^{*2}h^2 + \cdots + 2U_{12}a^*b^*hk + \cdots)\right]$ 

	<i>U</i> 11	$U_{22}$	U <sub>33</sub>	<i>U</i> <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
C1	677(13)	680(15)	501(12)	82(11)	175(11)	38(11)
C2	1219(25)	953(21)	820(20)	-212(19)	570(19)	90(16)
C3	1002(23)	1375(30)	610(17)	211(21)	103(16)	257(18)
C4	1457(32)	1086(25)	724(20)	307(22)	430(21)	-142(17)
S5	486(3)	481(3)	524(3)	0(2)	144(2)	-3(2)
06	722(10)	547(9)	770(11)	101(7)	299(9)	-42(8)
C7	495(11)	504(11)	527(12)	-57(9)	123(9)	-4(10)
C8	514(10)	503(11)	422(11)	-16(8)	179(9)	-16(9)
C9	630(13)	562(13)	675(15)	-110(10)	174(11)	34(11)
N10	554(9)	554(10)	537(10)	-20(8)	127(8)	90(8)
C11	592(12)	588(13)	552(13)	-34(10)	39(11)	18(10)
C12	701(15)	910(19)	606(15)	-29(14)	-17(12)	77(14)
C13	484(11)	906(19)	689(16)	-93(12)	57(11)	183(14)
C14	794(19)	1232(27)	971(24)	-302(18)	36(17)	384(20)
C15	770(24)	2303(60)	1280(41)	-471(34)	36(27)	890(39)
C16	848(29)	3298(111)	1398(50)	-398(47)	445(33)	527(55)
C17	1298(38)	2386(67)	1697(47)	91(39)	999(38)	-105(44)
C18	952(23)	1405(32)	1162(28)	-39(21)	604(22)	-75(25)

Refined hydrogen fractional coordinates ( $\times 10^3$ ) for 1

	<i>x</i>	у	Ζ	
H2A	484(4)	413(3)	47(3)	
H2B	603(3)	314(3)	66(3)	
H2C	531(4)	371(3)	-52(3)	
H3A	227(3)	362(3)	-65(2)	
H3B	172(4)	252(3)	-95(3)	
H3C	285(4)	305(3)	-142(3)	
H4A	461(4)	168(3)	-99(3)	
H4B	367(4)	104(3)	-48(2)	
H4C	538(4)	127(3)	9(3)	

	x	у	Z	_	
 H7	566(3)	239(2)	200(2)		
H9A	412(4)	-44(3)	249(3)		
H9B	305(4)	43(4)	219(3)		
H9C	354(4)	1(3)	158(4)		
H10	639(2)	3(2)	316(2)		
H11	725(2)	196(2)	349(2)		
H12A	890(3)	8(2)	414(2)		
H12B	948(3)	124(2)	452(2)		
H12C	817(3)	74(2)	476(2)		
H14	874(2)	292(2)	281(2)		
H15	1012(5)	290(4)	141(4)		
H16	1025(7)	147(5)	60(4)		
H17	941(3)	7(3)	117(3)		
H18	793(4)	-13(3)	205(3)		

Table 1. Continued

<sup>*a*</sup> Calculated from anisotropic thermal coefficients as  $B_{eq} = 8\pi^2 \cdot D_u^{1/3}$ , where  $D_u$  is the determinant of the  $U_{ii}$  matrix in orthogonal space.

<sup>b</sup>In this and next table the values in parentheses are estimated standard deviations.

One type of potential intermolecular hydrogen bonding was found in the crystal structure of 1. The hydrogen bonds involve the NH group as a donor and the O6 oxygen of the sulfoxide group in a neighboring molecule as the acceptor. The acceptor symmetry with respect to the identity symmetry of the donor is 1 - x,  $-\frac{1}{2} + y$ ,  $\frac{1}{2} - z$ . The geometry of the bond N10-H10  $\cdots$  O6 is as follows: N10-O10 0.73(2) Å, N10  $\cdots$ O6 2.872(2) Å, H10  $\cdots$  O6 2.15(2) Å and angle N10-H10  $\cdots$  O6 172(2)°. Thus, the molecules in the crystal form infinite chains along the screw axes, each chain containing the molecules of the same chir-



Fig. 1. Stereoplot of 1 showing molecular conformation of the E form.

**Table 2.** Selected geometrical parameters found from X-rayinvestigations of 1 compared with those of  $2^a$ 

	1	2
Bond lengths (Å)		
\$5-06	1.499(1)	1.520(4)
C1-S5	1.841(3)	1.788(5)
S5-C7	1.719(2)	1.723(7)
C7-C8	1.357(3)	1.367(8)
C8-N10	1.342(2)	1.349(10)
N10-H10	0.73(2)	
Bond angles (degrees)		
C1-S5-C7	101.5(1)	97.0(3)
C1-S5-O6	105.8(1)	104.2(2)
O6-S5-C7	107.8(1)	110.1(3)
C8-N10-H10	115(2)	
C11-N10-H10	115(2)	
C8-N10-C11	123.7(2)	123.4(5)
Torsion angles (degrees) <sup>b</sup>		
06-\$5-C7-C8	127.4(2)	-113.0(5)
C1-S5-C7-C8	-121.7(2)	139.1(5)
\$5-C7-C8-N10	-177.1(2)	-174.7(4)
H10-N10-C8-C7	-164.7(2)	
C9-C8-N10-C11	179.5(2)	-178.4(6)
H10-N10-C11-H11	-146(2)	
C8-N10-C11-C12	166.8(2)	
C8-N10-C11-C13	-69.4(3)	65.2(7)

<sup>a</sup>N-benzyl-1-phenylsulfinyl-1-propenyl-2-amine monohydrate (Z. Urbańczyk-Lipkowska *et al.* 1988a).

<sup>b</sup> For 2 the signs refer to the S configuration on sulfur.



Fig. 2. Parallel projection of two hydrogen bonded chains of molecules on to the *ab* plane of the crystal. Hydrogen bonds are distinguished by light lines. Two parallel chains contain opposite enantiomorphs each. The rectangular outline shows the projection face *ab* of the cell unit. Atom types are distinguished by increasing ball radii H < C < N < O < S.

ality. Figure 2 shows a parallel projection of chained molecules on the *ab* plane of the crystal.

To assign the configuration and conformations in a solution along the main bonds mentioned above we have attempted to develop a procedure of finding the best correlation between interproton distances in several stereochemical isomers and a set of respective nuclear Overhauser enhancements established in the <sup>1</sup>H NMR experiment.

The MMX-86 program (Allinger, 1986) was used to calculate the strain energy and interproton distances for minimum energy conformations for the Z and E isomers of both diastereoisomers u and l. The data are listed in Table 3. The conformations along the C1-S5 and N10-C11 bonds found from X-ray investigations were introduced as input for calculation of the lowest energy form for the u isomer. The energy was minimized down to 11.33 kcal (*E-RS*) and this was taken as the best conformation of the isolated molecule in the *E* form. Similarly, the conformations along S5-C7 and N10-C11 bonds were checked for minimum of strain energy in the Z form. The molecule at the lowest strain energy con-

formation (Z-RS) (Fig. 3) implies the existence of an intramolecular hydrogen-bond N10—H10  $\cdots$  O6 with following distances: N10  $\cdots$  O6 2.832 Å, H10  $\cdots$  2.045 Å, and N10—H10 0.96 Å. As compared with the corresponding intermolecular hydrogen bond in *E*-RS (crystal form) the above distances indicate the stronger hydrogen bond in Z-RS form. However, as judged from the IR or <sup>1</sup>H NMR spectra in chloroform or benzene solution, this intramolecular hydrogen bond is rather weak.

The shape of both diastereoisomers of the Z form differs distinctly as the distances between the *t*-butyl and phenyl ring are concerned; being 7.02 Å and 6.28 Å in Z-SS and Z-RS forms, respectively, if the average distance between C2, 3, 4 and C13 atoms are considered. If one takes into account a known relationship that steric compression results in <sup>1</sup>H NMR in high frequency shift, the observed chemical shifts of 1.22 and 0.79 ppm for RS and SS forms, respectively, are plausibly explained by the above distances.

Finally, we have used a method (Kozerski *et al.*, 1990) of a recognition of  ${}^{1}H{}-{}^{1}H$  interactions leading

	Structure <sup>b</sup> ( $\Delta E$ [kcal/mole]) <sup>c</sup>					
Torsion angle	Z - u (0)	Z - l (0.90)	E - u (1.36)	E - l (1.66)	$E - u (> 1.36)^d$	
06-\$5-C7-C8	+29	-52	+150	-70	+ 127.4	
C1-S5-C7-C8	+143	166	-98	+116	-121.7	
H10-N10-C8-C7	-12	+23	+178	+166	+164.7	
C9-C8-N10-C11	-39	-16	+179	+178	+179.5	
H10-N10-C12-H12	-163	-150	-115	-145	-146.8	
C8-N10-C11-C12	+160	+154	-178	+163	+166.8	
C8-N10-C11-C13	-77	-83	-55	-74	-69.9	
C8-N10-C11-C13	-77	-83	-55	-74	-69.9	

Table 3. Minimum strain energy conformations of diastereomers<sup>4</sup>

<sup>a</sup> Strain energy calculations were carried out using MMX-86 program (Allinger, 1986).

<sup>b</sup> Denotes the configuration at the double bond and relative configurations on sulfur and  $C_{\alpha}$  atoms.

<sup>c</sup> Excess of strain energy relative to the lowest energy form Z - u. The energy was optimized for various conformations along S5-C7 and N10-C11 bonds.

<sup>d</sup> Torsion angles found from X-ray investigations of 1 (see Table 2).

to NOE in homonuclear double resonance experiment. Thus we have attempted to interpret qualitatively a full set on NOE's in both diastereoisomers taking into account their linear relation to the interproton distances  $(r^{-6})$  if short irradiation time is applied (Sanders and Marsh, 1982). Several theoretical and experimental conditions must be met that the multispin system shows such a relationship (Noggle and Schirmer, 1971). Among the most important and hard to realize experimentally are the assumption of exclusive intramolecular dipolar relaxation in multispin system, isotropic molecular correlation time and the absence of spin diffusion effects (Werblow and Grant, 1977). With respect to this the experiment should provide the good means of a selective and instantaneous irradiation of a resonance transitions and equal time of irradiation if several irradiation sites are to be compared (Bothner-By and Noggle, 1979).



Fig. 3. Stereoplot of the molecule showing molecular conformation of the Z form assigned in solution.

The experimental conditions of the NOE measurements are discussed in experimental part and Table 4 gives the results together with interproton distances relevant to interacting nuclei. Several features emerge from the data if they are compared together with the distances in both forms, E and Z. The first three values of NOE in *u* isomer show decrease along with increasing  $r_z$  values while  $r_E$  distance remains nearly constant as seen in Table 4. In accord to that, the ratio of NOE values found at NH(10) and CH(11) (0.33) upon CH<sub>3</sub>(12) saturation is much closer to the ratio of inverse sixth power of relevant distances in Z form (0.48) than in E form (0.70). Furthermore, the NOE value on CH(11) in *l* isomer upon saturation of CH(7) is close to zero in agreement with the calculated distance in Z form  $(4.657 \text{ \AA})$  but much too low as expected for the E form where the above interproton distance is the shortest one in a whole molecule (2.236 Å). A confirmation to the above reasoning is the fact that the data of Table 4 correlate linearly according to the relationship NOE  $\approx a \cdot r_z^{-6} + b$  for the Z - l isomer, whereas such correlation is not observed for the E - l isomer if both sets of distances  $(r_z \text{ and } r_E)$  are subjected to a linear regression analysis. Such a correlation was not attempted in u isomer for three experimental points available which can be included in a regression analysis. Well known sensitivity of the NOE to the conformational differences may affect the results of such analysis. The reason is that the interproton distances were calculated on the basis of the prevailing rotamer established in the MMX program whereas several rotamers should be considered for the freely rotating groups. However, failure to meet the theoretical requirements in a standard experimental conditions is undoubtedly the main difficulty in that approach.

Isomer	Nuclear interaction	NOE <sup>b</sup> (%)	$r_Z^c$ (Å)	$r_E^c$ (Å)	$R_Z(n)$	$R_E(n)^d$
RS(u)	(d) <b>C12H</b> <sub>3</sub> -C11H	10.3	2.685	2.705		
	(d) $C12H_3 - N10H$	3.4	3.032	2.879		
	(s) C9H <sub>3</sub> -N10H	$2.8, 1.7^{e}$	3.835	2.877		
	(s) C2,3,4H <sub>9</sub> -C7H	8.2 <sup>f</sup>	3.86	4.177		
	(q) C11H-C7H	3.3 <sup>f</sup>	4.704	2.256		
SS(l)	(d) $C12H_3 - C11H$	$5.3, 0.3^{e}$	2.575	2.567	0.93	0.05
	(d) $C12H_3 - N10H$	$4.8, 0.7^{\circ}$	2.593	2.585	n	= 8
	(q) $C11H - C14H$ , C18H	1.5	3.102	3.109		
	(d) N10H-C14H, C18H	1.2	3.613	3.635		
	(d) $C12H_3 - C14H$ , C18H	1.1	3.738	3.72		
	(s) $C7H-C2, 3, 4H_9$	$0.3,^{e} 10.3^{f}$	3.817	3.77		
	(d) N10H-C9H <sub>3</sub>	1.8, 2.6	3.825	2.913		
	(s) $C7H-C11H$	0.1	4.657	2.236		
	(s) <b>C7H</b> -C14H, C18H	0.6	5.836	3.511		

**Table 4.** Correlation between Nuclear Overhauser Enhancements and relevant internuclear distances  $(r^{-6})$ in u and l forms of  $1^a$ 

<sup>a</sup>Irradiated signal is in bold print with indicated multiplicity.

<sup>b</sup>Second value corresponds to reverse irradiation.

<sup>c</sup>Distance to equivalent group of protons was calculated as a mean value of distances between all pairs of protons.

 $^{d}$  R denotes linear regression analysis coefficient for n points.

<sup>e</sup>Not included in correlation due to internal relaxation inside the methyl group.

<sup>f</sup> NOE on C7H proton was not included in a correlation due to contribution of other than intramolecular relaxation mechanism.

Finally one has to note the fact that dissolving the studied  $\beta$ -sulfinylenamine in aprotic solvents leads within few hours to establishment of the equilibrium between enamine and imine tautomers; the concentration of the latter reaches 25%. For a given diastereoisomer two isomeric imines are observed which correspond to geometrical isomers around C8=N10 bond (*E* and *Z* imines).

# Conclusion

The above discussion shows that  $\beta$ -sulfinylenamine studied exists as an enamine in the *E* configuration in the crystal, and as both a *Z* enamine and a mixture of *E* and *Z* imines in solution. The strain energy calculations indicate that *Z* isomer of the isolated molecule is favored by ca. 1.4 kcal/mol and 1.7 kcal/mol than corresponding *E* form of *u* and *l* diastereomers, respectively. These calculations also indicate that *Z* isomer of *u* diastereoisomer contains an intramolecular hydrogen bond which is shorter than the intermolecular hydrogen bond of the *E* form found in crystal. The interpretation of a full set of homonuclear NOE data available from the experiment for both diastereoisomers also point to the *Z* form in the solution, in particular, the linear correlation between interproton distances and relevant NOE values in  ${}^{1}\text{H}-{}^{1}\text{H}$  double resonance experiment is found for the Z - l isomer. Finally, the observed  ${}^{1}\text{H}$  NMR chemical shift of the *t*-butyl group in both diastereomers *u* and *l* are consistent with the spatial environment in both forms of the *Z* isomer.

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Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 60697 (16 pages).