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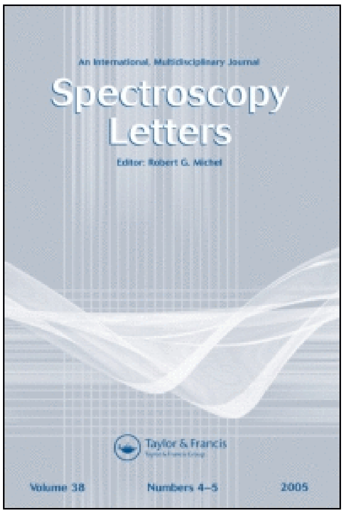

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Molecular Structure of Heterocycles: NMR Spectroscopy, Semiempirical MO Calculations and X-Ray Diffraction of 3,3a,4,5,6,7-Hexahydro-3-trichloromethyl[2,1]benzoisoxazole

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Molecular Structure of Heterocycles: NMR Spectroscopy, Semiempirical MO Calculations and X-Ray Diffraction of 3,3a,4,5,6,7-Hexahydro-3-trichloromethyl[2,1]benzoisoxazole

key words: [2,1]benzoisoxazoles, NMR, Crystal and molecular structure, MO calculations, AM1

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ABSTRACT

^{1}H and ^{13}C NMR data, AM1 calculations and X-ray diffraction in 3,3a,4,5,6,7-hexahydro-3-trichloromethyl[2,1]benzo isoxazole (**1**), obtained from the cyclization of trichloroacetyl cyclohexanone with hydroxylamine, are reported. ^{1}H and ^{13}C NMR data shown that only one pair of the diastereoisomers was

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obtained and the AM1 calculations indicated that **1a** (3*S*3a*S*/3*R*3a*R*) is 2.63 kcal.mol^{-1} more stable than **1b** (3*S*3a*R*/3*R*3a*S*). The X-Ray diffraction data confirmed that only the structure **1a** was obtained.

Crystals of 1 ($C_8H_{10}Cl_3NO_2$, M_r = 258.52) were obtained from acetone/n-hexane solution. The compound crystallizes in the monoclinic space group $P2_1/c$ with the cell dimensions a = 10.153(2), b = 8.271(2) and c = 14.225(3) Å, β = 103.8(3)°, V = 1160.0(4) Å^3, Z = 4, $D_{calcd.}$ = 1.480 Mg/m^3, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, = 0.764 mm^{-1}, $F(000)$ = 528, T = 293(2) K, R = 7.31 % and R_W = 17.91 % for an F^2 refinement on unique data with 2082 reflections and 1994 independent (R_{int} = 6.70%) were collected.

INTRODUCTION

As a part of our research program we have reported in a previous work that β-alkoxyvinyltrihalomethyl ketones react with hydroxylamine to give regiospecifically 5-halomethyl-4,5-dihydroisoxazoles[1-5]. On the other hand, when the 4,5-dihydroisoxazole ring bears an alkyl-substituent in the 4-position a ring with two chiral centers is formed. This fact suggests the presence of two pairs of diastereoisomers 3*S*4*S*/3*R*4*R* and 3*S*4*R*/3*R*4*S* as the reaction product.

The aim of this work is to study the molecular structure of a 4-alkyl substituted 4,5-dihydroisoxazole ring using ^1H and ^{13}C NMR spectroscopy, semiempirical MO calculations and X-ray diffraction tools. For this purpose we used the 3,3a,4,5,6,7-hexahydro-3-trichloromethyl-3-hydroxy-[2,*1*]-benzoisoxazole 1 as the substrate (**Scheme 1**). Experimental data of the molecular geometry of this compound in the gaseous, liquid, or solid phases are not available.

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RESULTS AND DISCUSSION

Synthesis

The synthesis of 3,3a,4,5,6,7-hexahydro-3-trichloromethyl-3-hydroxy-[*2,1*]-benzoisoxazole (**1**) from the cyclization of 2-trichloroacetylcyclohexanone with hydroxylamine hydrochloride was developed in our laboratory (**Scheme 1**)[3].

NMR Spectroscopy

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Although from the synthetic procedure was expected to obtain two pairs of the diastereoisomers for compound **1** [**1a** (3*S*3a*S*/3*R*3a*R*) and **1b** (3*S*3a*R*/3*R*3a*S*)], the ^1H and ^{13}C NMR spectra exhibited only a doublet of doublets for H3a (J^3\{H3a-H4*a*\} = 10.90 Hz and J^3\{H3a-H4*b*\} = 6.40 Hz) and just one line for each of these carbons on the proton noise decoupled spectrum ($^{13}C\{^1H\}$), Table 1. To obtain some additional information about the structure of compound **1**, theoretical Karplus curve[6] (Eq. 1) was used to calculate the coupling constants, J^3\{H3a-H4*a*\} and J^3\{H3a-H4*b*\}, of **1a** and **1b**.

$$J^3\{\text{H3a-H4}\} = 4.22 - 0.5 \cos \phi + 4.5 \cos 2\phi \qquad (1)$$

In the Eq. 1, ϕ is the dihedral angle (in degrees), H3a-H4*a* or H3a-H4*b*, obtained by AM1 calculations. Table 1 shows the calculated J^3\{H3a-H4*a*\} and J^3\{H3a-H4*b*\} coupling constants (Eq. 1) and the dihedral angles for **1a** and **1b**.

Considering that the original Karplus curve[6] (Eq. 1) has accounted that experimental values are generally 2-4 Hz higher than those obtained by theoretical calculations, we believe that the calculated J^3\{H3a-H4*a*\} and J^3\{H3a-H4*b*\} is in a good agreement with those observed experimentally (Table 1). However, these

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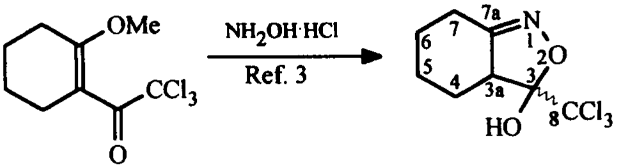

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Scheme 1

Table 1

Selected ^1H and ^{13}C NMR data[a] of compound 1.

^1H NMR δ	J^3 {H3a-H4} Hz exp.	calcd.[b] 1a	calcd.[b] 1b	Dihedral angle[c] (degrees) 1a	Dihedral angle[c] (degrees) 1b	^{13}C NMR δ C3	C3a	C7a	C8
	10.9	8.92	8.98	169.64	170.71 *ax.*				
3.41	6.4	2.84	2.89	51.88	51.55 *eq.*	109.5	52.1	160.9	102.9

[a] The NMR-spectra were recorded on a Bruker AC 80 (^1H at 80 MHz and ^{13}C at 20MHz) in chloroform-d_1/TMS.

[b] Calculated from Equation 1.

[c] Obtained from AM1 calculations (sec experimental). *ax.* = axial, *eq.* = equatorial.

results are not sufficient to assign which are the two pairs of the diastereoisomers (**1a** or **1b**) of compound **1**. Thus, the results obtained from the NMR spectroscopy suggest only one pair of diastereoisomers was obtained: **1a** (3*S*3a*S*/3*R*3a*R*) or **1b** (3*S*3a*R*/3*R*3a*S*).

Semiempirical MO Calculations and X-Ray Diffraction data

The bond lengths, bond angles and dihedral angles for compound **1** obtained from the AM1 calculations[7] and X-ray diffraction (in monocrystal, see experimental) are presented in Tables 2, 3, 4.

The AM1 calculations[7] performed showed that **1a** is 2,63 kcal.mol^{-1} more stable than **1b**. Although the influence of intermolecular interactions, which appear in a certain extent in the X-ray data, but not in the AM1 calculations, was observed that for most of the geometrical parameters the AM1 calculations done on **1a** gave very close values to those determined in crystal.

The simple linear regressions between experimental bond lengths, bond angles and dihedral angles (X-ray data) and those calculated (AM1 data) for **1a** and **1b** were made. The results show that both experimental and calculated bond lengths, bond angles present similar correlation coefficients for **1a** and **1b** [bond lengths (**1a**) r = 0.855, (**1b**) r = 846; bond angles (**1a**) r = 0.929, (**1b**) r = 0.923]. However, the dihedral angle correlation shows that only calculated data for **1a** exhibit an excellent correlation coefficient [dihedral angles (**1a**) r = 0.998, (**1b**) r = 0.772].

On the other hand, when some bond angles are compared (Table 3) is possible to observe an excellent agreement between the X-ray and AM1 calculation data of structure **1a** but not for **1b**. For example, while the bond angle of the atoms C3a-C3-C8 for **1a** obtained by AM1 calculations is 114.79° and determined by X-ray is 114.2°, the same bond angle for **1b** is 120.72°. Furthermore, the bond angle of the atoms C3a-C3-OH for **1a** obtained by AM1 calculations is 111.01° and determined by X-ray is 111.2°, the same bond angle for **1b** is 106.90°. Table 4 shows similar agreement when some dihedral angles determined by X-Ray diffraction with those calculated by AM1 for **1a** and **1b** were compared. The most illustrative data shown in Table 4 are the dihedral angles of the atoms C8-C3-C3a-C4 and HO-C3-C3a-C4 that have the X-ray data (-112.8° and 12.6°) similar to those obtained from AM1 calculations (-118.05° and 11.86°) for **1a** (3*S*3a*S*/3*R*3a*R*).

A perspective view of the molecular structure of **1a** and **1b** with optimized geometry by AM1 calculations is shown in Figure 1.

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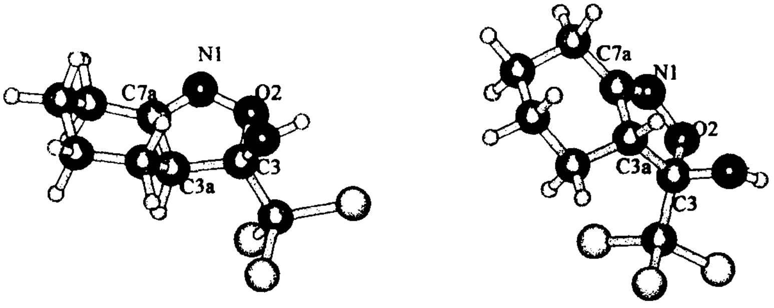

1a **1b**

Figure 1. Perspective view of the molecular structure of 3,3a,4,5,6,7-Hexahydro-3-trichloromethyl[2,1]benzoisoxazole (1). The optimized geometries were obtained by AM1 calculations .

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The isoxasole ring can be considered as essentially planar because the sum of the angles within the ring is 538.6(4)° and the root means square atomic displacements from the mean plane are 0.050 Å. This value is in good agreement with 539.8° obtained by AM1 calculations. The planarity of the isoxasole ring is attributed to the C-N double bond (1.277(7) Å). This conclusion agrees with the AM1 calculations that demonstrate a considerable deviation of the planarity of the isoxasole ring when a single bond order is attributed to the C-N bond. In this case, the geometry optimized molecule of *cis*-benzoisoxazolidine derivative showed the sum of the angles within the ring of 532.76°. Furthermore, when a simulation is carried out considering a double bound order for the C-N bond and excluding the cyclohexane ring of the molecule, the AM1 calculations furnish the sum of angles within the remaining five-membered ring is 539.9°. These observations reinforce the

Table 2

Selected bond lengths calculated by AM1 and determined by X-Ray diffraction for compound **1** (with e.s.d.'s in parenthesis).

Atoms	Bond Length (Å) Calcd. AM1 **1a**[a] (3*S*3a*S*/3*R*3a*R*)	Bond Length (Å) X-Ray[b]	Bond Length (Å) Calcd. AM1 **1b**[a] (3*S*3a*R*/3*R*3a*S*)
N1-O2	1.3198	1.431 (6)	1.3178
O2-C3	1.4785	1.436 (6)	1.4803
C3-C3a	1.5561	1.508 (6)	1.5619
C3a-C7a	1.5302	1.480 (8)	1.5299
C7a-N1	1.3165	1.277 (7)	1.3166
C3-C8	1.5493	1.549 (7)	1.5491
C3-OH	1.3931	1.384 (6)	1.3983
C3a-C4	1.5126	1.537 (7)	1.5091
C4-C5	1.5177	1.524 (8)	1.5194
C5-C6	1.5160	1.494 (10)	1.5151
C6-C7	1.5210	1.524 (10)	1.5195
C7-C7a	1.4822	1.477 (9)	1.4826

[a] **1a**, E= -2274.30 kcal.mol^{-1}; **1b**, E= -2271.67 kcal.mol^{-1}.
[b] See Experimental.

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conclusion that the planarity of the isoxasole ring can be attributed essentially to the C-N double bond.

The final position parameters for non-hydrogen atoms and the corresponding selected bond lengths and angles of **1** are given in Tables 5, 6, 2, and 3, respectively. An ORTEP[12] drawing of the structure of **1** is shown in Figure 2. The lists of the observed and calculated structure factors, anisotropic thermal parameters and hydrogen atom coordinates are available from the authors upon request.

The regiochemistry of the reaction can be explained from the intermediate **2** obtained in the cyclization process . This intermediate is 11.86 kcal.mol^{-1} less stable than **1a**, and can produce **1a** or **1b** by a tautomeric equilibrium (**Scheme 2**).

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Table 3

Selected bond angles calculated by AM1 and determined by X-Ray diffraction for compound **1** (with e.s.d.'s in parenthesis).

Atoms	Bond Angle (degrees) Calcd. AM1 **1a** (3*S*3a*S*/3*R*3a*R*)	Bond Angle (degrees) X-Ray[a]	Bond Angle (degrees) Calcd. AM1 **1b** (3*S*3a*R*/3*R*3a*S*)
N1-O2-C3	111.91	108.3 (4)	112.17
O2-C3-C3a	104.12	106.0 (4)	103.88
C3-C3a-C7a	99.71	101.0 (4)	99.73
C3a-C7a-N1	112.55	114.6 (5)	112.64
C7a-N1-O2	111.48	108.7 (5)	111.51
O2-C3-C8	109.18	105.3 (4)	108.09
C8-C3-OH	113.17	110.1 (5)	112.41
C3a-C3-C8	114.79	114.2 (4)	120.72
C3a-C3-OH	111.01	111.2 (4)	106.90
C3-C3a-C4	115.92	118.2 (5)	120.76
C3a-C4-C5	109.71	110.0 (5)	109.56
C4-C5-C6	112.18	111.9 (5)	112.00
C5-C6-C7	112.48	112.2 (6)	112.21
C6-C7-C7a	109.54	110.3 (6)	110.03
C7-C7a-N1	129.32	124.3 (6)	128.71

[a] See Experimental.

The theoretical and experimental data of the product obtained show that the tautomeric equilibrium yields only the structure **1a** (3*S*3a*S*/3*R*3a*R*), that has the most stable configuration (**1a** is 2.63 kcal.mol^{-1} more stable than **1b**). The configuration **1a** has the less strained condensed ring system, where the bulky CCl$_3$ group is *cis* to H3a and OH group is *cis* to the C-C bond of cyclohexane ring.

CONCLUSIONS

^{1}H and ^{13}C NMR spectroscopy method showed a poor contribution on the molecular geometry study of 3,3a,4,5,6,7-hexahydro-3-trichloromethyl-3-hydroxy-

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Table 4

Selected dihedral angles calculated by AM1 and determined by X-Ray diffraction for compound 1 (with e.s.d.'s in parenthesis).

Atoms	Dihedral Angle (Degrees) Calcd. AM1 **1a** (3*S*3a*S*/3*R*3a*R*)	Dihedral Angle (Degrees) X-Ray[a]	Dihedral Angle (Degrees) Calcd. AM1 **1b** (3*S*3a*R*/3*R*3a*S*)
N1-O2-C3-C3a	-4.88	-11.9 (5)	-2.71
O2-C3-C3a-C7a	4.36	10.6 (5)	2.76
C3-C3a-C7a-N1	-3.02	-6.2 (6)	-2.32
C3a-C7a-N1-O2	0.16	-1.0 (6)	0.79
C7a-N1-O2-C3	3.12	8.3 (5)	1.30
C8-C3-C3a-C4	-118.05	-112.8 (6)	3.27
OH-C3-C3a-C4	11.86	12.6 (7)	-126.82
C3-C3a-C4-C5	-164.90	-164.6 (5)	-167.49
C3a-C4-C5-C6	58.17	58.1 (7)	58.94
C4-C5-C6-C7	-57.37	-58.6 (8)	-58.59
C5-C6-C7-C7a	49.96	48.2 (9)	49.49
C6-C7-C7a-C3a	-48.40	-43.5 (8)	-45.76
C7-C7a-C3a-C4	50.96	44.6 (7)	47.97
C6-C7-C7a-N1	127.29	133.2 (7)	132.76

[a] See Experimental.

[2,*1*]-benzoisoxazole (**1**). The molecular geometry of the compound **1** was accurately determined by AM1 theoretical method. The differences found between X-ray and AM1 data are within the range of the standard deviations of the AM1 method and the influence of intermolecular interactions that appear in the crystal structure. Finally, from the X-ray diffraction were possible to conclude that the synthetic procedure used[3] yield only the pair of the diastereoisomers **1a** (3*S*3a*S*/3*R*3a*R*) of compound **1**.

Table 5

Crystal data and structure refinement for **1**, with e.s.d.'s in parenthesis.

Empirical formula	$C_8H_{10}Cl_3NO_2$
Formula weight	258.52
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å)	$a =$ 10.153(2) $b =$ 8.271(2) $c =$ 14.225(3) $\beta =$ 103.81(3)
Volume (Å^3), Z	1160.0(4), 4
Density (calculated) (Mg/m^3)	1.480
Absorption coefficient (mm^{-1})	0.764
F(000)	528
Crystal size (mm) / Colour	0.66 x 0.26 x 0.07 /colourless
Theta range for data collection (°)	3.17 to 24.95
Limiting indices	$-11 \leq h \leq 12$, $0 \leq k \leq 9$, $-16 \leq l \leq 0$
Reflections collected	2082
Independent reflections	1994 [R(int) = 0.0670]
Reflections observed	1168
Criterion for observation	[I>2sigma(I)]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1584 / 0 / 128
Goodness-of-fit on F^2	1.074
Final R indices [I>2sigma(I)]	$R_1 = 0.0731$, $wR_2 = 0.1791$
Maximal (Δ/σ)	0.000
Extinction coefficient	0.010(5)
Largest diff. peak and hole (e.Å^{-3})	0.519 and -0.680

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Table 6

Atomic coordinates ($\bullet 10^4$) and equivalent isotropic displacement parameters ($Å^2 \bullet 10^3$) for **1**, with e.s.d.'s in parenthesis.

Atom	x	y	z	U(eq)[a]
Cl(1)	4088(2)	141(2)	8794(1)	62(1)
Cl(2)	4012(2)	2476(2)	7285(2)	68(1)
Cl(3)	2327(2)	2892(3)	8633(2)	79(1)
O(2)	1175(4)	-351(5)	7871(3)	41(1)
O	1008(4)	1551(5)	6663(3)	45(1)
N(1)	998(5)	-1993(6)	7549(4)	44(1)
C(3)	1886(5)	499(7)	7263(4)	33(1)
C(3a)	2403(5)	-778(7)	6685(3)	32(1)
C(7a)	1676(6)	-2223(7)	6911(4)	39(1)
C(4)	2161(6)	-541(8)	5585(4)	49(2)
C(8)	3016(6)	1459(8)	7966(4)	45(2)
C(5)	2398(7)	-2126(9)	5105(5)	59(2)
C(7)	1701(8)	-3761(9)	6388(6)	65(2)
C(6)	1499(8)	-3445(10)	5307(5)	72(2)

[a]U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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EXPERIMENTAL

Compound

3,3a,4,5,6,7-Hexahydro-3-trichloromethyl-3-hydroxy-[*2,1*]-benzoisoxazole (**1**) was synthesized by the cyclization of 2-trichloroacetylcyclohexanone with hydroxylamine hydrochloride as reported in Reference 3.

NMR Spectroscopy

^1H and ^{13}C NMR spectra were recorded on a BRUKER AC-80 spectrometer (^1H at 80 MHz and ^{13}C at 20 MHz) in chloroform-d_1/TMS.

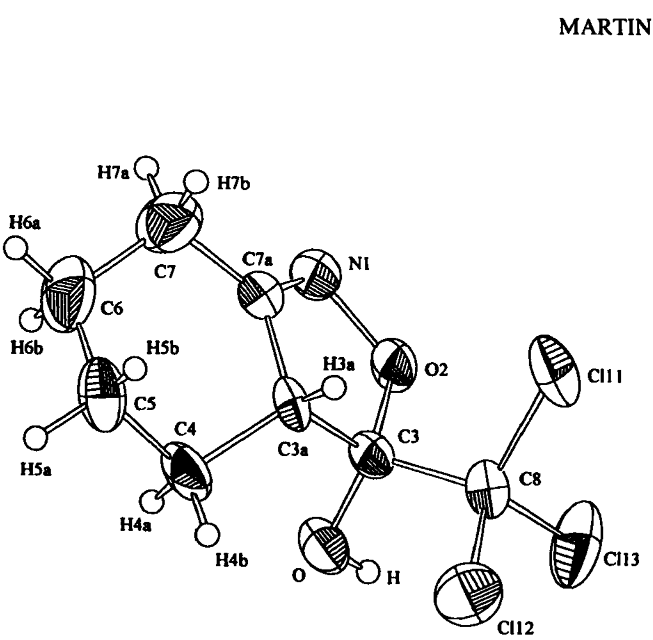
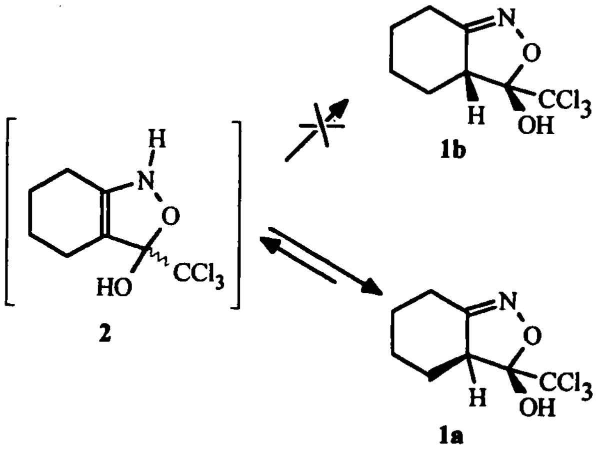


Figure 2. ORTEP[12] plot with atom-labeling scheme of the structure of **1**, displacement ellipsoids at the 50% level.



Scheme 2

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AM1 Calculations

The calculations were carried out by the Austin Model 1 (AM1) semiempirical method[7], implemented in the HyperChem 4.5 package (1995)[8]. Geometries were completely optimized without fixing any parameter, thus bringing all geometric variables to their equilibrium values. The energy minimization protocol employs the Polak-Ribiere algorithm, a conjugated gradient method[8]. Convergence to a local minimum is achieved when the energy gradient is $\leq$ 0.01 kcal.mol^{-1}. The calculations were performed on a PC Pentium-166MHz Megatropic computer equipped with an ink jet Epson Stylus Color II (720 dpi) printer.

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X-Ray diffraction

Table 5 summarizes the crystal data and structure refinement parameters for 1. Diffractometric intensity data were collected on an automatic four circle diffractometer (Enraf-Nonius CAD4)[9] using graphite-monochromated Mo$_{K\alpha}$ radiation and ϖ-2θ scans with a scan speed of 45 sec./reflection. At every 60 min. the orientation of the crystal was controlled by three standard reflections and no appreciable intensity loss was observed during the data collection. The structure were solved using the direct methods employing SHELXS-86 program[10] and all non-hydrogen atoms were located by subsequent Fourier difference synthesis. For structure refinement the SHELXL-93 program[11] was employed and the full-matrix least-squares method minimized on $\Sigma w(F_o^2 - F_c^2)^2$ where w is a weighting scheme detailed below. All non-hydrogen atoms were refined using anisotropic thermal parameters. The positions of the hydrogen atoms were calculated based on the geometry of the molecule and the thermal displacement parameters were refined isotropically on a groupwise basis. For the final refinement of the structure an isotropic extinction correction was included. Scattering factors for all atoms were as in the SHELXL-93 program[11].

A transparent colourless crystal of **1** with approximate dimensions 0.66 x 0.26 x 0.07 mm was used for intensity data collection at 293(2) K. The unit cell dimensions and the orientation matrix for the data collection resulted from a least square fit of 23 reflections in the range 17.66° 21.78°. The automatic intensity search and indexing method indicated a monoclinic cell symmetry. A total of 2082 reflections were collected involving one quarter of the Ewald sphere with the limiting indices $-11 \leq h \leq 12$, $0 \leq k \leq 9$, $-16 \leq l \leq 0$ and the theta range of 3.17 to 24.95. Based on the observed reflections conditions, E statistics and a successful structure solution, the space group was chosen to be $P2_1/c$. Lorentz and polarization correction was made on the intensity data and the observed intensity decay was less than 1.3%. After merging of the equivalent reflections ($R_{int.}$ = 6.70%), 1994 reflections were unique. Due to the observed low linear absorption coefficient (0.764 mm^{-1}), no absorption correction was made. The final refinement including 128 parameters gave R = 7.31% and R_w = 17.91% with the weighting scheme, $w = 1/[s^2(F_o^2) + (0.1398P)^2 + 0.00P]$ where $P = (F_o^2 + 2F_c^2)/3$ with a maximal shift/e.s.d. = 0.000.

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REFERENCES

1. M.A.P. Martins, A. Colla, G. Clar, P. Fischer, S. Krimmer, *Synthesis* **1991**, 6, 483-486.
2. M.A.P. Martins, A.N. Zoch, H.G. Bonacorso, N. Zanatta, G. Clar, *J. Heterocyclic Chem.* **1995**, 32, 739-741.
3. M.A.P. Martins, Alex F.C. Flores, Rogério Freitag, Nilo Zanatta, *J. Heterocyclic Chem.* **1995**, 32, 731-733.
4. M.A.P. Martins, G.M. Siqueira, G.P. Bastos, H.G. Bonacorso, N. Zanatta, *J.Heterocyclic Chem.* **1996**, 33, *in press.*
5. M.A.P. Martins, Alex F.C. Flores, Rogério A. Freitag, Nilo Zanatta, *J. Heterocyclic Chem.* **1996**, 33, *in press.*
6. M. Karplus, *J.Am.Chem.Soc.* **1963**, 85, 2870.
7. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, *J. Am. Chem. Soc.* **1990**, 107, 3902.
   J.J.P. Stewart, in *Reviews of Computational Chemistry*, K. Lipkovitz, D.B. Boyd (Eds.), VCM Publishers, New York, 1990.
8. Hypercube, Inc., HyperChem 4.5 package, Waterloo, Ontario, Canada, 1995.
   HyperChem Manual, *Computational Chemistry*, Waterloo, Ontario, Canada, 1994.
9. *CAD4, Automatic Four Circle Diffractometer ENRAF-NONIUS*, Delft, Holland.
10. G.M.Sheldrick, *SHELXS-86, Program for Crystal Structure Solution*, University of Göttingen, Germany (1986).
11. G.M.Sheldrick, *SHELXL-93, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1993).
12. C.K. Johnson, *ORTEP, A Thermal-Ellipsoid Plot Program.* Tennessee: Oak Ridge National Laboratory, 1965.

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