

## X-Ray Crystal Structure and AM1 Optimized Structure for 4-Methylamino-3-diphenylacetyl-3-penten-2-one

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4-Metilamino-3-difenilacetil-3-penten-2-ona cristaliza na configuração *E* com uma estrutura cristalina que consiste de ligações hidrogênio entre pares de moléculas feitas por uma operação de inversão de simetria. As ligações hidrogênio são intra e intermoleculares envolvendo O(2)--HN e O(2)---HN'. Enquanto os cálculos dos orbitais moleculares são consistentes com ligações hidrogênio intramoleculares na configuração *E*, que é a mais estável, o mesmo não ocorre para a forma *Z*. Neste caso, fatores estéricos parecem ser importantes.

4-Methylamino-3-diphenylacetyl-3-penten-2-one crystallizes in the *E* configuration with a crystal structure that consists of hydrogen bonded pairs of molecules made by an inversion symmetry operation. The hydrogen bonds are intra- and intermolecular, involving O(2)--HN and O(2)---HN'. While molecular orbital calculations are consistent with intramolecular hydrogen bonding in the more stable *E* configuration, the same is not true for the *Z* form. In this case steric factors seem to be important.

**Keywords:** *X-ray crystal structure, AM1 calculations,  $\alpha$ -ketoenaminone*

### Introduction

Although there are a considerable number of studies involving the chemistry of simple enaminones, the same is not true for  $\alpha$ -acyl enaminones. In the few cases reported, the two carbonyl functions are of different types and with known differences in reactivity<sup>1</sup>. Recently we showed that diphenylketene reacts with primary and secondary enaminones to form  $\alpha$ -diphenylacetyl enaminones as the principal products<sup>2</sup>. Since then, other  $\alpha$ -ketoenaminones have been obtained<sup>3</sup>. Our continuing interest in the structure-reactivity relationships of enaminones<sup>2,4</sup> has led us to examine the chemistry of 4-amino-3-penten-2-ones with acetyl derivatives in the 3-position. As part of this study, it has become necessary to determine the structures of these compounds in greater detail than was obtained by spectroscopic data.

In the present article we report the X-ray crystal structure of 4-methylamino-3-diphenylacetyl-3-penten-2-one (**1**) together with molecular orbital (MO) calculations for

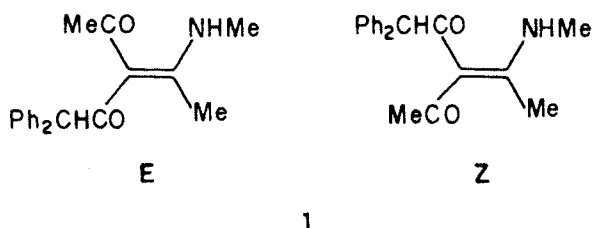
comparison. Although the N-H chemical shift of **1** shows that it is intramolecularly hydrogen bonded, it is not possible to determine which carbonyl is involved and thus *cis* with respect to nitrogen<sup>1</sup>. Another aspect of the structure which we consider important to its reactivity involves the conformation of the second carbonyl with respect to the conjugated enaminone system.

### Experimental Details

#### *X-ray crystal structure analysis*

The compound was prepared according to the literature procedure<sup>2</sup> and was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to give needles, m.p. 120-120 °C.

The cell dimensions and the intensity data were obtained using a crystal with dimensions 0.75x0.20x0.15 mm, CAD-4 automated diffractometer, MoK $\alpha$  radiation,  $\omega$ -2 $\theta$  scan mode (2 $\theta$  up to 24.98; -17  $\leq$  h  $\leq$  17, 0  $\leq$  k  $\leq$  7, 0  $\leq$  l  $\leq$  22), variable scan rate. A total of 2,880 independent reflections were collected, 827 with  $|F_0| \geq 3\sigma(|F_d|)$  were



considered observed and used for the structure determination. The intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods and defined by a least-squares method using the SHELX-76 programs. The hydrogen atoms were included in the final refinement model at their calculated position (C–H 1.08 Å) with an overall isotropic parameter of  $U = 0.06 \text{ \AA}^2$ . The final full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms converged to  $R = 0.0625$  and  $R_w = 0.0674$ , and the residual densities in the final difference Fourier synthesis was  $0.19 \text{ e \AA}^{-3}$ . The minimized function was  $\sum w (|F_o| - |F_c|)^2$ , and  $w = [\sigma^2(F_o) + 0.01137 F_o^2]^{-1}$ .

#### Crystal data

The following crystal data were obtained for  $C_{20}H_{21}NO_2$ :  $M = 307.4$ , monoclinic,  $P2_1/c$ ,  $a = 14.645(3)$ ,  $b = 6.065(4)$ ,  $c = 19.141(5) \text{ \AA}$ ,  $\beta = 92.19(2)^\circ$ ,  $V = 1698(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $F(000) = 656.00$ ,  $\mu = 0.43 \text{ cm}^{-1}$ ,  $D_C = 1.202 \text{ g cm}^{-3}$ . The final position parameters for the non-hydrogen atoms are listed in Table 1. The bond distances, bond angles and torsional angles are reported in Table 2, Table 3 and Table 4 respectively. Other geometrical data are shown in Table 5. Anisotropic thermal parameters for the non-hydrogen atoms, positional parameters for the hydrogen atoms, and a table of structure factors are available from the authors upon request.

#### Theoretical calculations

Quantum chemical calculations using the AM1 (Austin Model 1)<sup>5</sup> semi-empirical method were carried out using the AMPAC package<sup>6</sup> which was modified locally to handle a larger number of atoms. Geometries were fully optimized without imposing any symmetry constraints. Standard bond angles and bond lengths<sup>7</sup> were used as input and intramolecular hydrogen bonding was assumed in both geometric forms [Input S]. X-ray data was also used as input for the configuration which corresponds to the solid state structure of 1. Optimized bond lengths, bond angles and torsional angles are shown in Table 2, Table 3 and Table 4, respectively.

**Table 1.** Fractional atomic coordinates and isotropic equivalent temperature factors ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses.

Atom	X/A	Y/B	Z/C	Beq ( $\text{\AA}^2$ )
O(1)	0.1905(4)	0.1829(7)	0.2436(3)	4.8(2)
O(2)	0.0815(3)	0.0935(8)	0.0408(3)	5.1(2)
N	0.0099(3)	-0.2532(9)	0.0977(3)	3.8(2)
C(1)	0.2683(4)	-0.200(1)	0.3174(4)	3.0(2)
C(2)	0.2375(5)	-0.389(1)	0.3489(4)	4.5(3)
C(3)	0.2413(6)	-0.414(1)	0.4204(5)	5.1(4)
C(4)	0.2808(6)	-0.251(2)	0.4638(5)	5.5(4)
C(5)	0.3146(5)	-0.063(1)	0.4323(4)	4.8(3)
C(6)	0.3067(5)	-0.033(1)	0.3616(4)	3.9(3)
C(7)	0.3465(4)	-0.127(1)	0.2013(3)	2.8(2)
C(8)	0.3818(5)	-0.288(1)	0.1590(4)	4.2(3)
C(9)	0.4600(6)	-0.249(2)	0.1248(5)	6.0(4)
C(10)	0.5061(6)	-0.054(2)	0.1297(5)	6.2(4)
C(11)	0.4712(5)	0.109(2)	0.1726(5)	5.6(3)
C(12)	0.3928(5)	0.075(1)	0.2073(4)	4.5(3)
C(13)	0.2587(4)	-0.173(1)	0.2387(3)	2.7(2)
C(14)	0.1893(4)	0.002(1)	0.2134(4)	3.5(3)
C(15)	0.1292(4)	-0.038(1)	0.1527(3)	2.9(2)
C(16)	0.0638(4)	-0.215(1)	0.1516(4)	3.0(2)
C(17)	0.0525(5)	-0.350(1)	0.2170(4)	3.8(3)
C(18)	-0.0588(5)	-0.427(1)	0.0939(5)	5.0(3)
C(19)	0.1321(4)	0.109(1)	0.0940(4)	3.5(3)
C(20)	0.2039(5)	0.291(1)	0.0932(5)	4.7(3)

## Results and Discussion

A three dimensional view of the molecule in the solid state is given in Fig. 1. It crystallizes in the *E* configuration, and the crystal structure consists of hydrogen bonded pairs of molecules made by an inversion symmetry operation, as shown in Fig. 2. The hydrogen bonds are intra- and intermolecular, involving O(2)---HN [1.771(7) Å] and O(2)---HN' [2.273(8) Å] respectively. The dihedral angle between the O(1)C(14) carbonyl and C(15)C(16) is approximately  $123^\circ$ . The data in Table 2 show that the C(15) - C(16) and the C(15)-C(19) bond lengths (1.438(9) Å and 1.436(9) Å respectively) are the same, i.e. in between standard single and double  $C(sp^2) - C(sp^2)$  bond lengths. Another deviation involves the C(16)-N bond length of 1.296(9) Å which is considerably shorter than the standard single C(16)-N value of 1.40 Å. Distortions of these bonds from standard values have been observed in simple enaminones<sup>8</sup> and in other  $\alpha$ -ketoenaminones<sup>9-12</sup>. Together with the planarity of the enaminone system, as observed in this compound for

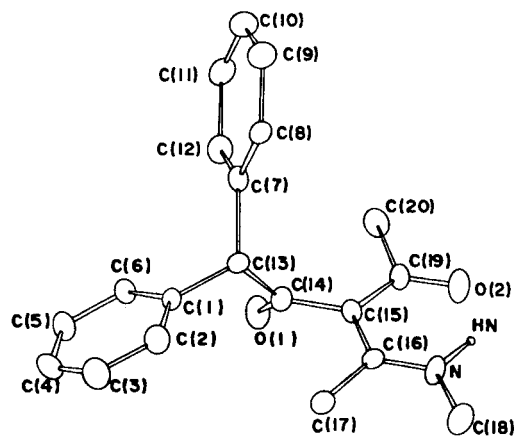


Figure 1. Three dimensional view as obtained from X-ray analysis.

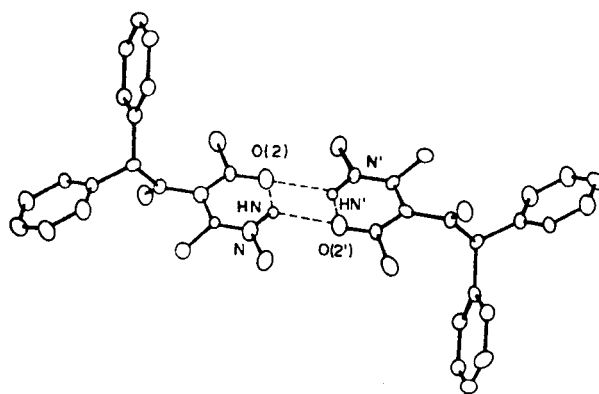


Figure 2. Three dimensional view showing crystal structure which consists of hydrogen bonded pairs of molecules made by an inversion symmetry operation.

Table 2. Bond lengths.

Bond	Length (Å)				
	X-Ray	Input S	Config. E Optim S	Optim X	Config. Z
O(2)-C(19)	1.240(8)	1.22	1.245	1.246	1.241
C(15)-C(19)	1.436(9)	1.46	1.462	1.461	1.464
C(15)-C(16)	1.438(9)	1.34	1.384	1.386	1.381
C(16)-C(17)	1.52(2)	1.52	1.502	1.503	1.499
C(14)-C(15)	1.451(9)	1.46	1.479	1.481	1.481
C(19)-C(20)	1.52(1)	1.52	1.498	1.497	1.499
N-C(16)	1.296(9)	1.40	1.370	1.367	1.375
N-C(18)	1.46(1)	1.47	1.429	1.427	1.426
O(1)-C(14)	1.240(8)	1.22	1.237	1.235	1.238
C(14)-C(13)	1.536(9)	1.52	1.532	1.527	1.531
C(1)-C(13)	1.52(1)	1.52	1.499	1.500	1.501
C(1)-C(2)	1.38(2)	1.34	1.405	1.402	1.404
C(2)-C(3)	1.38(1)	1.34	1.391	1.393	1.392
C(3)-C(4)	1.40(1)	1.34	1.395	1.395	1.396
C(4)-C(5)	1.39(1)	1.34	1.392	1.394	1.393
C(5)-C(6)	1.37(1)	1.34	1.396	1.394	1.396
C(6)-C(1)	1.42(2)		1.398		1.397
C(7)-C(8)	1.38(1)		1.398	1.400	1.399
C(7)-C(12)	1.403(9)		1.402		1.402
C(7)-C(13)	1.52(9)	1.52	1.497	1.501	1.493
C(8)-C(9)	1.36(1)	1.34	1.395	1.393	1.395
C(9)-C(10)	1.36(1)	1.34	1.393	1.393	1.393
C(10)-C(11)	1.39(1)	1.34	1.394	1.395	1.394
C(11)-C(12)	1.36(1)	1.34	1.392	1.392	1.393
N-HN	1.08(1)		1.001	1.001	0.995

**Table 3.** Bond angles.

Angle	Value (Å)				
	Config. E			Config. Z	
	X-Ray	Input S	Optim S	Optim X	
O(2)-C(19)-C(15)	124.1(6)	120	123.7	123.5	124.2
C(16)-C(15)-C(19)	119.4(6)	120	123.6	124.3	124.6
C(15)-C(16)-C(17)	119.1(6)	120	120.0	119.7	122.4
C(14)-C(15)-C(16)	121.3(6)	120	120.5	119.9	119.9
C(15)-C(19)-C(20)	119.9(6)	120	116.1	116.7	114.8
N-C(16)-C(15)	122.0(6)	120	122.9	122.9	120.8
C(16)-N-C(18)	124.6(6)	120	122.2	123.0	123.0
O(1)-C(14)-C(15)	121.2(6)	120	121.2	122.1	121.1
O(1)-C(14)-C(13)	117.9(6)				
C(13)-C(14)-C(15)	120.7(6)	120	121.2	115.5	121.3
C(1)-C(13)-C(14)	115.0(5)	120	112.3	112.9	109.4
C(7)-C(13)-C(14)	106.6(5)	120	114.1	110.8	115.0
C(14)-C(15)-C(19)	119.2(6)				
N-C(16)-C(17)	118.8(6)				
O(2)-C(19)-C(20)	115.9(6)				
C(2)-C(1)-C(6)	117.4(7)		117.8	119.9	117.6
C(2)-C(1)-C(13)	120.4(6)				
C(6)-C(1)-C(13)	122.3(7)				
C(1)-C(2)-C(3)	121.7(7)	120	120.5	120.5	120.8
C(2)-C(3)-C(4)	120.8(8)	120	120.1	120.1	119.9
C(3)-C(4)-C(5)	117.9(8)	120	119.8	119.8	119.5
C(4)-C(5)-C(6)	121.5(8)	120	120.2	120.2	120.7
C(1)-C(6)-C(5)	120.7(7)				
C(8)-C(7)-C(12)	118.3(6)				
C(8)-C(7)-C(13)	119.2(6)	120	123.3	119.9	122.9
C(12)-C(7)-C(13)	122.4(6)				
C(7)-C(8)-C(9)	120.0(7)	120	120.5	120.0	120.5
C(8)-C(9)-C(10)	122.8(9)	120	120.3	121.1	120.2
C(9)-C(10)-C(11)	117.6(9)	120	119.7	118.8	119.7
C(10)-C(11)-C(12)	120.9(9)	120	120.0	120.7	120.1
C(7)-C(12)-C(11)	120.4(7)				
C(1)-C(13)-C(7)	116.1(6)				

atoms O(2)-C(19)-C(15)-C(16)-N-HN (Table 5, plane 3), these data show electron delocalization from nitrogen in this push-pull system.

The deviations from standard bond lengths obtained in a geometry optimization study of simple enamines using the AM1 semi-empirical molecular orbital method are much smaller than those obtained from X-ray data for this system. Thus, X-ray data (bond lengths, angles and torsional angles) were used as input (Input X) for geometry

optimization in the MO calculation to compare with the results obtained when standard values (Input S) are used. The results given in Tables 2 and 3 (Optim X and Optim S) show similar bond lengths and bond angles with the two different inputs. In both cases the C(15)-C(16) bond length is slightly longer than a double bond (1.34 Å) and the C(15)-C(19) is shorter than a single bond (1.54 Å). The C(16)-N bond length of 1.37 Å is a little longer than a double bond. Similar results were obtained with simple

Table 4. Torsional angles.

Angle	Value (Å)				Config. Z
	X-Ray	Input S	Config. E		
			Optim S	Optim X	
O(2)C(19)C(15)C(16)	-1(1)	0	-20.9	1.3	-29.8
C(19)C(15)C(16)C(17)	-172.0(6)	180	-169.0	-172.7	3.3
C(15)C(16)C(17)H(171)	14(1)	0	1.9	9.0	-5.1
C(15)C(16)C(17)H(172)	131.4(7)	120	121.8	128.9	115.1
C(15)C(16)C(17)H(173)	-111.1(8)	-120	-118.1	-111.1	-125.8
C(17)C(16)C(15)C(14)	4.9(9)	0	4.7	3.9	176.1
C(14)C(15)C(19)C(20)	6(1)	0	-16.3	4.1	-22.9
O(2)C(19)C(20)H(201)	2(1)	0	1.7	42.1	-173.7
O(2)C(19)C(20)H(202)	120.2(8)	120	122.3	163.4	-52.6
O(2)C(19)C(20)H(203)	-123.2(8)	-120	-118.5	-76.8	66.4
C(19)C(15)C(16)N	4(1)	0	12.0	8.0	
C(15)C(16)NH(N)	1.5(1)	0	-5.7	-6.5	-0.7
C(17)C(16)NC(18)	-3.5(1)	0	13.7	8.0	-2.0
C(16)NC(18)H(181)	-56(1)	-60	-56.9	-54.2	-65.9
C(16)NC(18)H(182)	64(1)	60	63.7	66.4	54.3
C(16)NC(18)H(183)	-173.2(7)	-180	-176.2	-173.7	174.3
C(16)C(15)C(14)O(1)	-122.8(7)	-90	-92.5	-112.0	-81.7
C(16)C(15)C(14)C(13)	62.0(9)	90	88.9	69.7	96.6
O(1)C(14)C(13)H(131)	157.0(7)	0	-0.3	168.2	-14.7
O(1)C(14)C(13)C(1)	45.2(8)	120	113.6	50.5	97.2
H(131)C(13)C(1)C(2)	-7.4(9)	30	30.0	14.9	46.0
C(13)C(1)C(2)H(21)	1(1)	30	4.5	0.8	2.6
C(13)C(1)C(2)C(3)	-176.9(7)	180	-174.9	-179.4	-176.8
H(21)C(2)C(3)H(31)	2(1)	0	0.2	0.7	2.6
C(1)C(2)C(3)C(4)	-3(1)	0	-1.2	0.5	-0.2
H(31)C(3)C(4)H(41)	-1(1)	0	-2.3	-1.4	1.2
H(31)C(3)C(4)C(5)	178.7(9)	180	179.0	178.5	-178.3
H(41)C(4)C(5)H(51)	-1(1)	0	1.7	0.2	0.4
H(41)C(4)C(5)C(6)	-178.0(9)	180	-177.4	-179.8	-179.3
H(51)C(5)C(6)H(61)	2(1)	0	0.2	-0.8	-0.6
O(1)C(14)C(13)C(7)	-85.0(7)	-120	-115.6	-74.9	-131.8
H(131)C(13)C(7)C(8)	-1.3	180	-167.8	-15.7	-173.7
C(13)C(7)C(8)H(81)	-1(1)	0	0.7	-0.3	1.7
C(13)C(7)C(8)C(9)	179.6(7)	180	-179.7	-179.9	-179.2
H(81)C(8)C(9)H(91)	0(2)	0	-0.1	0.3	-0.1
C(7)C(8)C(9)C(10)	-1(1)	0	0.2	0.3	-0.1
H(91)C(9)C(10)H(101)	0(2)	0	-0.2	0.2	-0.6
H(91)C(9)C(10)C(11)	-180(1)	180	179.8	-179.8	179.1
H(101)C(10)C(11)H(111)	1(1)	0	-0.1	-0.2	-0.1
C(9)C(10)C(11)C(12)	-1(1)	0	-0.1	0.0	0.0
H(111)C(11)C(12)H(121)	-1(1)	0	0.0	0.3	0.0
C(14)C(15)C(16)N	-179.8(6)				-3.0

**Table 5.** Least-squares planes through selected atoms and deviations of atoms from the planes.

## (a) Deviations (Å) from the planes

Plane 1	C(1)	-0.001(6)	C(2)	0.017(8)	C(3)	-0.014(8)
	C(4)	-0.004(9)	C(5)	0.20(8)	C(6)	-0.017(7)
Plane 2	C(7)	-0.001(6)	C(8)	0.001(7)	C(9)	-0.002(9)
	C(10)	0.004(9)	C(11)	-0.005(9)	C(12)	0.003(8)
Plane 3	O(2)	-0.037(5)	N	-0.019(5)	H(N)	0.049(5)
	C(15)	0.024(6)	C(16)	-0.025(6)	C(19)	0.008(5)
Plane 4	O(1)	0.088(5)	C(13)	0.001(6)	C(14)	0.001(7)
	C(15)	0.001(6)				

## (b) Equation of the planes

Plane	A	B	C	D
1	0.9014	-0.4270	-0.0725	3.4110
2	-0.5116	0.3581	-0.7810	-5.8026
3	0.7124	-0.5814	-0.3931	0.2298
4	0.7050	0.3939	-0.5898	-0.5582

The equation of the planes is of the form  $Ax + By + Cz + D = 0$ .

## (c) Dihedral angles (°) between selected planes

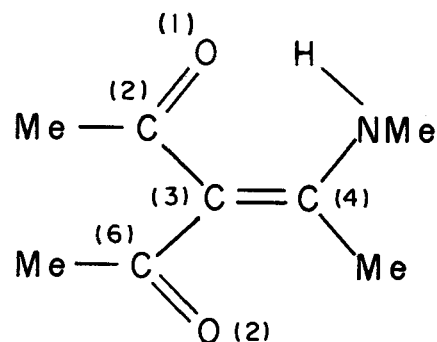
Planes	
1-2	123.9(3)
1-3	23.2(4)
1-4	59.3(4)
3-4	59.7(4)
2-4	106.8(5)

enaminones<sup>4</sup>. The largest differences between the two optimizations occur in torsional angles (Table 3). As an example, the optimized torsional angle O(2)C(19)C(15)C(16) of 1.3° obtained using input X is closer to the X-ray value of -1° than is the value obtained when standard values (Input S) were used (-20.9°). This is true, even though an angle of zero degrees was used in Input S for optimization. The information obtained from the two calculations can be used to give better estimates for input data in calculations of similar systems for which X-ray data is not available.

The final structure obtained using Input X is slightly more stable than that obtained using Input S (-11.6 kcal vs. -7.2 kcal).

Molecular structure optimization was also performed starting from the Z configuration and assuming: (1) hydrogen bonding between O(1) and HN; (2) O(1)C(14)C(15)C(16)N lies in a plane; and (3) O(2)C(19) is perpendicular to this plane. The torsional angle of -29.8° for O(2)C(19)C(15)C(16) shows that the O(2)-C(19) carbonyl is, in fact, closer to being in a plane with C(15)C(16)N than is O(1)C(14) [O(1)C(14)C(15)C(16) torsional angle = -81.7°]. This means that even in the Z configuration the acetyl carbonyl [O(2)C(19)] is the one that is conjugated.

If this were the correct configuration in solution, there would essentially be no hydrogen bonding as can be seen by comparison of the O(1)C(14)...HN distance in the Z configuration (2.775 Å) with that of O(2)C(19)...HN in the E form (2.060 Å). The chemical shift of 12.2 ppm for NH in the <sup>1</sup>NMR spectrum (in CDCl<sub>3</sub>) for this compound is consistent with a hydrogen bonded proton. This, together with the absence of any signal which could indicate another isomer, suggests that the E configuration is the only isomer in solution. The heat of formation for the Z configuration is larger (-5.14 kcal) than for the E configuration.



The results obtained show that, whichever the configuration, the diphenylacetyl group tends to be approximately perpendicular to the plane of the enaminone, most likely because of steric factors. To remove the difference in steric requirements of the two carbonyl groups, geometry optimization was performed on 4-methylamino-3-acetyl-3-penten-2-one.

Optimization was performed using standard bond angles and bond lengths and assuming intramolecular hydrogen bonding. In calculation A, the acetyl group which is *trans* to nitrogen was placed 90° out of the O(1)C(2)C(3)C(4)N plane and in calculation B, it was placed in the plane with the O(2)C(6)C(3)C(4) dihedral angle at 0°. The optimized structure in the two cases differed. In A, the O(1)C(2)C(3)C(4) dihedral angle is -7° while the O(2)C(6)C(3)C(4) angle is -93°. In B, these same angles are 14° and 53°, respectively. However, the enthalpies of formation are practically the same (-72.03 kcal in A vs. -71.7 kcal in B). Both calculations show a greater tendency for the intramolecularly chelated carbonyl to be more planar. Therefore, the fact that the opposite occurs in the calculation using configuration *Z* for compound **1** is most likely a steric effect.

## References

- (a) P. Plath and W. Rohr, *Synthesis* **318** (1982).
- (b) L. F. Tietze, A. Bergman, G. Brill, K. Brueggeman, U. Hartfiel and E. Voss, *Chem. Ber.* **122**, 83 (1989).
- M. N. Eberlin, Y. Takahata and C. Kascheres, *J. Org. Chem.* **55**, 5150. (1990)
- Unpublished results.
- M. N. Eberlin, Y. Takahata and C. Kascheres, *J. Mol. Struct. (Theochem)* **207**, 143 (1990).
- M. J. S. Dewar, E.G. Zoebisch, E.F. Healy and J.J.P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
- M. J. S. Dewar, Research Group, *QCPE Bull.*, Program no. 506 (1986).
- J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw, New York, 1970).
- J. -P. Célérier and G. Lhomme, *J. Heterocycl. Chem.* **19**, 481 (1982).
- B. Corain, C. Crotti, A. Del Pra, F. Filira and G. Zanotti, *Inorg. Chem.* **20**, 2044 (1981).
- C. Stevansson, I. Ymén and B. Yom-Tov, *Acta Chem. Scand.* **B36**, 71 (1982).
- M. J. Diáñez, A. López-Castro and R. Márquez, *Acta Cryst.* **C41**, 149 (1985).
- P. N. Bourosh, Yu. A. Simonov, V. B. Arion, A. N. Sobolev, N.V. Gérébéleu and V.S. Pakhopol, *Sov. Phys. Crystallogr.* **34**, 380 (1989).