# The Structures of 2-(4,5-Dihydro-5-aryl-3-isoxazolyl)-1-arylethanone Oximes. An Unusual Behaviour in its <sup>1</sup>H-NMR and Mass Spectra [1]

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The reaction of dibenzalacetones substituted on the aromatic ring with hydroxylamine hydrochloride and potassium hydroxide in refluxing ethanol affords several compounds. Herein, we report the structures and spectral properties of several oximes of 2-(4,5-dihydro-5-aryl-3-isoxazolyl)-1-arylethanones 6. Unusual behaviour on its 'H-nmr and mass spectra was observed. Single crystal X-ray diffraction was performed on compound 6d to support our structural considerations abouth the title compounds.

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### Introduction.

The reaction of dibenzalacetone la with hydroxylamine hydrochloride and potassium hydroxide under phasetransfer conditions gives several six-membered ring products 2, 3a and 4a [2]. When the same reaction of 1 was conducted in refluxing ethanol [3] besides a mixture of 3 and

## Scheme 1

4, the 2-isoxazoline derivatives 5 and 6 were obtained [4] (Scheme 1). The later products show interesting spectral

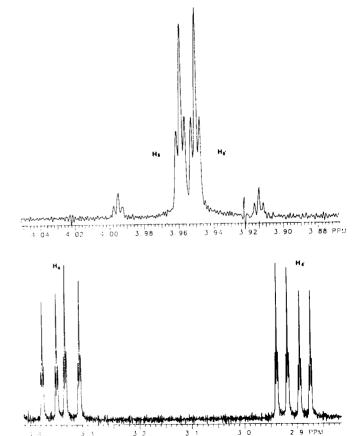


Figure 1. 400-MHz <sup>1</sup>H-nmr spectrum of **6a**; A) C-6 methylene protons; B) C-4 methylene protons.

3 0

Table 1

[a] dd, doublet of doublets; td, triplet of doublet; tdd, triplet of doublet of doublets.

Table 2

Mass Spectral Data of Compounds 6 [a]

m/z

Compound	[ M ]+·	[ M - 17 ] <sup>+</sup>	[ M - 32 ] <sup>+</sup>	[ 67 + R ] <sup>+</sup>	[ R CO ]*	[ R CHCH <sub>2</sub> ] <sup>+</sup>	[ R CN ]*	[ <b>R</b> ]⁺
6a	280 (17%)	263 (4%)	248 (69%)	144 (81%)	105 (44%)	104 (67%)	103 (55%)	77 (100%)
<b>6a</b> [b]	280 (13%)	263 (4%)	248 (100%)	144 (86%)	105 (21%)	104 (18%)	103 (9%)	77 (4%)
6Ь	348 (10%)	331 (1%)	316 (68%)	178 (92%)	139 (56%)	138 (59%0	137 (34%)	111(100%)
6c	368 (18%)	351 (1%)	336 (10%)	188 (7%)	149 (58%)	148 (100%)	147 (56%)	121 (13%)
6 <b>d</b>	316 (5%)	299 (0.5%)	284 (24%)	162 (72%)	123 (50%)	122 (100%)	121 (55%)	95 (82%)
<b>6d</b> [b]	316 (14%)	299 (1%)	284 (100%)	162 (40%)	123 (12%)	122 (5%)	121(3%)	95 (2%)

[a] 70 eV, 190 °C. [b] 12 eV, 190°C.

Table 3 Fractional Coordinates  $(x10^4)$  for the Non-hydrogen Atoms,  $(x10^4)$  for the Hydrogen Atoms and the Equivalent Ueq  $(\mathring{A}^2x10^3)$  Isotropic Thermal Factor

atom	X	Y	Z	Ueq
01	4477(4)	2235(2)	3696	60(1)
N2	4630(4)	1603(2)	4156(1)	46(1)
C3	2895(5)	736(3)	4195(1)	42(1)
C4	1263(6)	635(3)	3767(1)	52(1)
C5	2661(7)	1484(3)	3403(1)	54(1)
C6	2573(5)	-108(3)	4633(1)	47(1)
C7	4818(6)	-137(3)	4957(1)	44(1)
N1	6642(4)	-951(3)	4887(1)	52(1)
02	6250(4)	-1762(3)	4477(1)	69(1)
C8	4995(5)	781(3)	5374(1)	43(1)
C9	3290(6)	1820(3)	5441(1)	53(1)
C10	3434(6)	2658(3)	5839(1)	61(1)
C11	5294(7)	2462(3)	6156(1)	62(1)
C12	7051(7)	1472(4)	6099(1)	67(1)
F1	5463(5)	3299(2)	6542(1)	97(1)
C13	6885(6)	629(4)	5707(1)	59(1)
C14	4045(6)	720(3)	3022(1)	49(1)
C15	5741(6)	-289(3)	3139(1)	55(1)
C16	7130(7)	-929(4)	2792(1)	63(1)
C17	6786(7)	-553(4)	2326(1)	68(1)
C18	5111(8)	401(4)	2195(1)	82(2)
F2	8184(5)	-1162(2)	1981(1)	104(1)
C19	3733(7)	1034(3)	2544(1)	70(1)
H4a	1104	-290	3662	60
H4b	-362	1003	3830	60
H5	1480	2018	3226	60
H6a	1189	247	4812	60
H6b	2213	-1022	4535	60
H2	7335(69)	-2190(37)	4500(13)	60
H9	1990	1960	5210	60
H10	2231	3366	5888	60
H12	8373	1365	6328	60
H13	8102	-76	5664	60
H15	5949	-544	3468	60
H16	8309	-1624	2875	60
H18	4889	633	1864	60
H19	2529	1708	2454	60

features. Here, we describe the structures of several 2-(4,5-dihydro-5-aryl-3-isoxazolyl)-1-arylethanone oximes 6, obtained by the reaction of the substituted dibenzalacetones 1 with hydroxylamine hydrochloride and potassium hydroxide in refluxing ethanol. High resolution nmr, mass spectral data and X-ray crystallography were used to confirm its structures.

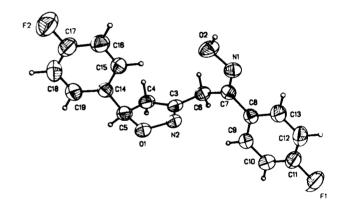


Figure 2. ORTEP-like view of 6d.

Results and Discussion.

The <sup>1</sup>H- and <sup>13</sup>C-nmr spectral data of compounds **6** are presented on Table 1. Although the aromatic moiety shows different substituents, the chemical shifts and coupling constants of the remaining protons are very similar in the different compounds. For example, the <sup>1</sup>H-nmr spectrum of **6a** showed multiplets at  $\delta_{\rm H}=7.713$  (2H), 7.340 (3H), 7.245 (3H) and 7.178 (2H), assigned to the aromatic protons and a doublet of doublets at  $\delta_{\rm H}=5.459$  (H-5) as part an ABX pattern. The AB moiety was localized at  $\delta_{\rm H}=3.350$  and 2.903 (H-4 and H-4'). Each peak of this AB signals showed an additional  $4\sigma$  coupling (<sup>4</sup>J = 1.1 Hz) with the protons H-6 and H-6' (Figure 1). These methylene protons were localized as an A'B' pattern at  $\delta_{\rm H}=$ 

3.967 and 3.941 split into small triplets ( ${}^{2}J_{A'B'} = -14.9 \text{ Hz}$ ). Although the nmr chemical shifts are in agreement with the structure, the unusual  $4\sigma$  long range coupling observed on the methylene protons in each of the compounds encouraged us to perform a detailed spectroscopic study.

The  $4\sigma$  coupling has been previously described [5]. The mechanism of this "isopropylidenic coupling" along this path is believed to involve  $\sigma$ - $\pi$  orbital overlap and the magnitudes of the coupling constant fall off rapidly as the system loses coplanarity. In order to confirm this situation for the compounds  $\bf 6$ , a single crystal X-ray data study of compound  $\bf 6d$  was carried out. The evidences on the specific dihedral angles between H4-C4-C6-H6′ = -6.5° and H4′-C4-C6-H6 = -5.5° shown a high degree of coplanarity. An ORTEP-like view of  $\bf 6d$  is shown in Figure 2. X-ray crystallographic features are listed on Tables 3-7.

Table 4
Selected Bond Distances (Å) and Angles (°)

O1-N2	1.431(2)	O1-C5	1.471(4)
N2-C3	1.267(4)	C3-C4	1.484(4)
C3-C6	1.489(4)	C4-C5	1.515(4)
C5-C14	1.501(4)	C6-C7	1.507(4)
C7-N1	1.280(4)	C7-C8	1.477(4)
N1-O2	1.412(4)	C8-C9	1.385(4)
C8-C13	1.384(4)	C9-C10	1.386(5)
C10-C11	1.348(5)	C11-C12	1.365(5)
C11-F1	1.360(4)	C12-C13	1.377(5)
C14-C15	1.386(4)	C14-C19	1.378(5)
C15-C16	1.376(5)	C16-C17	1.365(5)
C17-C18	1.350(5)	C17-F2	1.360(4)
C18-C19	1.373(5)		
N2-O1-C5	108.6(2)	O1-N2-C3	109.1(2)
N2-C3-C4	114.3(3)	N2-C3-C6	122.0(3)
C4-C3-C6	123.7(2)	C3-C4-C5	102.2(2)
O1-C5-C4	103.4(2)	O1-C5-C14	108.6(3)
C4-C5-C14	116.4(2)	C3-C6-C7	114.3(2)
C6-C7-N1	122.1(3)	C6-C7-C8	120.9(3)
N1-C7-C8	117.3(3)	C7-N1-O2	111.4(2)
C7-C8-C9	121.1(3)	C7-C8-C13	120.7(3)
C9-C8-C13	118.2(3)	C8-C9-C10	120.8(3)
C9-C10-C11	118.9(3)	C10-C11-C12	122.5(3)
C10-C11-F1	118.9(3)	C12-C11-F1	118.6(3)
C11-C12-C13	118.6(3)	C8-C13-C12	121.1(3)
C5-C14-C15	121.1(3)	C5-C14-C19	120.9(3)
C15-C14-C19	118.0(3)	C14-C15-C16	121.1(3)
C15-C16-C17	118.3(3)	C16-C17-C18	122.4(3)
C16-C17-F2	118.7(3)	C18-C17-F2	118.9(3)
C17-C18-C19	118.8(3)	C14-C19-C18	121.3(3)

On the other hand, an unusual fragmentation pattern was observed in the mass spectra of compounds 6 and it is of particular interest in view of the uncommon nature of this valence tautomerism system. The relative abundance of relevant ions obtained as primary fragmentation products are shown in Table 2. The fragmentation pattern of

the compounds discussed can be adequately explained by the iminium valence tautomer obtained by hydrogen transfer to the oxime nitrogen atom (Scheme 2). The primary loss of radical OH [M-17]<sup>+</sup> in oximes [6], is almost absent. Elimination of radical NH-OH [M-32]<sup>+</sup> is present leading to a general fragmentation pattern. These cleavage of the C-C bond in the  $\alpha$ -position to the carbon-nitrogen double bond and the loss of two hydrogen atoms lead to the ions at m/z [67+R]<sup>+</sup>. Such fragmentation pathway is not thermal and is the major process observed in the mass spectra of compounds 6. Other significant fragment ions

Table 5
Selected Torsion Angles(°)

C6-C3-C4-H4a	-50.8	H4a-C4-H4b-C6	96.3
C6-C3-C4-H4b	71.5	C3-C4-C6-H4a	-133.7
C6-C3-C4-C6	0.0	C3-C4-C6-H4b	116.0
C4-C3-C6-H6a	-76.3	H4a-C4-C6-H4b	-110.3
C4-C3-C6-H6b	42.3	C3-C6-H6a-H6b	117.8
C4-C3-C6-C4	0.0	C3-C6-H6a-C4	27.7
C3-C4-C6-C3	0.0	C4-C6-H6a-H6b	90.1
C3-C4-C6-H6a	110.6	C3-C6-H6b-H6a	-117.9
C3-C4-C6-H6b	-140.2	C3-C6-H6b-C4	-18.5
H4a-C4-C6-C3	133.7	C4-C6-H6b-H6a	-99.3
H4a-C4-C6-H6a	-115.8	H4a-C3-C4-H4b	122.4
H4a-C4-C6-H6b	-6.5	H4a-C3-C4-C6	50.8
H4b-C4-C6-C3	-116.0	H4b-C3-C4-C6	-71.5
H4b-C4-C6-H6a	-5.5	H6a-C3-C6-H6b	118.6
H4b-C4-C6-H6b	103.8	C4-C3-C6-H6a	-76.3
C3-C4-H4a-H4b	123.4	С4-С3-С6-Н6Ь	42.3
C3-C4-H4a-C6	21.5	C3-C4-C6-H6a	110.6
H4b-C4-H4a-C6	-101.9	C3-C4-C6-H6b	-140.2
C3-C4-H4b-H4a	-123.4	H6a-C4-C6-H6b	109.2
C3-C4-H4b-C6	-27.1		

derived from the molecular ion are [R.CO]<sup>+</sup>, and [R.CH-CH<sub>2</sub>]<sup>+</sup> base peak in compounds **6c** and **6d**. The [R]<sup>+</sup> ion is the base peak in compounds **6a** and **6b**. Finally, the ion [R.CN]<sup>+</sup> can be derived from the ion at m/z [M-17]<sup>+</sup>. When the energy of the electron beam is lowered to 12 eV in compounds **6a** and **6d**, the [M-32]<sup>+</sup> ions are converted in the peak base.

The mechanism of formation of **3.6** can be postulated as shown in Scheme 3. The dihydroxylamino ketone produced by 1,4-addition of two molecules of hydroxylamine to **1**, in the first step of the process, reacts with a second molecule of **1** to give a disubstituted hydroxylamine. Oximation of this compound produces a dioxime-hydroxylamine intermediate which decomposes to yield **5** and a

Scheme 2

$$\begin{bmatrix} & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

#### Scheme 3

Table 6
Crystallographic Data for **6d** 

molecular formula	$C_{17}H_{14}N_2O_2F_2$		
molecular weight	316.29		
crystal size/mm <sup>3</sup>	$0.22 \times 0.16 \times 0.06$		
space group	$\operatorname{Pb}_{\mathbf{n}}2_{1}$		
cells dimentions			
a/Å	5.364(5)		
b/Å	9.846(1)		
c/Å	27.923(4)		
α/deg	90(1)		
β/deg	90(1)		
νdeg	90(1)		
$vol/Å^3$	1474.7(3)		
z	4		
ρ <sub>meand</sub> /g cm <sup>-3</sup>			
ρ <sub>measd</sub> /g cm <sup>-3</sup> ρ <sub>calcd</sub> /g cm <sup>-3</sup>	1.42		

Table 7

Data Collection and Refinement Details for **6d** 

diffractometer	Nicolet P3/F
radiation	CuKα (1.5418 Å)
monochromator	Ni filtered Cu radiation
scan type	2θ: θ
scan speed, deg min <sup>-1</sup>	variable; slow 4.29, fast 29.3
background	
2θ scan limit, deg	110
"standard" reflections	50
indices	(0,2,5)(0,2,4)
crystal stability	2 every 50 reflections
unique reflections with I > O (I)	881
R factor	0.027
$R_{vv}$	0.029

isoxazoline-hydroxylamine precursor of 6. Oxidation of the latter compound by atmospheric oxygen leads to 6. On the other hand, single 1,4-addition of hydroxylamine to 1 forms a hydroxylamino ketone that by cyclization and oximation produces 3 and 4.

#### **EXPERIMENTAL**

Melting points were taken on a Culatti melting point apparatus and are uncorrected. The ir spectra were recorded on a Nicolet FT 5SX instrument. The 'H and '3C nmr spectra were obtained either on a Varian VXR-300S spectrometer equipped with a 5 mm multi-nuclear probe or on a Varian FT-80A spectrometer. The spectra were determined at room temperature for ca. 20 mg samples in 0.5 ml of deuteriochloroform. Mass spectra were measured on a Hewlett-Packard 5985A quadrupole mass spectrometer at 70 eV (unless specified otherwise) at 190°. Compounds 1b-d used as starting materials were obtained following the procedure described to prepare dibenzalacetone 1a [7].

General Procedure for the Reaction of Substituted Dibenzalacetones 1 with Hydroxylamine Hydrochloride.

To a solution of 4 g (0.071 mole) of potassium hydroxide in 50 ml of 95% ethanol, 1.2 g (0.0172 mole) of hydroxylamine hydrochloride and 1 g (0.0043 mole) of dibenzalacetone  ${\bf la}$  were added. The resulting solution was heated at reflux for 2 hours. After cooling, the mixture was filtered and the filtrate was evaporated under vacuum. The residue was solved in 50 ml of ethyl acetate and washed with water (2 x 25 ml) and brine (2 x 25 ml). The organic solution was dried (sodium sulfate) and evaporated. The residue was purified by column chromatography in silica gel using ethyl acetate-hexane as eluent. From the fractions eluted with

2% ethyl acetate-hexane, **5a** was obtained. From the fractions eluted with 5% ethyl acetate-hexane a residue was obtained and it was recrystallized to give **6a**. The fractions eluted with 10% ethyl acetate-hexane gives a residue containing a mixture of **3a** and **4a** [2].

(E)-5-Phenyl-3-(2-phenylethenyl)-2-isoxazoline (5a).

This compound was obtained as colorless needles (acetone-hexane) in 24% yield, mp 106-107°; ir (chloroform):  $\nu$  1630 (w), 1492, 1367 cm<sup>-1</sup>; <sup>1</sup>H nmr:  $\delta$  3.10 (dd, J = -17.5 and 8 Hz, 1H), 3.60 (dd, J = -17.5 and 10 Hz, 1H), 5.63 (dd, J = 10 and 8 Hz, 1H), 6.67 (d, J = 17 Hz, 1H), 7.10 (d, J = 17 Hz, 1H), 7.20-7.55 (m, 10H, phenyl protons); ms: 249 (M\*, 39), 248 (100), 115 (52), 91 (57), 77 (63).

Anal. Calcd. for C<sub>17</sub>H<sub>18</sub>NO: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.84; H, 6.20; N, 5.64.

2-(4,5-Dihydro-5-phenyl-3-isoxazolyl)-1-phenylethanone Oxime (6a).

This compound was obtained as colorless needles (acetone-hexane) in 4% yield, mp 151-152°; ir (potassium bromide):  $\nu$  3322, 1632 (w), 1422 cm<sup>-1</sup>; for 'H nmr and mass spectra see Tables 1 and 2.

Anal. Calcd. for  $C_{17}H_{16}N_2O_2$ : C, 72.84; H, 5.75; N, 9.99. Found: C, 72.55; H, 5.83; N, 10.09.

(E)-5-(3-Chlorophenyl)-3-[2-(3-chlorophenyl)ethenyl]-2-isoxazoline (5b).

This compound was obtained as colorless needles (acetone-hexane) in 12% yield, mp 76-77°; 'H nmr:  $\delta$  3.10 (dd, J = -16 and 8 Hz, 1H), 3.60 (dd, J = -16 and 10 Hz, 1H), 5.58 (dd, J = 10 and 8 Hz, 1H), 6.53 (d, J = 16 Hz, 1H), 7.05 (d, J = 16 Hz, 1H), 7.10-7.40 (m, 8H, phenyl protons); ms: 321 (M\*+4, 4), 320 (M\*+3, 12), 319 (M\*+2, 25), 318 (M\*+1, 62), 317 (M\*, 35), 316 (M\*-1, 100), 149 (29).

Anal. Calcd. for C<sub>17</sub>H<sub>13</sub>Cl<sub>2</sub>NO: C, 64.17; H, 4.12; N, 4.40. Found: C, 64.10; H, 4.26; N, 4.49.

2-[4,5-Dihydro-5-(3-chlorophenyl)-3-isoxazolyl]-1-(3-chlorophenyl)-ethanone Oxime (6b).

This compound was obtained as colorless needles (acetone-hexane) in 5% yield, mp 118-121°; for 'H nmr and mass spectra see Tables 1 and 2.

Anal. Calcd. for  $C_{17}H_{14}Cl_2N_2O_2$ : C, 58.47; H, 4.04; N, 8.02. Found: C, 58.13; H, 4.10; N, 8.09.

(E)-5-(3,4-Methylenedioxyphenyl)-3-[2-(3,4-methylenedioxyphenyl)ethenyl]-2-isoxazoline (5c).

This compound was obtained as colorless needles (acetone-hexane) in 7% yield, mp 150-151°; 'H nmr:  $\delta$  3.14 (dd, J = -16 and 8 Hz, 1H), 3.59 (dd, J = -16 and 11 Hz, 1H), 5.57 (dd, J = 11 and 8 Hz, 1H), 5.97 (s, 1H), 6.01 (s, 1H), 6.67 (d, J = 16 Hz, 1H), 6.92 (d,

J = 16 Hz, 1H), 6.80-7.02 (m, 6H, phenyl protons); ms: 337 (M\*, 36), 336 (64), 148 (100), 147 (58).

Anal. Calcd. for C<sub>19</sub>H<sub>15</sub>NO<sub>5</sub>: C, 67.65; H, 4.48; N, 4.15. Found: C. 67.39: H. 4.49: N. 4.11.

2-[4,5-Dihydro-5-(3,4-methylenedioxyphenyl)-3-isoxazolyl]-1-(3,4-methylenedioxyphenyl)ethanone Oxime (6c).

This compound was obtained as colorless needles (acetone-hexane) in 8% yield, mp 156-158°; for 'H nmr and mass spectra see Tables 1 and 2.

Anal. Calcd. for  $C_{19}H_{16}N_2O_6$ : C, 61.96; H, 4.38; N, 7.61. Found: C, 62.18; H, 4.40; N, 7.34.

2-[4,5-Dihydro-5-(4-fluorophenyl)-3-isoxazolyl]-1-(4-fluorophenyl)-ethanone Oxime (6d).

This compound was obtained as colorless needles (acetone-hexane) in 12% yield, mp 170-171°; for 'H nmr and mass spectra see Tables 1 and 2.

Anal. Calcd. for  $C_{17}H_{14}F_2N_2O_2$ : C, 64.55; H, 4.46; N, 8.86. Found: C, 64.70; H, 4.48; N, 8.75.

(E)-1,5-Bis-(4-fluorophenyl)-5-hydroxy-1-penten-3-one Oxime (7).

This compound was obtained as colorless needles (acetone-hexane), in 15% yield, mp 167-168°; <sup>1</sup>H nmr (acetone-d<sub>6</sub>):  $\delta$  2.99 (dd, J = -13 and 6 Hz, 1H), 3.07 (dd, J = -13 and 7.5 Hz, 1H), 4.51 (d, J = 4 Hz, 1H, 0H), 5.11-5.21 (m, 1H), 6.69 (d, J = 17 Hz, 1H), 6.86 (d, J = 17 Hz, 1H), 7.01-7.18 (m, 4H, phenyl protons), 7.44-7.56 (m, 4H, phenyl protons), 10.50 (s, 1H, N-OH); ms: 303 (M\*, 22), 302 (27), 286 (25), 284 (50), 179 (61), 178 (56), 162 (58), 125 (100), 97 (67), 95 (47).

Anal. Calcd. for C<sub>17</sub>H<sub>15</sub>F<sub>2</sub>NO<sub>2</sub>: C, 67.32; H, 4.98; N, 4.62. Found: C, 67.39; H, 4.98; N, 4.60.

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