Structure of the intermediate in the synthesis of 6-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile

Nikolay Yu. Gorobets,* Yuriy V. Sedash, Svetlana V. Shishkina, Oleg V. Shishkin, Sergey A. Yermolayev, and Sergey M. Desenko

Department of Chemistry of Heterocyclic Compounds, State Scientific Institution 'Institute for Single Crystals' of National Academy of Science of Ukraine, Lenin Ave. 60, Kharkiv 61001, Ukraine
E-mail: gorobets@isc.kharkov.com

The X-Ray Diffraction Study.

The crystals of 1-*s*-*cis* **6aa** ($C_9H_{13}ON_3$) are triclinic. At 293 K a = 6.710(3), b = 7.952(3), c = 9.183(7) Å, α = 99.09(5)°, β = 106.26(6)°, γ = 99.96(4)°, V = 452.1(4) Å^3, M_r = 179.22, space group $P\bar{1}$, Z = 2, d_{calc} = 1.317 g/cm^3, μ(MoKα) = 0.090 mm^{-1}, F(000) = 192. Intensities of 1945 reflections (1409 independent, R_{int}=0.026) were measured on the «Xcalibur-3» diffractometer (graphite monochromated MoK_α radiation, CCD detector, ω-scaning, $2\Theta_{max}$ = 50°).

The crystals of 1-*s*-*trans* **6aa** ($C_9H_{13}ON_3 \cdot C_2H_4O_2$) are monoclinic. At 100 K a = 10.189(5), b = 12.790(5), c = 10.726(5) Å, β = 116.318(5)°, V = 1253(1) Å^3, M_r = 239.28, space group $P2_1/n$, Z = 4, d_{calc} = 1.269 g/cm^3, μ(MoKα) = 0.094 mm^{-1}, F(000) = 512. Intensities of 4284 reflections (2129 independent, R_{int}=0.031) were measured on the «Xcalibur-3» diffractometer (graphite monochromated MoK_α radiation, CCD detector, ω-scaning, $2\Theta_{max}$ = 50°).

The structures were solved by direct method using SHELXTL program package.[24] Position of the hydrogen atoms were located from electron density difference maps and refined by "riding" model with $U_{iso} = nU_{eq}$ of non-hydrogen atom bonded with given H-atom (n = 1.5 for methyl and hydroxyl groups and n = 1.2 for other hydrogen atoms).

For the structure 1-*s*-*cis* **6aa** full-matrix least-squares refinement against F^2 in anisotropic approximation using 1360 reflections was converged to wR_2 = 0.135 (R_1 = 0.055 for 789 reflections with F>4σ(F), S = 0.892).

The final atomic coordinates, and crystallographic data for 1-*s*-*cis* **6aa** have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition number CCDC 743446.

For the structure 1-*s*-*trans* **6aa** full-matrix least-squares refinement against F^2 in anisotropic approximation using 2114 reflections was converged to wR_2 = 0.133 (R_1 = 0.053 for 1203 reflections with F>4σ(F), S = 0.868).

The final atomic coordinates, and crystallographic data for 1-*s*-*trans* **6aa** have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) and are available on request quoting the deposition number CCDC 743446.

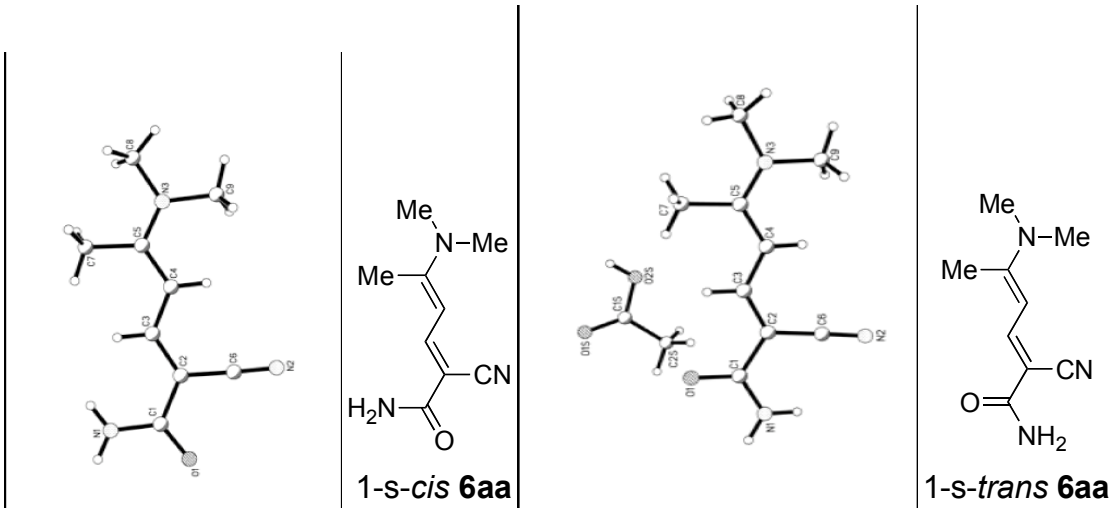


Figure 1. Molecular structures of rotational isomers of the compound **6aa:** 1s-*cis*-(2*E*,4*E*)-2-cyano-5-(dimethylamino)hexa-2,4-dienamide (1-*s*-*cis* **6aa**) and 1s-*trans*-(2*E*,4*E*)-2-cyano-5-(dimethylamino)hexa-2,4-dienamide (1-*s*-*trans* **6aa**) obtained by single crystal X-ray analysis (atom numbering as used in the Structural Analysis).

Table 1. The shortened intramolecular contacts in the rotational isomers 1-*s*-*cis* **6aa** and 1-*s*-*trans* **6aa** determined by the X-ray diffraction data and quantum-chemical calculations using MP2/aug-cc-pvdz method.

Contact	Distance [Å]			
	1-*s*-*cis* **6aa**		1-*s*-*trans* **6aa**	
	Experimental	Calculated	Experimental	Calculated
H(3)···N(1)	2.53*	2.53		
H(3)···H(1Na)	1.96	2.23		
H(3)···C(7)	2.59	2.73	2.60	2.74
H(3)···H(7b)	1.91	1.94	1.95	1.94
H(4)···C(6)	2.53	2.50	2.65	2.55
H(4)···C(9)	2.40	2.40	2.45	2.41
H(4)···H(9b)	2.26	2.31	2.29	2.32
	2.19	2.10	2.23	2.10
H(1Na)···C(3)	2.52	2.72		
H(7b)···C(3)	2.50	2.59	2.56	2.57
H(9b)···C(4)	2.76	2.68	2.79	2.88
H(9a)···C(4)	2.70	2.87	2.75	2.68
H(7a)···C(8)	2.59	2.79		
H(7a)···H(8a)	2.22	2.19	2.28	2.19
H(8a)···C(7)	2.68	2.46	2.41	2.46
H(7c) ···C(8)	2.72	2.79	2.59	2.78
H(7c)···H(8b)	2.30	2.32		2.32
H(8b)···C(7)	2.65			
H(9c)···H(8c)	2.01	2.21	2.26	2.20
H(1Na)···C(6)			2.39	2.40
H(8a···H(7c)			2.15	

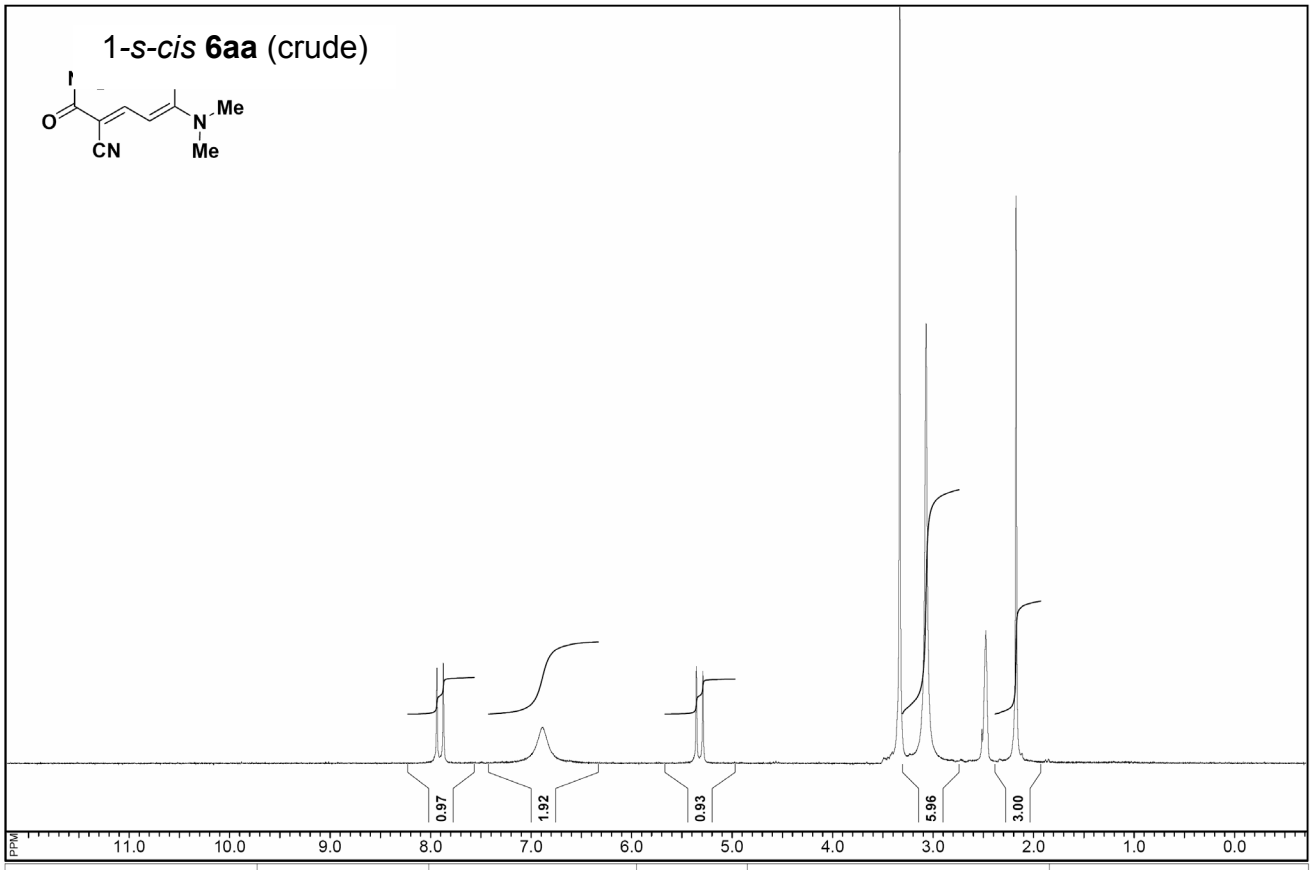
*Van der Waals radii sum:[25] 2.87 Å for H···C, 2.34 Å for H···H and 2.67 Å for H···N.

Table 2. The bond lengths (Å) in 1-*s*-*cis* **6aa** and 1-*s*-*trans* **6aa** determined by the X-ray diffraction data and quantum-chemical calculations using MP2/aug-cc-pvdz method.

Bond	1-*s*-*cis* **6aa**		1-*s*-*trans* **6aa**	
	Experimental	Calculated	Experimental	Calculated
N(1)–C(1)	1.322(3)	1.391	1.338(3)	1.371
N(2)–C(6)	1.132(3)	1.191	1.158(3)	1.192
N(3)–C(5)	1.301(3)	1.379	1.333(3)	1.377
N(3)–C(8)	1.432(3)	1.464	1.469(3)	1.464
N(3)–C(9)	1.438(3)	1.461	1.472(3)	1.461
O(1)–C(1)	1.224(3)	1.233	1.266(3)	1.236
C(1)–C(2)	1.427(4)	1.494	1.453(4)	1.499
C(2)–C(3)	1.351(3)	1.380	1.376(4)	1.376
C(2)–C(6)	1.402(4)	1.438	1.430(4)	1.435
C(3)–C(4)	1.365(3)	1.432	1.383(3)	1.429
C(4)–C(5)	1.359(3)	1.389	1.397(4)	1.390
C(5)–C(7)	1.479(4)	1.511	1.507(4)	1.511

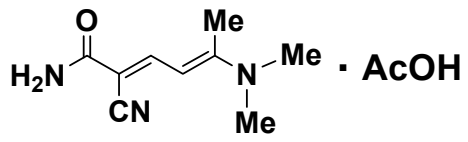
References

24. Sheldrick G.M. *SHELXTL PLUS. PC Version. A system of computer programs for the determination of crystal structure from X-ray diffraction data.* Rev. 5.1. 1998.
25. Zefirov, Yu. V. // Kristallografiya (Russian), **1997**, *42*, 936.

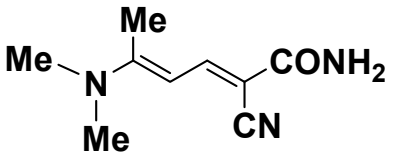


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1-*s-trans* **6aa** (acetic acid solvate)

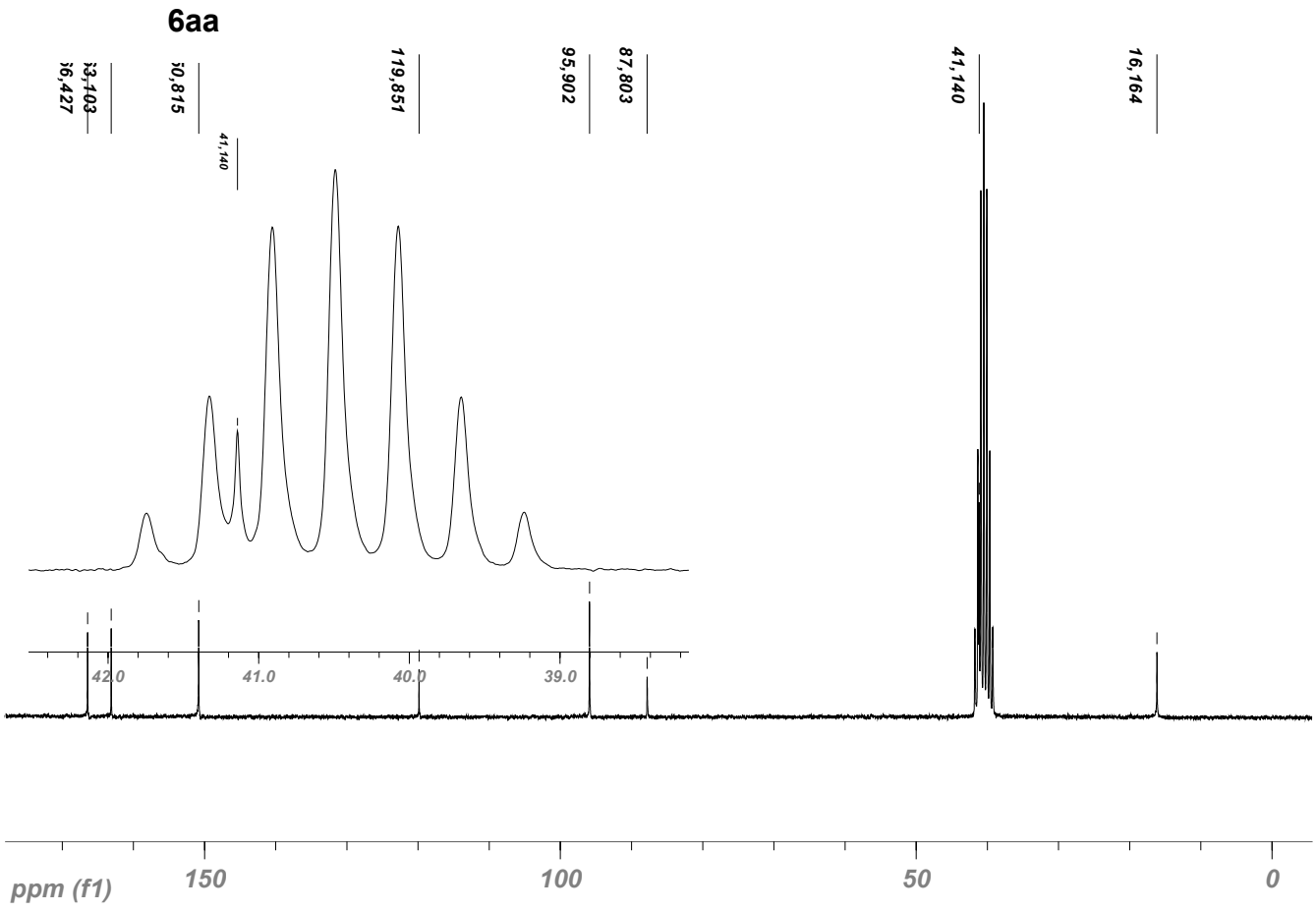


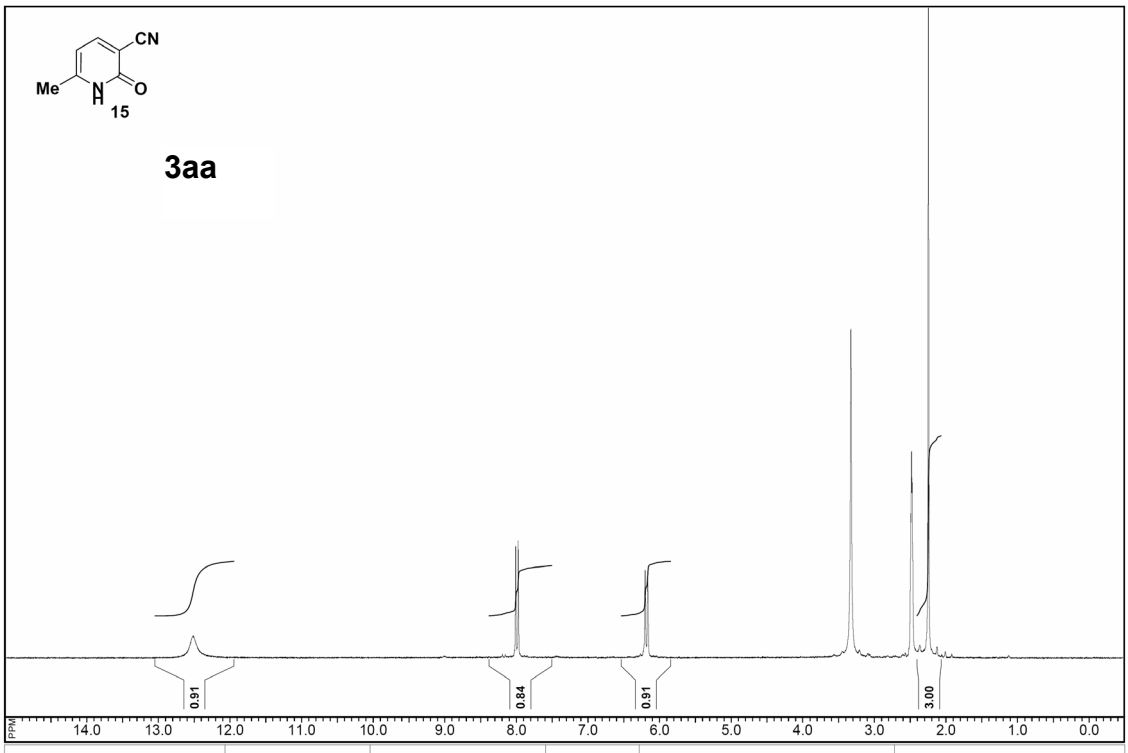
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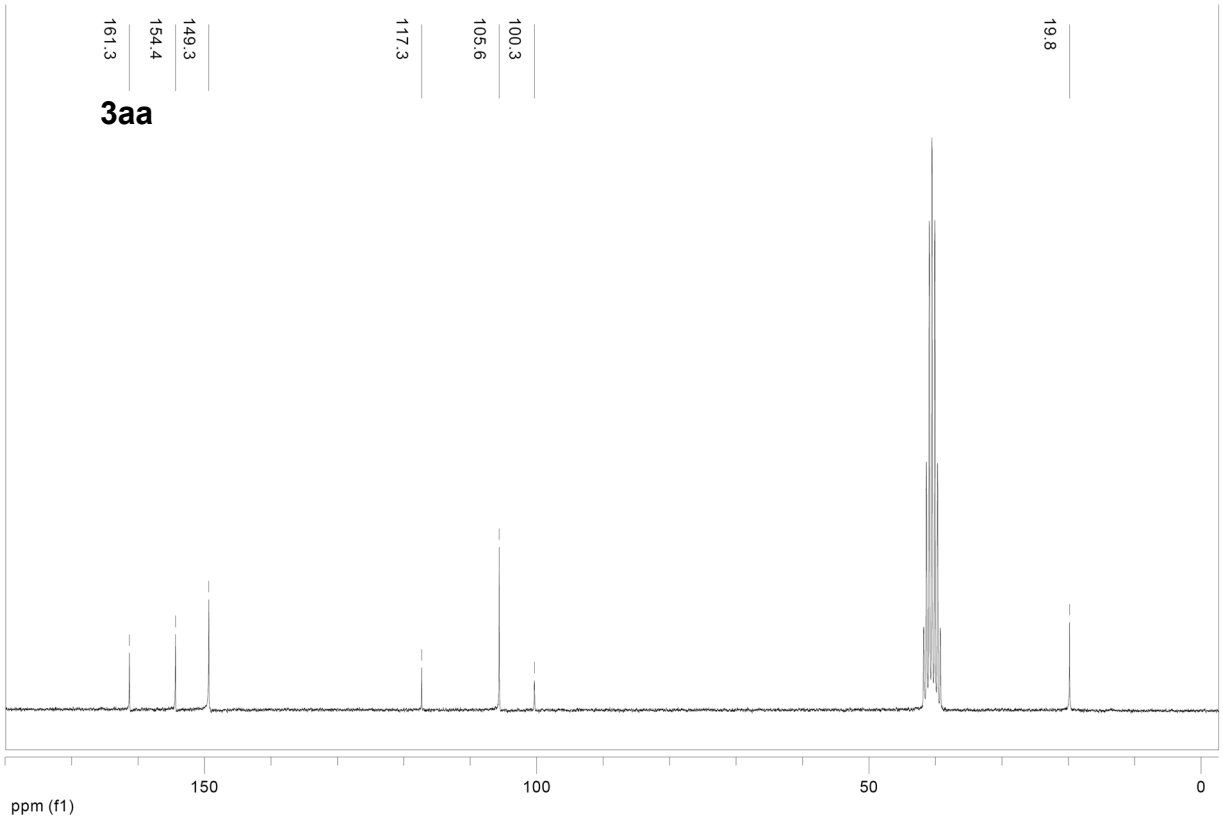
6aa

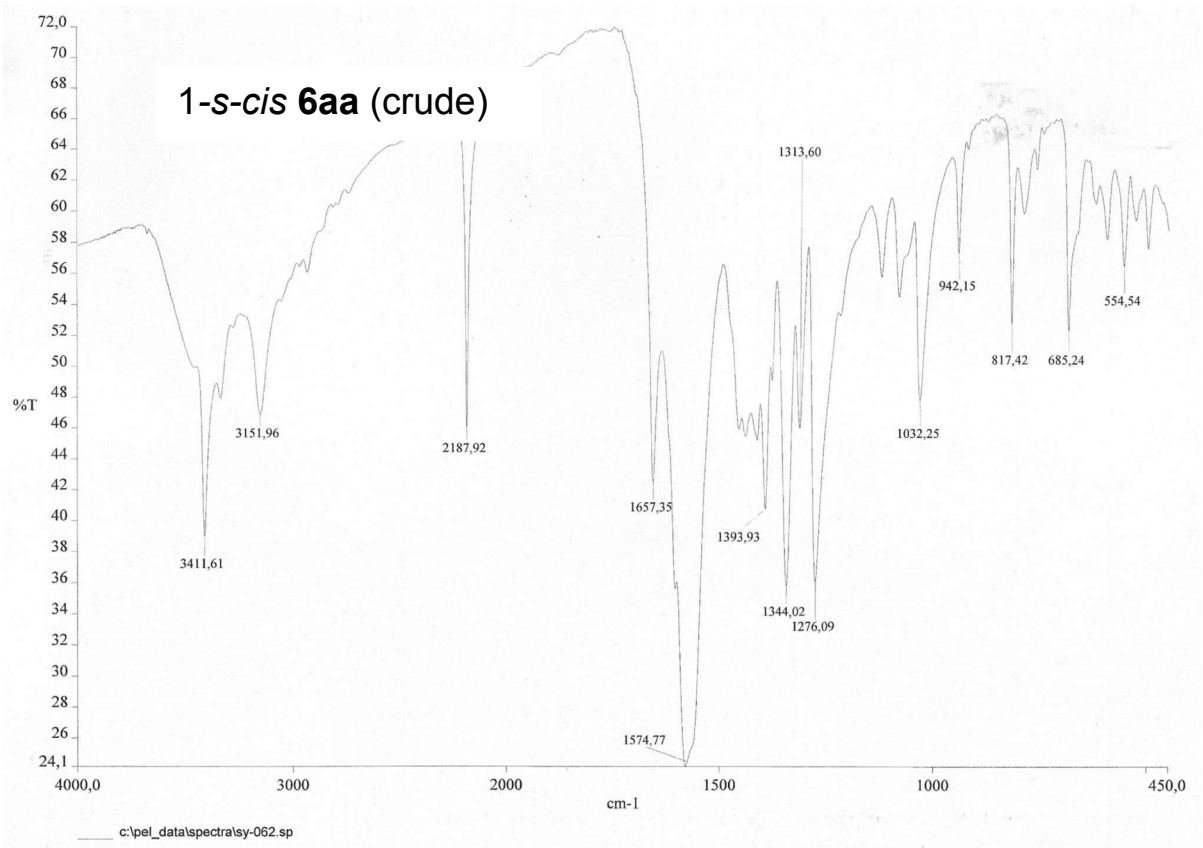
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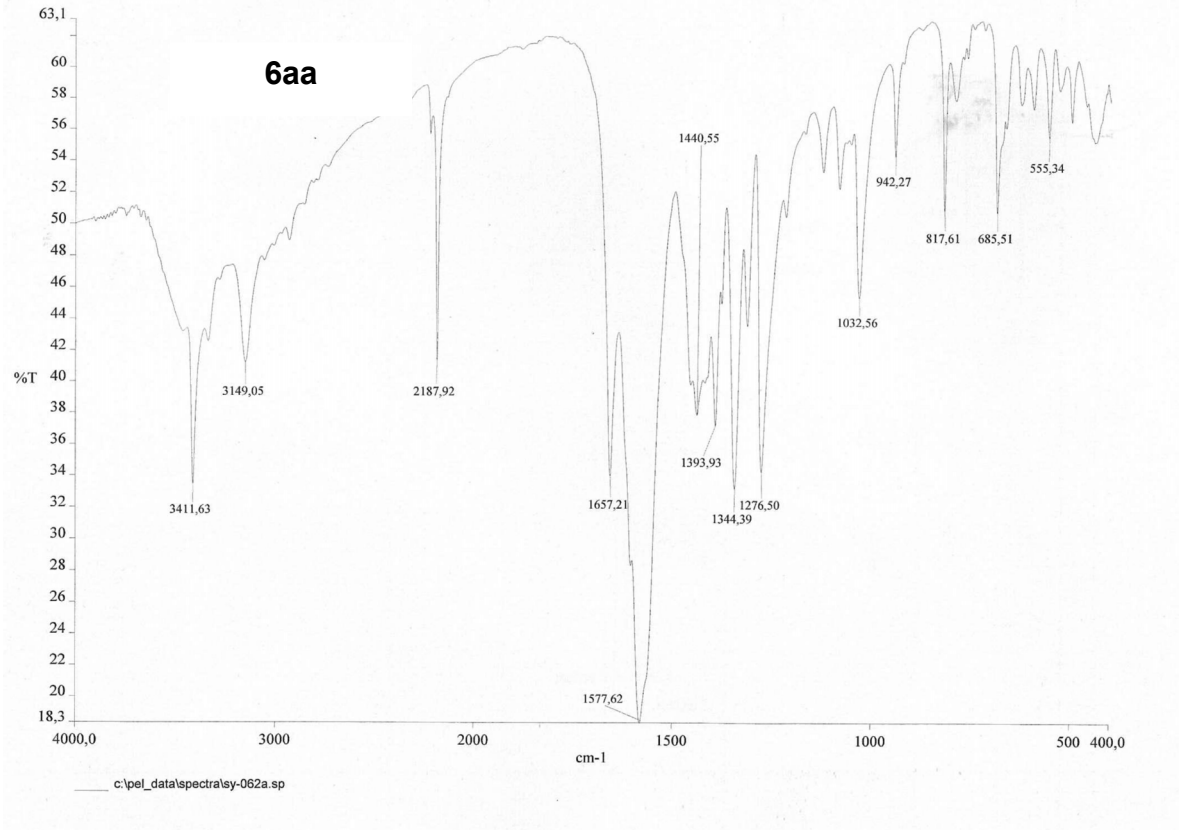

6aa
i6,427
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i0,815
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41,140
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41.0
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39.0
ppm (f1)
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50
0

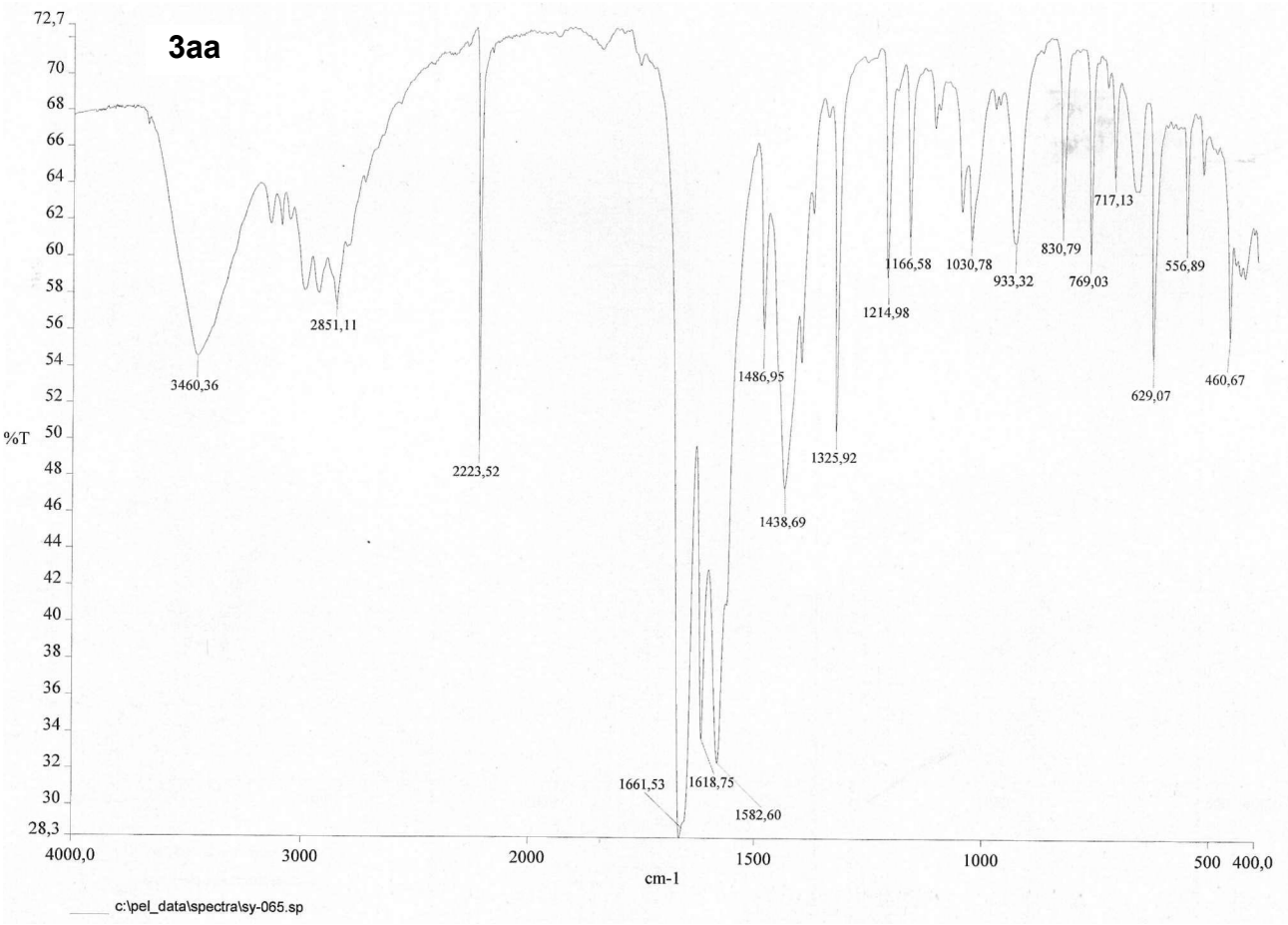


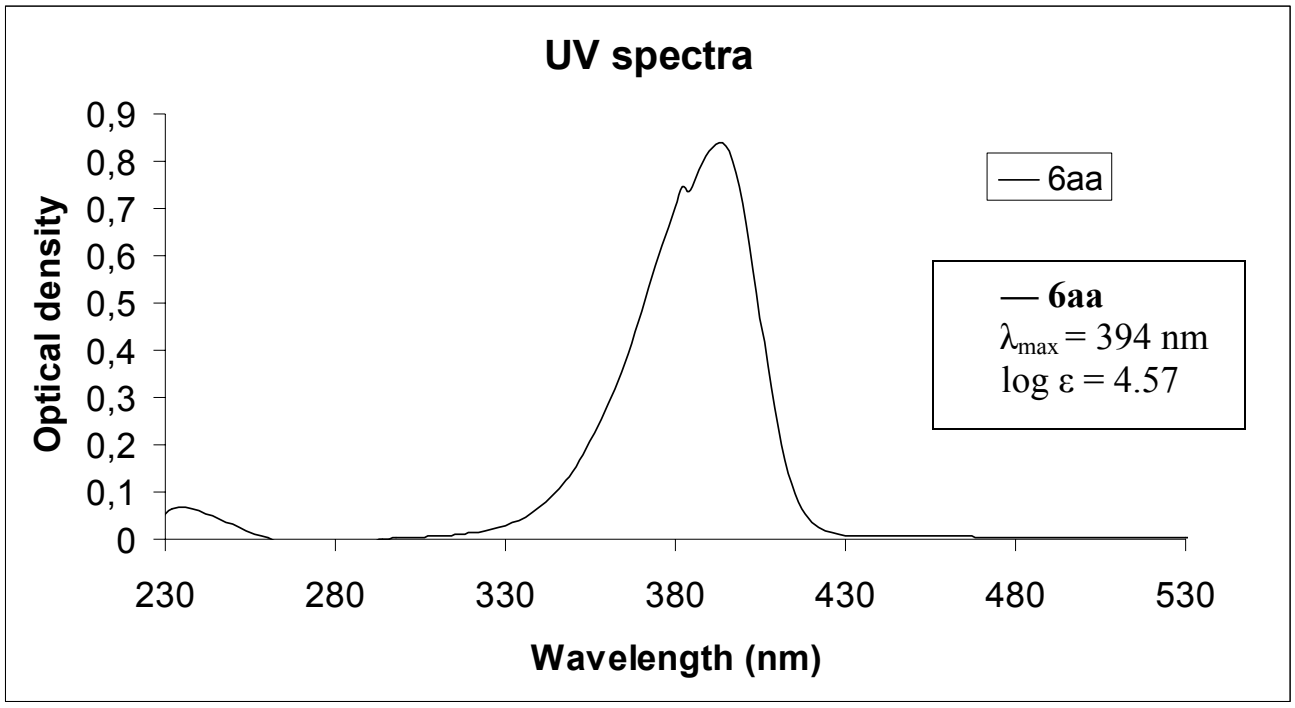
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1-*s*-*cis* **6aa** (crude)
%T
cm-1
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1657,35
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1393,93
1344,02
1276,09
1313,60
1032,25
942,15
817,42
685,24
554,54
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6aa
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933,32
830,79
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717,13
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460,67
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UV spectra
Optical density
Wavelength (nm)
6aa
— 6aa
λmax = 394 nm
log ε = 4.57