

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

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The X-Ray Diffraction Study.

The crystals of 1-*s-cis* **6aa** (C₉H₁₃ON₃) are triclinic. At 293 K $a = 6.710(3)$, $b = 7.952(3)$, $c = 9.183(7)$ Å, $\alpha = 99.09(5)^\circ$, $\beta = 106.26(6)^\circ$, $\gamma = 99.96(4)^\circ$, $V = 452.1(4)$ Å³, $M_r = 179.22$, space group P $\bar{1}$, $Z = 2$, $d_{\text{calc}} = 1.317$ g/cm³, $\mu(\text{MoK}\alpha) = 0.090$ mm⁻¹, $F(000) = 192$. Intensities of 1945 reflections (1409 independent, $R_{\text{int}} = 0.026$) were measured on the «Xcalibur-3» diffractometer (graphite monochromated MoK α radiation, CCD detector, ω -scanning, $2\Theta_{\text{max}} = 50^\circ$).

The crystals of 1-*s-trans* **6aa** (C₉H₁₃ON₃ · C₂H₄O₂) are monoclinic. At 100 K $a = 10.189(5)$, $b = 12.790(5)$, $c = 10.726(5)$ Å, $\beta = 116.318(5)^\circ$, $V = 1253(1)$ Å³, $M_r = 239.28$, space group P2₁/n, $Z = 4$, $d_{\text{calc}} = 1.269$ g/cm³, $\mu(\text{MoK}\alpha) = 0.094$ mm⁻¹, $F(000) = 512$. Intensities of 4284 reflections (2129 independent, $R_{\text{int}} = 0.031$) were measured on the «Xcalibur-3» diffractometer (graphite monochromated MoK α radiation, CCD detector, ω -scanning, $2\Theta_{\text{max}} = 50^\circ$).

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 $U_{\text{iso}} = nU_{\text{eq}}$ 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 $F > 4\sigma(F)$, $S = 0.892$).

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 $F > 4\sigma(F)$, $S = 0.868$).

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.

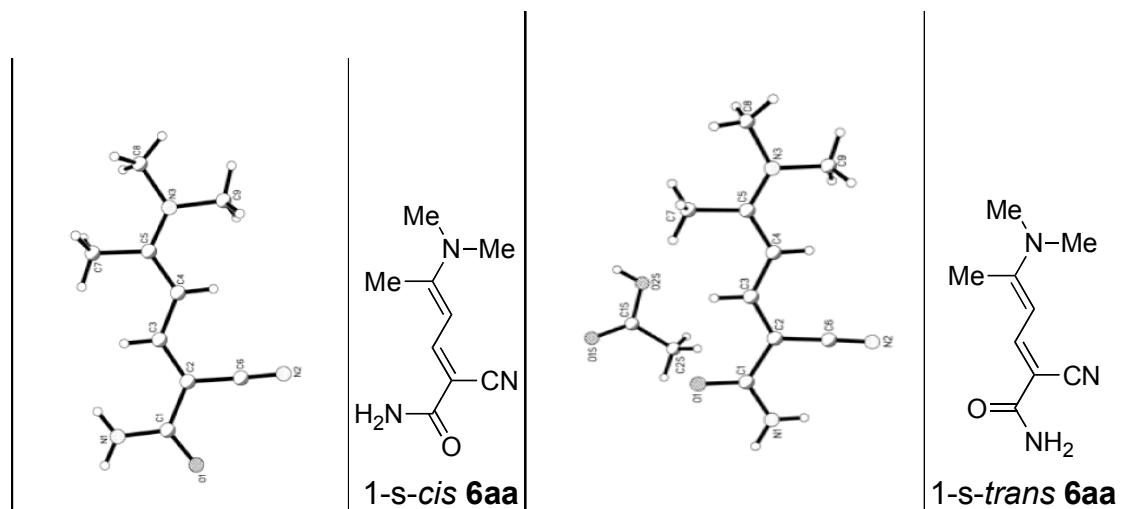


Figure 1. Molecular structures of rotational isomers of the compound **6aa**: *1s-cis*-(*2E,4E*)-2-cyano-5-(dimethylamino)hexa-2,4-dienamide (*1-s-cis* **6aa**) and *1s-trans*-(*2E,4E*)-2-cyano-5-(dimethylamino)hexa-2,4-dienamide (*1-s-trans* **6aa**) obtained by single crystal X-ray analysis (atom numbering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

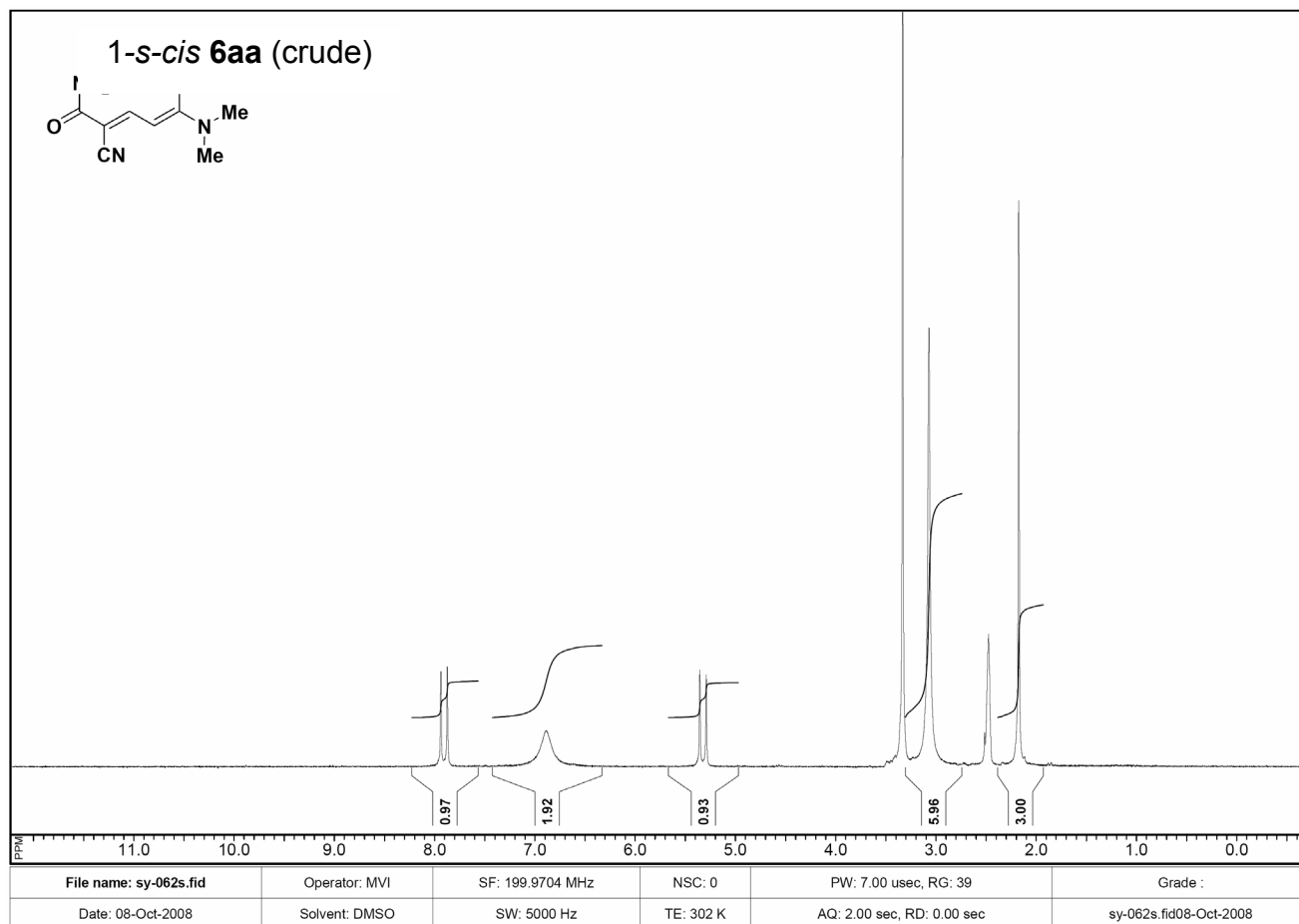
*Van der Waals radii sum:²⁵ 2.87 Å for H···C, 2.34 Å for H···H and 2.67 Å for H···N.

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- <i>s-cis</i> 6aa		1- <i>s-trans</i> 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

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