# Crystal structure of 4-aza-2-(hydroxyimino)-3-methyl-5-(2-pyridyl)pent-3-ene, $C_{10}H_{13}N_3O$

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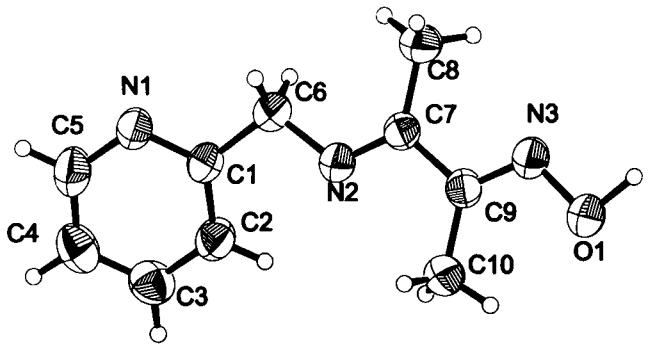


**Abstract**

$C_{10}H_{13}N_3O$, monoclinic, $P12_1/c1$ (No. 14), $a = 7.1477(9)$ Å, $b = 18.768(2)$ Å, $c = 7.651(1)$ Å, $\beta = 91.36(1)°$, $V = 1026.1$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.045$, $wR_{all}(F^2) = 0.157$, $T = 291$ K.

**Source of material**

5 g (49.5 mmol) of biacethyl monoxime were dissolved in 20 mL of diisopropylic ether with 4.7 mL (5 g, 46.2 mmol) of 2-(2-aminomethyl)pyridine. The mixture was refluxed by one hour and cooled, then filtered and the resulting product washed with ethyl alcohol. Colourless needle crystals were obtained after recrystallization from ethanol at 277 K. Crystals were separated by filtration, washed with ehtyl ether and dried under vacuum (mp 416 K).

**Discussion**

The C6–C10,N2,N3,O1 moiety is almost planar (rms deviation of the best least square plane through them being 0.040 Å) making an angle of 28.39(6)° with the pyridine ring. It is interesting to note that the molecule exhibits two intramolecular short contacts: C10–H10A···O1 ($d$(H···O) = 2.23 Å; ∠C–H···O = 107°) and C2–H2···N2 ($d$(H···N) = 1.51 Å, ∠C–H···N = 99°) which are responsible for the particular arrangement of the molecule. In order to study the influence of these short contacts in the molecular conformation a series of Potential Energy Surfaces (PES) calculations were performed (MOPAC7.01 [1,2] and GAMESS98 [3]). The geometry optimization calculations, using AM1 and 6-31G*, showed that there is a change in the conformation, the N2–C6–C1–N1 torsion angle changes from 156.1(2)° to 180°. This involves the C2–H2···N2 interaction, in fact the H2···N2 distance shortens from 2.51 Å to 2.48 Å. As the molecules are joined through a classical hydrogen bond involving the pyridyl N atom and the hydroxyl group: $d$(H1O1···N1$^i$) = 1.66 Å, ∠O1–H1O1···N1$^i$ = 177° ($i = 1-x, 0.5+y, 0.5-z$). We can postulate that, in this case, the molecular conformation is driven more by the intermolecular interaction. Whether all the mentioned C–H···X interactions are true hydrogen bonds is difficult to assert because, as pointed out by *Cotton et al.* [4], 'the field is getting muddier and muddier as the definition of a hydrogen bond is relaxed'. In any case, we have only take into account those with H···X distance less than the sum of the van der Waal's radii [5] plus 10% and with an C–H···O angle greater than, or very close to 100°.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | colourless, irregular, size 0.10 × 0.20 × 0.25 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| μ: | 0.84 cm$^{-1}$ |
| Diffractometer, scan mode: | CAD-4 Mach 3, ω/2θ |
| $2\theta_{max}$: | 51.8° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 2129, 1980 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 1070 |
| $N(param)_{refined}$: | 129 |
| Programs: | SIR92 [6], MolEn [7], SHELXL-97 [8] PARST95[9], ZORTEP [10], WinGX [11] PLATON [12] |

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1O1) | 4e | 0.4774 | 0.6749 | 0.3921 | 0.075 |
| H(6A) | 4e | 0.4794 | 0.3494 | 0.0214 | 0.060 |
| H(6B) | 4e | 0.5113 | 0.3198 | 0.2119 | 0.060 |
| H(5) | 4e | 0.8199 | 0.1355 | 0.0093 | 0.072 |
| H(10A) | 4e | 0.8604 | 0.5825 | 0.3170 | 0.090 |
| H(10B) | 4e | 0.8760 | 0.5232 | 0.1740 | 0.090 |
| H(10C) | 4e | 0.8725 | 0.5022 | 0.3722 | 0.090 |
| H(8A) | 4e | 0.2805 | 0.4164 | 0.1434 | 0.089 |
| H(8B) | 4e | 0.2652 | 0.4987 | 0.1749 | 0.089 |
| H(8C) | 4e | 0.2797 | 0.4465 | 0.3345 | 0.089 |
| H(3) | 4e | 1.1404 | 0.2998 | –0.1124 | 0.073 |
| H(2) | 4e | 0.9076 | 0.3750 | –0.0154 | 0.067 |
| H(4) | 4e | 1.0971 | 0.1774 | –0.0928 | 0.076 |

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**Table 3.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| O(1) | 4*e* | 0.5960(2) | 0.64319(8) | 0.3570(2) | 0.056(1) | 0.0436(9) | 0.089(1) | –0.0010(7) | 0.0041(9) | –0.0137(9) |
| N(3) | 4*e* | 0.5032(3) | 0.58012(9) | 0.3090(2) | 0.052(1) | 0.041(1) | 0.057(1) | –0.0002(8) | 0.0047(9) | –0.0023(8) |
| N(2) | 4*e* | 0.6418(2) | 0.41251(9) | 0.1715(2) | 0.047(1) | 0.040(1) | 0.056(1) | –0.0004(8) | 0.0045(8) | –0.0038(9) |
| N(1) | 4*e* | 0.7019(2) | 0.22682(9) | 0.0587(2) | 0.054(1) | 0.038(1) | 0.052(1) | –0.0004(8) | –0.0023(8) | 0.0001(8) |
| C(1) | 4*e* | 0.7292(3) | 0.2974(1) | 0.0528(3) | 0.050(1) | 0.039(1) | 0.038(1) | –0.0025(9) | 0.0001(9) | –0.0001(9) |
| C(7) | 4*e* | 0.5290(3) | 0.4611(1) | 0.2173(3) | 0.042(1) | 0.040(1) | 0.043(1) | –0.0002(9) | 0.0065(9) | 0.0048(9) |
| C(6) | 4*e* | 0.5717(3) | 0.3432(1) | 0.1152(3) | 0.048(1) | 0.043(1) | 0.060(1) | –0.004(1) | 0.005(1) | 0.001(1) |
| C(9) | 4*e* | 0.6163(3) | 0.5295(1) | 0.2741(3) | 0.045(1) | 0.041(1) | 0.046(1) | 0.0025(9) | 0.0053(9) | 0.0021(9) |
| C(5) | 4*e* | 0.8385(4) | 0.1845(1) | 0.0044(3) | 0.073(2) | 0.041(1) | 0.067(2) | 0.006(1) | –0.002(1) | –0.007(1) |
| C(10) | 4*e* | 0.8250(3) | 0.5348(1) | 0.2853(3) | 0.048(1) | 0.052(1) | 0.080(2) | 0.001(1) | 0.006(1) | –0.011(1) |
| C(8) | 4*e* | 0.3198(3) | 0.4552(1) | 0.2175(3) | 0.046(1) | 0.056(1) | 0.077(2) | –0.004(1) | 0.011(1) | –0.008(1) |
| C(3) | 4*e* | 1.0307(3) | 0.2812(1) | –0.0680(3) | 0.055(2) | 0.068(2) | 0.058(2) | 0.002(1) | 0.014(1) | –0.003(1) |
| C(2) | 4*e* | 0.8917(3) | 0.3258(1) | –0.0109(3) | 0.058(1) | 0.046(1) | 0.063(2) | –0.004(1) | 0.012(1) | 0.002(1) |
| C(4) | 4*e* | 1.0046(4) | 0.2089(1) | –0.0581(3) | 0.064(2) | 0.065(2) | 0.061(2) | 0.017(1) | 0.004(1) | –0.011(1) |

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## References

1. Csern, I.: MOPAC7.01 for linux (public domain version). Institute of Nucl. Research of Hung. Acad. Sci. H-4001 Debrecen POB 51, Hungary.
2. Stewart, J. J. P.: MOPAC: A Semiempirical Molecular Orbital Program. J. Comput. Aid. Mol. Des. **4** (1990) 1-105.
3. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T., Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. S.; Dupuis, M.; Montgomery, J. A.: GAMESS98: J. Comput. Chem. **14** (1993) 1347-1363.
4. Cotton, F. A.; Daniels, L. M.; Jordan, G. T.; Murillo, C. A.: The crystal packing of bis(2,2'-dipyridylamido)cobalt(II), $Co(dpa)_2$, is stabilized by C–H···N bonds: are there any real precedents? J. Chem. Soc. Chem. Commun. (1997) 1673-1674.
5. Paulig, L.: The Nature of the Chemical Bond. 3rd. Ed., Cornell University Press, Ithaca, NY 1960.
6. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.: Completion and refinement of crystal structures with SIR92. J. Appl. Crystallogr. **26** (1993) 343-350.
7. Fair, C. K.: MolEn. An Interactive Intelligent System for Crystal Structure Analysis. Enraf-Nonius, Delft, The Netherlands 1990.
8. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
9. Nardelli, M.: PARST95 - an update to PARST: a system of Fortran routines for calculating molecular structure parameters from the result of crystal structure analyses. J. Appl. Crystallogr. **28** (1995) 659.
10. Zsolnai, L.: ZORTEP. An Interactive Molecular Graphics Program. University of Heidelberg, Germany 1995.
11. Farrugia, L. J.: WinGX suite for small-molecule single-crystal crystallography. J. Appl. Crystallogr. **32** (1999) 837-838.
12. Spek, A.L.: PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands 1998.