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Crystal structure of *rel*-(3a*R*,6a*S*)-6-methyl-3,6a-diphenyl-3a,4,6,6a-tetrahydro-isoxazolo[5,4-*c*]isoxazole, $C_{17}H_{16}N_2O_2$

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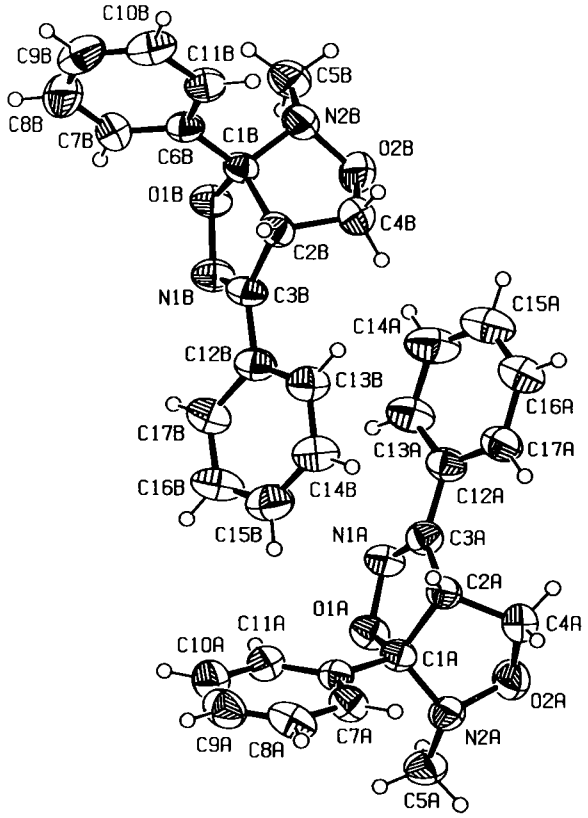

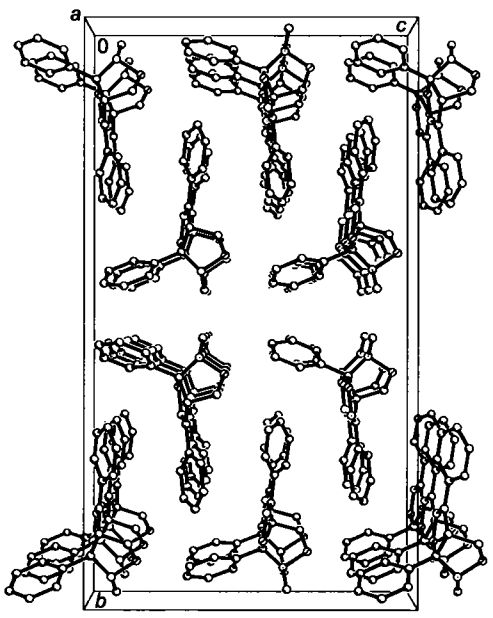

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Abstract

$C_{17}H_{16}N_2O_2$, orthorhombic, $Pca2_1$ (no. 29), a = 5.6406(8) Å, b = 30.292(4) Å, c = 16.925(3) Å, V = 2891.9 Å^3, Z = 8, $R_{gt}(F)$ = 0.084, $wR_{ref}(F^2)$ = 0.236, T = 293 K.

Source of material

The title compound has been obtained by 1,3-dipolar cycloaddition of 2-methyl-3-phenyl-2,5-dihydroisoxazole and benzhydroximoyl chloride in the presence of triethylamine as a base [1-7]. Purification by chromatography (ethyl acetate/petroleum ether) and crystallization from ethanol gave the title cyclo-adduct in the form of colorless crystals (m.p. 403-405 K) [1,2,4].

Experimental details

The rather high remaining electron density (0.43 eÅ^{-3}) correlates with the R_{gt} and wR_{ref} values being larger than expected. The reason of this behavior results from the poor crystal quality represented by broad reflection profiles and instabilities of the orientation matrix of the crystal during the measurement.

Discussion

The compound crystallizes with two independent molecules in the asymmetric unit. The N1=C3 double bond of the isoxazole moiety is clearly identified by the distances of 1.279(7) Å and 1.273(8) Å, respectively. The dihedral angles of the bicyclic systems are 73.2(3)° and 75.4(3)°. The tetrahydroisoxazole parts of the bicyclic systems show an envelope conformation, where O2 is out of plane (figure, top). In the cell plot we observe an antiparallel orientation of the molecules along the c axis. We also find non-polar layers in the a,c plane stacked along the b axis generated by the phenyl moieties. The b,c view of the cell plot also shows a face-to-face orientation of the molecules along the a axis (figure, bottom).

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.05 × 0.40 × 0.50 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	6.90 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{max}$:	134.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4723, 4515
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2370
$N(param)_{refined}$:	380
Programs:	SHELXS-97 [8], SHELXL-97 [9], SHELXTL-Plus [10]

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

Atom	Site	x	y	z	U_{iso}
H(2A)	4*a*	1.2230	0.3506	0.2834	0.066
H(4A1)	4*a*	1.1478	0.3443	0.4376	0.087
H(4A2)	4*a*	1.3100	0.3822	0.4034	0.087
H(5A1)	4*a*	0.8084	0.4806	0.3997	0.113
H(5A2)	4*a*	0.6308	0.4439	0.3720	0.113
H(5A3)	4*a*	0.7498	0.4752	0.3097	0.113
H(7A)	4*a*	1.3178	0.4399	0.2417	0.075
H(8A)	4*a*	1.4142	0.4690	0.1203	0.097
H(9A)	4*a*	1.1709	0.4610	0.0150	0.102
H(10A)	4*a*	0.8230	0.4241	0.0282	0.103
H(11A)	4*a*	0.7021	0.3968	0.1503	0.078
H(13A)	4*a*	0.6576	0.2482	0.2699	0.099
H(14A)	4*a*	0.7484	0.1743	0.2864	0.124
H(15A)	4*a*	1.0894	0.1530	0.3480	0.116
H(16A)	4*a*	1.3602	0.2051	0.3879	0.098
H(17A)	4*a*	1.2854	0.2797	0.3718	0.095

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(2B)	4*a*	1.2854	0.1486	0.0311	0.071
H(4B1)	4*a*	1.3668	0.1163	0.1509	0.090
H(4B2)	4*a*	1.2092	0.1549	0.1849	0.090
H(5B1)	4*a*	0.8447	0.0199	0.1478	0.123
H(5B2)	4*a*	0.7848	0.0254	0.0579	0.123
H(5B3)	4*a*	0.6734	0.0576	0.1201	0.123
H(7B)	4*a*	0.7553	0.1072	–0.1020	0.087
H(8B)	4*a*	0.8560	0.0797	–0.2242	0.106
H(9B)	4*a*	1.1957	0.0416	–0.2409	0.109
H(10B)	4*a*	1.4435	0.0289	–0.1362	0.102
H(11B)	4*a*	1.3601	0.0581	–0.0112	0.077
H(13B)	4*a*	1.3554	0.2188	0.1241	0.090
H(14B)	4*a*	1.4362	0.2930	0.1447	0.098
H(15B)	4*a*	1.1874	0.3459	0.0955	0.105
H(16B)	4*a*	0.8407	0.3269	0.0343	0.115
H(17B)	4*a*	0.7370	0.2533	0.0186	0.101

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(1A)	4*a*	0.6975(7)	0.3784(1)	0.2858(3)	0.049(2)	0.053(2)	0.078(3)	–0.004(2)	0.001(2)	0.007(2)
N(1A)	4*a*	0.6961(9)	0.3319(2)	0.2950(3)	0.060(3)	0.046(3)	0.075(4)	0.000(2)	0.005(3)	0.004(3)
C(1A)	4*a*	0.9371(9)	0.3956(2)	0.2905(4)	0.049(3)	0.047(3)	0.060(4)	–0.005(2)	0.004(3)	0.004(3)
O(2A)	4*a*	0.975(1)	0.4015(2)	0.4225(3)	0.093(4)	0.080(3)	0.058(3)	0.013(3)	0.002(3)	0.001(2)
N(2A)	4*a*	0.9710(9)	0.4284(2)	0.3505(3)	0.072(3)	0.057(3)	0.052(3)	0.004(3)	0.007(3)	–0.004(2)
C(2A)	4*a*	1.084(1)	0.3556(2)	0.3171(4)	0.056(3)	0.049(3)	0.060(4)	0.000(3)	–0.003(3)	0.001(3)
C(3A)	4*a*	0.906(1)	0.3189(2)	0.3113(4)	0.057(3)	0.053(3)	0.062(4)	–0.009(3)	0.004(3)	0.003(3)
C(4A)	4*a*	1.153(1)	0.3694(2)	0.4020(4)	0.084(5)	0.071(4)	0.061(5)	0.003(4)	–0.007(4)	0.001(4)
C(5A)	4*a*	0.773(1)	0.4598(2)	0.3587(4)	0.084(5)	0.062(4)	0.081(5)	0.018(4)	0.008(4)	–0.011(4)
C(6A)	4*a*	0.999(1)	0.4152(2)	0.2100(4)	0.056(3)	0.045(3)	0.055(4)	0.000(3)	0.004(3)	0.001(3)
C(7A)	4*a*	1.214(1)	0.4369(2)	0.1996(4)	0.054(4)	0.060(4)	0.074(5)	–0.008(3)	0.001(3)	0.010(3)
C(8A)	4*a*	1.272(1)	0.4540(2)	0.1263(5)	0.076(5)	0.063(4)	0.103(7)	0.011(4)	0.022(5)	0.022(4)
C(9A)	4*a*	1.128(2)	0.4494(2)	0.0638(5)	0.113(7)	0.073(5)	0.067(6)	0.012(5)	0.023(5)	0.016(4)
C(10A)	4*a*	0.920(2)	0.4278(2)	0.0720(5)	0.117(7)	0.077(5)	0.063(5)	0.011(5)	–0.005(5)	0.004(4)
C(11A)	4*a*	0.848(1)	0.4108(2)	0.1451(4)	0.070(4)	0.061(4)	0.064(5)	0.001(3)	0.000(4)	–0.004(3)
C(12A)	4*a*	0.959(1)	0.2719(2)	0.3211(4)	0.066(4)	0.054(4)	0.067(5)	–0.003(3)	0.012(3)	0.008(3)
C(13A)	4*a*	0.799(1)	0.2399(2)	0.2942(5)	0.084(5)	0.056(4)	0.107(7)	–0.003(4)	0.008(5)	0.010(4)
C(14A)	4*a*	0.854(2)	0.1957(2)	0.3044(6)	0.099(6)	0.057(4)	0.153(9)	–0.007(4)	0.005(7)	0.004(5)
C(15A)	4*a*	1.058(2)	0.1828(3)	0.3402(6)	0.106(7)	0.059(4)	0.125(8)	0.009(5)	0.030(6)	0.012(5)
C(16A)	4*a*	1.219(2)	0.2141(2)	0.3647(5)	0.084(5)	0.063(4)	0.097(6)	0.009(4)	0.014(5)	0.015(4)
C(17A)	4*a*	1.175(1)	0.2588(2)	0.3555(5)	0.087(5)	0.060(4)	0.089(6)	0.002(4)	–0.010(5)	0.009(4)
O(1B)	4*a*	0.7539(8)	0.1229(1)	0.0360(3)	0.047(2)	0.052(2)	0.081(3)	0.008(2)	0.010(2)	–0.004(2)
N(1B)	4*a*	0.759(1)	0.1694(2)	0.0470(4)	0.053(3)	0.052(3)	0.084(4)	0.005(3)	0.010(3)	–0.005(3)
C(1B)	4*a*	0.988(1)	0.1047(2)	0.0358(4)	0.049(3)	0.045(3)	0.061(4)	0.009(2)	–0.001(3)	0.001(3)
N(2B)	4*a*	1.020(1)	0.0715(2)	0.0971(3)	0.077(4)	0.057(3)	0.063(4)	0.003(3)	0.000(3)	0.010(3)
O(2B)	4*a*	1.027(1)	0.0981(2)	0.1700(3)	0.105(4)	0.082(3)	0.052(3)	–0.003(3)	0.000(3)	0.001(2)
C(2B)	4*a*	1.146(1)	0.1439(2)	0.0646(4)	0.053(3)	0.058(4)	0.067(5)	0.007(3)	–0.005(3)	0.005(3)
C(3B)	4*a*	0.972(1)	0.1813(2)	0.0603(4)	0.064(4)	0.044(3)	0.076(5)	0.013(3)	0.010(4)	–0.001(3)
C(4B)	4*a*	1.211(2)	0.1298(2)	0.1493(4)	0.095(6)	0.067(4)	0.064(5)	–0.004(4)	–0.005(4)	0.005(4)
C(5B)	4*a*	0.812(1)	0.0408(2)	0.1066(5)	0.104(6)	0.061(4)	0.081(6)	–0.013(4)	0.007(5)	0.016(4)
C(6B)	4*a*	1.048(1)	0.0856(2)	–0.0437(4)	0.058(3)	0.045(3)	0.060(4)	0.004(3)	0.012(3)	–0.004(3)
C(7B)	4*a*	0.897(1)	0.0918(2)	–0.1084(4)	0.087(5)	0.067(4)	0.063(5)	0.004(4)	–0.008(4)	0.007(3)
C(8B)	4*a*	0.956(2)	0.0751(3)	–0.1814(5)	0.118(7)	0.095(6)	0.052(5)	–0.002(5)	0.011(5)	–0.004(4)
C(9B)	4*a*	1.157(2)	0.0525(3)	–0.1913(5)	0.136(8)	0.072(5)	0.064(6)	–0.036(5)	0.035(6)	–0.013(4)
C(10B)	4*a*	1.306(2)	0.0453(2)	–0.1286(5)	0.091(6)	0.061(4)	0.103(7)	–0.003(4)	0.018(5)	–0.019(4)
C(11B)	4*a*	1.256(1)	0.0624(2)	–0.0532(4)	0.061(4)	0.060(4)	0.072(5)	0.013(3)	0.010(3)	–0.010(3)
C(12B)	4*a*	1.036(1)	0.2278(2)	0.0709(4)	0.065(4)	0.052(3)	0.075(5)	0.007(3)	0.012(4)	–0.002(3)
C(13B)	4*a*	1.249(1)	0.2402(2)	0.1073(5)	0.078(4)	0.059(4)	0.088(6)	0.005(4)	0.002(4)	–0.005(4)
C(14B)	4*a*	1.299(1)	0.2847(2)	0.1181(5)	0.085(5)	0.063(4)	0.098(6)	–0.001(4)	0.007(5)	–0.008(4)
C(15B)	4*a*	1.149(2)	0.3163(3)	0.0897(5)	0.104(6)	0.065(4)	0.094(6)	0.002(4)	0.017(5)	–0.011(4)
C(16B)	4*a*	0.941(2)	0.3049(2)	0.0529(6)	0.105(7)	0.049(4)	0.133(8)	0.011(4)	0.008(6)	0.003(5)
C(17B)	4*a*	0.879(1)	0.2609(2)	0.0430(5)	0.094(5)	0.062(4)	0.097(6)	0.017(4)	–0.004(5)	0.004(4)

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References

1. Sunitha, S.: Dissertation, University Stuttgart (planned).
2. Sunitha, S.; Bathich, Y.; Henneböhle, M.; Le Roy, P.-Y.; Jäger, V.: *N*-Methylisoxazolium salts: Building Blocks for the Stereoselective Synthesis of Branched Amino Polyols and Amino Acids. 7th Conference on Iminium Salts (ImSaT-7) Bartholomä (Germany) September 5-8, 2005, Book of Abstracts, p. 141.
3. Le Roy, P.-Y.: Neue Reaktionen von Isoxazolinen und Isoxazolinium-Salzen: Reduktion, stereoselektive CC-Verknüpfung durch Addition von Nucleophilen. Synthese ungewöhnlicher Aminohydroxysäuren. Dissertation, Universität Stuttgart 1997.
4. Gibert, J. P.; Petrus, C.; Petrus, F.: Action de l'oxyde de benzonitrile sur les isoxazolines-D_3. Synthèse et comportement chimique de mèthyl-6-diphenyl-3,6a tètrahydro-3a,4,6,6a-isoxazolo[5,4-*c*]isoxazoles. J. Chem. Res. (M) (1978) 2101-2118.
5. Shatzmiller, S.; Shalom, E.; Lidor, R.; Tartkovski, E.: Synthese und Umsetzungen von 3-Isoxazolinen. Liebigs Ann. Chem. (1983) 906-912.
6. Jäger, V.; Le Roy, P.-Y.; Henneböhle, M.; Bathich, Y.; Remen, L.; Imerhasan, M.: *N*-Methylisoxazolinium Salts: An Inconspicuous Class of Compounds with High Potential for Organic Synthesis. 6th Conference on Iminium Salts (ImSaT-6) Stimpfach-Rechenberg September 16-18, 2003, Book of Abstracts, p. 99-107.
7. Henneböhle, M.; Le Roy, P.-Y.; Hein, M.; Ehrler, R.; Jäger, V.: Isoxazolinium Salts in Asymmetric Synthesis. 1. Stereoselective Reduction Induced by a 3'-Alkoxy Stereocentre. A New Approach to Polyfunctionalized β-Amino Acids. Z. Naturforsch. **59b** (2004) 451-467.
8. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
9. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
10. Sheldrick, G. M.: SHELXTL-Plus. Structure Determination Software Suite. Release 4.1. Siemens Analytical Systems, Madison, Wisconsin, USA 1991.