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Synthesis and Crystal Structure Characterization of (6*R*,7a*S*)-1,1-Diphenyl-6-(4-vinylbenzyloxy)tetrahydropyrrolo[1,2-c]oxazol-3(*1H*)-one

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The title compound, (6R,7aS)-1,1-Diphenyl-6-(4-vinylbenzyloxy)tetrahydropyrrolo [1,2-c]oxazol -3(1H)-one, was synthesized and characterized by ^{1}H and ^{13}C NMR and high-resolution mass spectrometry (HRMS). Its molecular configuration was investigated by X-ray crystallography. The crystal structure is devoid of any classical hydrogen bonding, and molecules are linked by weak C—H···O contacts. In the 4-vinylbenzyloxy group, the three H atoms and one C atom are disordered over two sets of sites, with site occupancy factors of 0.75 and 0.25.

Keywords Chirality; Jørgensen–Hayashi catalyst; single crystal; X-ray diffraction

Introduction

(S)-α, α-Diarylprolinol silyl ethers, also known as Jørgensen–Hayashi catalysts, were proven to be promising organocatalysts [1]. Therefore, novel synthetic routes to such new kind of compounds are of interest. In this paper, the title compound, as an intermediate to some functional Jørgensen–Hayashi catalysts, was synthesized. Furthermore, the title compound, (6R,7aS)-1,1-Diphenyl-6-(4-utetrahydropyrrolo[1,2-c]oxazol-3(*1H*)-one, (Fig. 1), was characterized by H and ^{13}C NMR, and HRMS spectroscopy. Its crystal structure was investigated by X-ray single-crystal diffraction analysis.

Experimental

^{1}H and ^{13}C NMR were recorded in $CDCl_3$ on Bruker AVANCE III (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Proton chemical shifts (δ) are relative to tetramethylsilane

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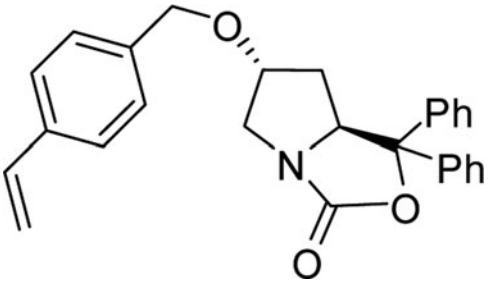


Figure 1. Structure of the title compound.

Table 1. Crystal data and structure refinement parameters of compound **1**

Parameter	Value	
CCDC deposition number	1026620	
Empirical formula	C27 H25 N O3	
Formula weight	411.48	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 15.279(8) Å	$\boldsymbol{a} = 90^\circ$
	b = 10.115(6) Å	$\beta = 107.785(8)^\circ$
	c = 14.709(9) Å	$\gamma = 90^\circ$
Volume	2165(2) Å3	
Z	4	
Density (calculated)	1.263 Mg/m3	
Absorption coefficient	0.082 mm-1	
F(000)	872	
Crystal size	0.187 × 0.123 × 0.056 mm3	
Theta range for data collection	2.452 to 25.476°.	
Index ranges	$-15 <= h <= 18$, $-11 <= k <= 12$, $-10 <= l <= 17$	
Reflections collected	5444	
Independent reflections	3760 [R(int) = 0.0278]	
Completeness to theta = 25.242°	96.6%	
Absorption correction	Semiempirical from equivalents	
Max. and min. transmission	0.7456 and 0.2435	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3760/21/289	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0689, $wR2$ = 0.1116	
R indices (all data)	R1 = 0.1197, $wR2$ = 0.1237	
Absolute structure parameter	1.0(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.219 and −0.177 e.Å-3	

Table 2. Atomic coordinates and equivalent thermal parameters of the nonhydrogen atoms (Å^2). $U_{eq} = (1/3) \sum i \sum j\ Uij a_i^* a_j^* (a_i . a_j)$

Atom	*x*	*y*	*z*	*U*eq	*Occ. (<1)*
N(1)	1.0044(3)	0.3955(5)	0.7640(4)	0.057(1)	
O(1)	1.0745(3)	0.5022(5)	0.6667(3)	0.088(2)	
O(2)	0.9793(3)	0.3317(4)	0.6133(3)	0.064(1)	
O(3)	0.8764(3)	0.5094(5)	0.8919(3)	0.080(1)	
C(1)	1.0239(4)	0.4190(7)	0.6811(5)	0.063(2)	
C(2)	0.9236(4)	0.2451(5)	0.6514(4)	0.049(2)	
C(3)	0.9196(4)	0.3196(5)	0.7402(4)	0.051(2)	
C(4)	0.8477(4)	0.4259(6)	0.7298(5)	0.063(2)	
C(5)	0.8941(4)	0.5285(6)	0.8050(5)	0.066(2)	
C(6)	0.9976(5)	0.5062(7)	0.8230(4)	0.077(2)	
C(7)	0.7934(5)	0.5728(7)	0.8950(6)	0.088(2)	
C(8)	0.8031(5)	0.7180(7)	0.9031(5)	0.067(2)	
C(9)	0.8695(5)	0.7744(8)	0.9762(5)	0.086(2)	
C(10)	0.8782(6)	0.9085(9)	0.9834(6)	0.096(2)	
C(11)	0.8208(5)	0.9916(8)	0.9193(5)	0.072(2)	
C(12)	0.7553(5)	0.9351(9)	0.8473(6)	0.089(2)	
C(13)	0.7463(5)	0.8006(9)	0.8390(5)	0.086(2)	
C(14)	0.8263(7)	1.1351(9)	0.9259(7)	0.107(3)	
C(15)	0.8872(9)	1.1982(13)	0.9966(9)	0.124(4)	0.75
C(15′)	0.8370(30)	1.2510(30)	0.9550(30)	0.131(7)	0.25
C(16)	0.8314(4)	0.2308(6)	0.5762(4)	0.051(2)	
C(17)	0.7618(5)	0.1634(7)	0.5963(4)	0.071(2)	
C(18)	0.6766(5)	0.1538(7)	0.5308(5)	0.077(2)	
C(19)	0.6585(5)	0.2122(7)	0.4447(5)	0.078(2)	
C(20)	0.7269(6)	0.2808(7)	0.4233(5)	0.083(2)	
C(21)	0.8130(5)	0.2895(6)	0.4883(5)	0.066(2)	
C(22)	0.9745(4)	0.1154(6)	0.6743(4)	0.051(2)	
C(23)	0.9582(4)	0.0260(7)	0.7379(4)	0.068(2)	
C(24)	1.0016(6)	−0.0930(7)	0.7553(5)	0.084(2)	
C(25)	1.0610(6)	−0.1289(8)	0.7075(6)	0.093(3)	
C(26)	1.0781(5)	−0.0430(8)	0.6443(6)	0.095(3)	
C(27)	1.0359(4)	0.0775(7)	0.6277(5)	0.075(2)	

($\delta = 0.0$) as internal standard and expressed in parts per million. Spin multiplicities are given as *s* (singlet), *d* (doublet), *t* (triplet), and *q* (quartet) as well as *b* (broad). Coupling constants (*J*) are given in hertz. High-resolution mass spectrometry (HRMS) data were measured on an Agilent 6120 LC/TOF-MS with ESI source.

Synthesis of (6*R*,7a*S*)-1,1-Diphenyl-6-(4-vinylbenzyloxy)tetrahydropyrrolo[1,2-c]oxazol-3(*1H*) -one **1** Sodium hydride (1.69 g, 0.044 mmol, 4.4 eq, 60 (*ω*%)) was added in a N_2-filled round-bottom flask containing 30 mL dried N,N-dimethylformamide (DMF) at room temperature with stirring for 10 min. Then, the solution of **2** [2] (3.41 g, 0.01 mmol, 1 eq) in 9 mL of dried DMF was added in 30 min at 0°C. After an hour, 1-(chloromethyl)-4-vinylbenzene (1.67 g, 0.011 mmol, 1.1 eq) was added slowly using a septum. The resulting

Table 3. bond lengths (A°) for the title compound **1**

Atoms	Length	Atoms	Length
N(1)-C(1)	1.361(7)	C(12)-H(12)	0.9300
N(1)-C(6)	1.440(7)	C(13)-H(13)	0.9300
N(1)-C(3)	1.455(7)	C(14)-C(15′)	1.24(2)
O(1)-C(1)	1.205(7)	C(14)-C(15)	1.328(12)
O(2)-C(1)	1.350(7)	C(14)-H(14)	0.9601
O(2)-C(2)	1.448(6)	C(14)-H(14′)	0.9675
O(3)-C(5)	1.399(6)	C(15)-H(15A)	0.9300
O(3)-C(7)	1.434(7)	C(15)-H(15B)	0.9300
C(2)-C(22)	1.510(7)	C(15')-H(15C)	0.9300
C(2)-C(16)	1.510(7)	C(15')-H(15D)	0.9300
C(2)-C(3)	1.524(7)	C(16)-C(17)	1.368(8)
C(3)-C(4)	1.512(7)	C(16)-C(21)	1.372(7)
C(3)-H(3)	0.9800	C(17)-C(18)	1.367(8)
C(4)-C(5)	1.524(8)	C(17)-H(17)	0.9300
C(4)-H(4A)	0.9700	C(18)-C(19)	1.346(9)
C(4)-H(4B)	0.9700	C(18)-H(18)	0.9300
C(5)-C(6)	1.538(8)	C(19)-C(20)	1.368(9)
C(5)-H(5)	0.9800	C(19)-H(19)	0.9300
C(6)-H(6A)	0.9700	C(20)-C(21)	1.373(9)
C(6)-H(6B)	0.9700	C(20)-H(20)	0.9300
C(7)-C(8)	1.478(9)	C(21)-H(21)	0.9300
C(7)-H(7A)	0.9700	C(22)-C(27)	1.376(7)
C(7)-H(7B)	0.9700	C(22)-C(23)	1.376(8)
C(8)-C(13)	1.356(9)	C(23)-C(24)	1.360(9)
C(8)-C(9)	1.358(9)	C(23)-H(23)	0.9300
C(9)-C(10)	1.364(10)	C(24)-C(25)	1.356(9)
C(9)-H(9)	0.9300	C(24)-H(24)	0.9300
C(10)-C(11)	1.363(9)	C(25)-C(26)	1.355(10)
C(10)-H(10)	0.9300	C(25)-H(25)	0.9300
C(11)-C(12)	1.343(10)	C(26)-C(27)	1.366(9)
C(11)-C(14)	1.456(11)	C(26)-H(26)	0.9300
C(12)-C(13)	1.369(10)	C(27)-H(27)	0.9300

reaction mixture was allowed to react with stirring at ambient temperature. Subsequently, the reaction was quenched with diethyl ether (10 mL) and water (10 mL). The layers were separated and the aqueous phase was extracted with diethyl ether several times. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 85:15) to afford the title compound **1** as colorless solid, yield: 18.5 g, 90%. b**^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.58−7.56 (m, 2H), 7.45−7.42 (m, 2H), 7.41−7.37 (m, 6H), 7.35−7.27 (m, 4H), 6.76−6.72 (q, J = 11.0, 17.5 Hz, 1H), 5.81−5.78 (m, 1H), 5.31−5.28 (m, 1H), 4.90−4.93 (q, J = 5.0, 11.5 Hz, 1H), 4.48 (s, 2H), 4.18 (t, J = 5.5 Hz, 1H), 4.08−4.05(q, J = 5.5, 12.5 Hz, 1H), 3.38−3.35 (m, 1H), 1.96−1.92 (q, J = 5.0, 13.5 Hz, 1H), 1.25−1.19 (m, 1H) ppm; **^{13}C**

Table 4. Bond angles (°) for the title compound **1**

Atoms	Angle	Atoms	Angle
C(1)-N(1)-C(6)	118.7(5)	C(11)-C(12)-C(13)	121.6(7)
C(1)-N(1)-C(3)	107.4(5)	C(11)-C(12)-H(12)	119.2
C(6)-N(1)-C(3)	109.4(4)	C(13)-C(12)-H(12)	119.2
C(1)-O(2)-C(2)	109.5(5)	C(8)-C(13)-C(12)	121.7(7)
C(5)-O(3)-C(7)	112.7(5)	C(8)-C(13)-H(13)	119.2
O(1)-C(1)-O(2)	122.2(6)	C(12)-C(13)-H(13)	119.2
O(1)-C(1)-N(1)	127.4(7)	C(15′)-C(14)-C(11)	165(2)
O(2)-C(1)-N(1)	110.4(6)	C(15)-C(14)-C(11)	122.9(11)
O(2)-C(2)-C(22)	106.8(4)	C(15)-C(14)-H(14)	118.7
O(2)-C(2)-C(16)	107.6(5)	C(11)-C(14)-H(14)	118.4
C(22)-C(2)-C(16)	112.5(5)	C(15′)-C(14)-H(14′)	96.2
O(2)-C(2)-C(3)	102.4(4)	C(11)-C(14)-H(14′)	98.9
C(22)-C(2)-C(3)	113.0(5)	C(14)-C(15)-H(15A)	120.0
C(16)-C(2)-C(3)	113.7(5)	C(11)-C(14)-H(14′)	120.0
N(1)-C(3)-C(4)	102.4(5)	C(14)-C(15)-H(15A)	120.0
N(1)-C(3)-C(2)	101.6(4)	C(14)-C(15)-H(15B)	120.0
C(4)-C(3)-C(2)	118.9(5)	H(15A)-C(15)-H(15B)	120.0
N(1)-C(3)-H(3)	111.0	C(14)-C(15′)-H(15C)	119.7
C(4)-C(3)-H(3)	111.0	C(14)-C(15′)-H(15D)	120.3
C(2)-C(3)-H(3)	111.0	H(15C)-C(15′)-H(15D)	120.0
C(3)-C(4)-C(5)	104.4(5)	C(17)-C(16)-C(21)	118.0(6)
C(3)-C(4)-H(4A)	110.9	C(17)-C(16)-C(2)	120.2(5)
C(5)-C(4)-H(4A)	110.9	C(21)-C(16)-C(2)	121.7(5)
C(3)-C(4)-H(4B)	110.9	C(18)-C(17)-C(16)	121.3(6)
C(5)-C(4)-H(4B)	110.9	C(18)-C(17)-H(17)	119.4
H(4A)-C(4)-H(4B)	108.9	C(16)-C(17)-H(17)	119.4
O(3)-C(5)-C(4)	113.0(5)	C(19)-C(18)-C(17)	120.6(7)
O(3)-C(5)-C(6)	107.3(5)	C(19)-C(18)-H(18)	119.7
C(4)-C(5)-C(6)	104.6(5)	C(17)-C(18)-H(18)	119.7
O(3)-C(5)-H(5)	110.6	C(18)-C(19)-C(20)	119.2(7)
C(4)-C(5)-H(5)	110.6	C(18)-C(19)-H(19)	120.4
C(6)-C(5)-H(5)	110.6	C(20)-C(19)-H(19)	120.4
N(1)-C(6)-C(5)	105.7(5)	C(19)-C(20)-C(21)	120.6(7)
N(1)-C(6)-H(6A)	110.6	C(19)-C(20)-H(20)	119.7
C(5)-C(6)-H(6A)	110.6	C(21)-C(20)-H(20)	119.7
N(1)-C(6)-H(6B)	110.6	C(20)-C(21)-C(16)	120.4(6)
C(5)-C(6)-H(6B)	110.6	C(20)-C(21)-H(21)	119.8
H(6A)-C(6)-H(6B)	108.7	C(16)-C(21)-H(21)	119.8
O(3)-C(7)-C(8)	112.3(6)	C(27)-C(22)-C(23)	116.6(6)
O(3)-C(7)-H(7A)	109.1	C(27)-C(22)-C(2)	120.9(5)
C(8)-C(7)-H(7A)	109.1	C(23)-C(22)-C(2)	122.4(5)
O(3)-C(7)-H(7B)	109.1	C(24)-C(23)-C(22)	122.0(6)
C(8)-C(7)-H(7B)	109.1	C(24)-C(23)-H(23)	119.0

(Continued on next page)

Table 4. Bond angles (°) for the title compound **1***(Continued)*

Atoms	Angle	Atoms	Angle
H(7A)-C(7)-H(7B)	107.9	C(22)-C(23)-H(23)	119.0
C(13)-C(8)-C(9)	117.1(7)	C(25)-C(24)-C(23)	120.3(7)
C(13)-C(8)-C(7)	122.0(8)	C(25)-C(24)-H(24)	119.8
C(9)-C(8)-C(7)	120.9(8)	C(23)-C(24)-H(24)	119.8
C(8)-C(9)-C(10)	120.7(8)	C(26)-C(25)-C(24)	118.9(8)
C(8)-C(9)-H(9)	119.6	C(26)-C(25)-H(25)	120.5
C(10)-C(9)-H(9)	119.6	C(24)-C(25)-H(25)	120.5
C(11)-C(10)-C(9)	122.2(8)	C(25)-C(26)-C(27)	121.0(7)
C(11)-C(10)-H(10)	118.9	C(25)-C(26)-H(26)	119.5
C(9)-C(10)-H(10)	118.9	C(27)-C(26)-H(26)	119.5
C(12)-C(11)-C(10)	116.7(7)	C(26)-C(27)-C(22)	121.1(7)
C(12)-C(11)-C(14)	119.4(8)	C(26)-C(27)-H(27)	119.4
C(10)-C(11)-C(14)	123.8(8)	C(22)-C(27)-H(27)	119.4

NMR (125 MHz, $CDCl_3$): δ = 160.4, 143.0, 140.2, 137.4, 137.2, 136.4 (×2), 128.7 (×2), 128.5 (×2), 128.0 (×2), 127.8, 126.4 (×2), 126.1 (×2), 125.5 (×2), 114.2, 85.8, 78.4, 71.1, 67.5, 53.8, 36.2 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{26}NO_3$ 412.1913; found 412.1922.

Crystal Structure Analysis

The crystal structure of the title compound was solved by direct methods and was refined anisotropically by full matrix least-squares method on F^2. All H atoms were placed in their calculated positions and included in the refinement using the riding model. A summary of the salient crystallographic data is given in Table 1.

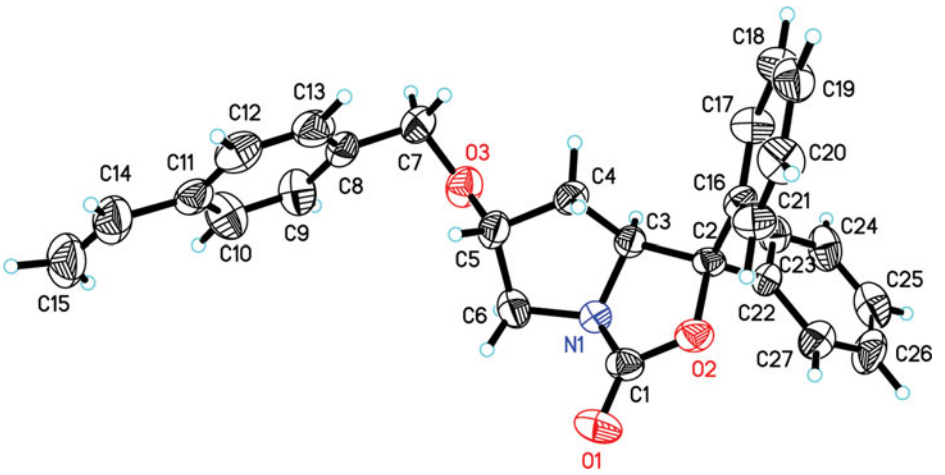


Figure 2. ORTEP of the molecule with thermal ellipsoids drawn at 50% probability.

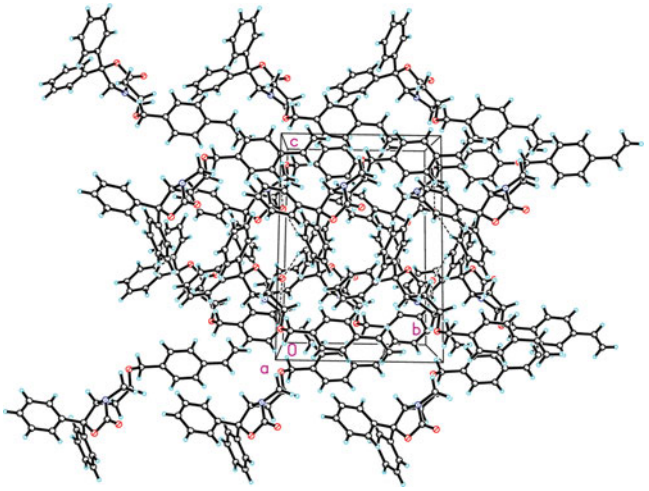
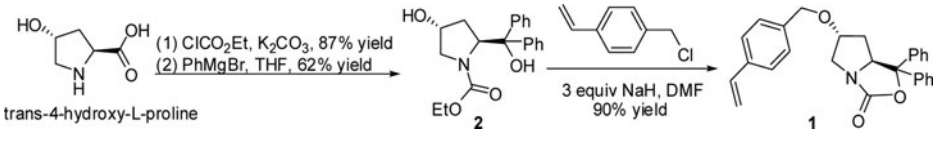


Figure 3. The crystal packing of the title compound **1**.

A single crystal suitable for X-ray diffraction obtained in acetonitrile and methanol (V/V = 1:4) was colorless and block. The single crystal XRD of the crystal was collected on a PROCESS-AUTO [3] diffractometer at 273(2) K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The cell was refined on a PROCESS-AUTO [3] and the data were reducted on a CrystalStructure [4] and corrected for absorption using multiscan [5]. The structure was solved by direct methods using SHELXS-97 and refined by a full-matrix least-squares procedure using the program SHELXL-97 [6]. Subsequent refinements were carried out with anisotropic thermal parameters for nonhydrogen atoms. H atoms were placed in calculated positions with C—H = 0.96 Å (sp^3), C—H = 0.93 Å (aromatic). All H atoms included in the final cycles of refinement using a riding model, with Uiso(H) = 1.5 Ueq(sp^3) or 1.2 Ueq of the carrier atoms. A molecular plot was prepared with ORTEP-3 for Windows [7]. The software used to prepare material for publication was WINGX [8]. Table 2 gives the atomic coordinates and equivalent thermal parameters of the nonhydrogen atoms. Tables 3 and 4 give the list of bond lengths and bond angles, respectively.

The ORTEP of the molecule with thermal ellipsoids drawn at 50% probability is shown in Fig. 2. The crystal structure is devoid of any classical hydrogen bonding, and molecules are linked by weak intermolecular C—H···O interactions. In the 4-vinylbenzyloxy group, the three H atoms and one C atom are disordered over two sets of sites, with site occupancy factors of 0.75 and 0.25. The title compound has two 5-membered rings, both of them are not on the same plane, and a chair conformation is adopted by the two fused five-membered rings. The angle is 12.1(1)° between the plane of the C(15)–C(14)–C(11) and the C(14)–C(11)–C(10) plane. The torsion angle of C(1)-N(1)-C(3)-C(2) is 28.9(6)°. The



Scheme 1. Synthesis of the title compound **1**.

C(1)-N(1)-C(6) and O(3)-C(7)-C(8) bond angles are 118.7(5)° and 112.3(6)°, respectively. The Packing diagram of (3) is given in Fig. 3.

Conclusion

The title compound, (6*R*,7a*S*)-1,1-Diphenyl-6-(4-vinylbenzyloxy)tetrahydropyrrolo [1,2-c]oxazol-3(*1H*)-one, was synthesized and characterized by ^{1}H, ^{13}C NMR, and HRMS spectroscopy. We summarized the results from X-ray diffraction measurements for compound **1** single crystal. X-ray analysis revealed that the molecules are linked by weak intermolecular C—H···O interactions. The three H atoms and one C atom are disordered over two sets of sites.

Supplementary Information

CCDC 1026620 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax:+44(0)1223-336033. E-mail: deposit@ccdc.cam.ac.uk.

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