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Crystal and Molecular Structure of Bibenzyl-4-yl- [5,6-dihydro-6-oxo-1-(4-pentenyl)pyridine-3-carboxylate]-4′-yl-(6-methoxypyridine-3- carboxylate) Obtained by Rearrangement of a Pentenyl Group at a Pyridine Ring

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Crystal and Molecular Structure of Bibenzyl-4-yl-[5,6-dihydro-6-oxo-1-(4-pentenyl)pyridine-3-carboxylate]-4′-yl-(6-methoxypyridine-3-carboxylate) Obtained by Rearrangement of a Pentenyl Group at a Pyridine Ring

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Bibenzyl-4-yl-[5,6-dihydro-6-oxo-1-(4-pentenyl)pyridine-3-carboxylate]-4′-yl-(6-methoxypyridine-3-carboxylate) (Z-EFH) crystallizes in a triclinic space group of P-1 with $a = 6.118(2)$ Å, $b = 15.821(6)$ Å, $c = 16.910(6)$ Å, $\alpha = 116.65(2)^\circ$, $\beta = 96.31(2)^\circ$, $\gamma = 92.55(2)^\circ$, $V = 1445.9(9)$ Å^3 at ambient temperature. The compound was obtained by synthesis of a targeted compound with a pentenyloxy derivatized pyridine ring at one end of the molecule which was rearranged during synthesis by transferring the pentenyl group to the nitrogen of the pyridine ring and thus creating a derivative of a newly formed 2-pyridone ring. The packing arrangement is dominated by strong dipolar carbonyl–carbonyl interaction.

Keywords Carbonyl–carbonyl interaction; conformation; packing arrangement; single crystal analysis

Introduction

The separations of polycyclic aromatic hydrocarbons and polycyclic aromatic sulfur heterocycles, which are formed by the burning of crude oil and of coal tar, have been investigated by Boberg et al. [1,2] with gas chromatography (GC) for many years. They used e.g. liquid crystalline materials as stationary phase, synthesized and optimized compounds with the goal of establishing low melting and high clearing points due to the necessity to separate the mixtures of the mobile phases at high temperature. Following this line, Feder-Holz [3] investigated in her doctoral thesis especially liquid crystalline esters of benzoic acid and esters of pyridine-3-carboxylic acid of bibenzyl-4–4′-diols. One of the compounds synthesized and characterized was bibenzyl-4-yl-[5,6-dihydro-6-oxo-1-(4-pentenyl)pyridine-3-carboxylate]-4′-yl-(6-methoxypyridine-3-carboxylate) (Z-EFH), which could be crystallized and the molecular shape and interactions between the rod-like molecules determined by single crystal analysis. The actual obtained constitution of the compound deviates from the targeted one, which was expected to contain two pyridine rings at each end of the molecule with attached methyloxy and pentenyloxy terminal groups in

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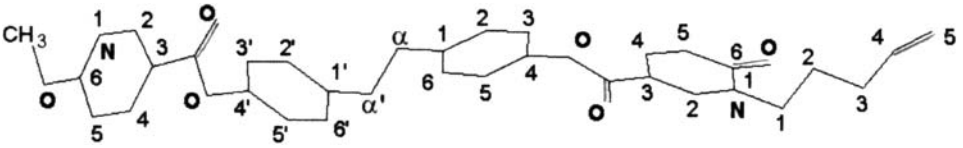
6-position. Actually, a rearrangement occurred during synthesis of one pyridine ring to be transferred to a 2-pyridone ring with a terminal pentenyl group attached to the nitrogen.

Experimental – Structure Determination and Refinement

The synthesis of bibenzyl-4-yl-[5,6-dihydro-6-oxo-1-(4-pentenyl)pyridine-3-carboxylate]-4′-yl-(6-methoxypyridine-3-carboxylate) **1** is described in the thesis of Feder-Holz [3] despite the fact that the targeted compound was a different one. During the synthesis, the terminal pentenyl end of the pentenyloxy group attached at the 6-position of the pyridine ring was transferred to the nitrogen and created a 2-pyridone ring (Scheme 1). The two compounds discussed cannot be differentiated by ^{1}H-NMR spectroscopy, rather by evaluation of the conformation of single crystal X-ray data, as presented in this investigation.



Scheme 1. Scheme of compound **1**: Bibenzyl-4-yl-[5,6-dihydro-6-oxo-1-(4-pentenyl)pyridine-3-carboxylate]-4′-yl-(6-methoxypyridine-3-carboxylate).

Single crystals of sufficient size were grown by solvent evaporation of a methanol-pyridine solution. The single crystal X-ray data were collected with a CAD4 instrument of Enraf-Nonius and the data processed with the computer programs from the MolEN package, Enraf-Nonius, including the unit cell refinement with CELDIM [4]. The intensity data reduction was carried out with XCAD4NV [5], the structure solution procedure with SIR97 [6], structure refinement with SHELXL-97 [7], and the molecular graphics with SCHAKAL-92, -99 [8,9].

A summary of the basic crystal structure data is listed in Table 1. The coordinates, bond lengths and angles, torsion angles, and further crystallographic data are collected in a CIF file and deposited at the Cambridge Crystallographic Data Centre (CCDC No. 908232).

Results and Discussion

Molecular Geometry and Conformation

The conformation of **1** and atom labeling are represented in Fig. 1. The center part of the molecule is symmetrical and the heterocycles at both ends are almost planar. The geometry of the ring with the pentenyl terminal group corresponds closely the 2-pyridone ring determined by Yang & Craven [10] at 123 K and the geometry of both rings are compared in Table 2. The planarity of the ring is confirmed by the values of the torsion angles. The bond length of C24-O6 corresponds to a double bond and that of N2-C27 to a single bond. The pentenyl terminal group is in trans position, except the vinyl end group that exhibits a disordered split position, and the attached hydrogens are omitted in the refinement procedure.

Table 1. Summary of crystallographic data collected of **1** at ambient temperature

	1
Molecular formula	$C_{32}H_{30}N_2O_6$
Formula mass/g*mol^{-1}	538.58
Crystal system	triclinic
Space group/ No. Int. Tab.	P-1 / 2
a/Å	6.118(2)
b/Å	15.821(6)
c/Å	16.910(6)
α/°	116.65(2)
ß/°	96.31(2)
γ/°	92.55(2)
V/Å^3	1445.9(9)
D_{cal}/g*cm^{-3}	1.237
Z (asymmetric unit)	2
MoK$_\alpha$/Å	0.71073
μ(MoK$_\alpha$)/cm^{-1}	0.086
Number of reflections used for lattice parameter refinement	25
Scan range	$10^o < \theta < 23^\circ$
F(000)	568
Reflections collected	4147
Unique data	3700 ($R_{int} = 0.0131$)
Significant I's ($>2\sigma$)	2636
Data collection	$1.3^\circ \leq \theta \leq 23.0^\circ$
Parameters refined/restraints	455/2
R_1	0.049
wR_2	0.140
Goodness-of-fit on F^2	1.043
Highest peak/e*Å^{-3}	0.21
Crystal colour	colorless
Crystal shape	rod-like

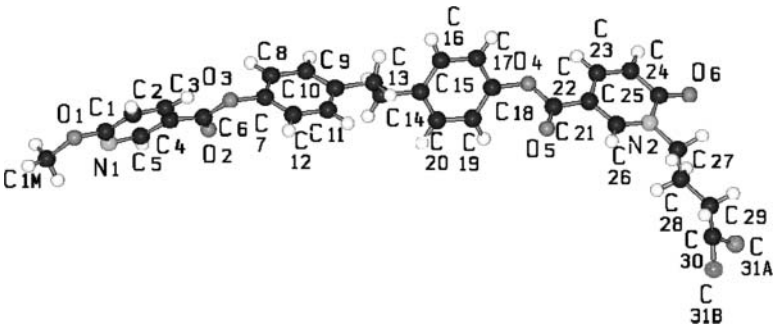


Figure 1. Representation of the conformation and atom labeling of **1**. Note the partial occupancy of C31 (C31A and C31B) due to disorder. The hydrogen atoms of the terminal vinyl group are omitted.

Table 2. Bond lengths, angles, and torsion angles of the 2-pyridone group

(a) Intramolecular bond lengths of 2-pyridone at 123 K (1) according to ref. [10] and values of present study (2) at ambient temperature. Numbering of atoms according to Scheme 1 except the pentenyl terminal group of the present study (2) according to Fig. 1.

	(1)	(2)
N1-C6	1.379 (1)	1.414 (4)
C6-O6	1.251 (1)	1.215 (3)
C6-C5	1.437 (1)	1.421 (4)
C5-C4	1.370 (1)	1.345 (4)
C4-C3	1.417 (1)	1.423 (4)
C3-C2	1.366 (1)	1.356 (4)
C2-N1	1.362 (1)	1.335 (3)
N2-C27		1.474(4)
C27-C28		1.498(5)
C28-C29		1.505(5)
C29-C30		1.465(9)
C30-C31B		1.223(10)
C30-C31A		1.22(2)
(b) Intramolecular bond angles	(1)	(2)
N1-C6-C5	115.0 (1)	114.0 (3)
C6-C5-C4	121.1 (1)	122.7 (3)
C5-C4-C3	121.0 (1)	120.6 (3)
C4-C3-C2	117.8 (1)	117.0 (3)
C3-C2-N1	121.0 (1)	122.7 (3)
C6-N1-C2	124.2 (1)	122.9 (2)
C5-C6-O6	124.8 (1)	125.8 (3)
N1-C6-O6	120.2 (1)	120.2 (3)
C26-N2-C27		120.3(3)
C25-N2-C27		116.8(2)
N2-C27-C28		112.3(3)
C27-C28-C29		111.2(4)
C30-C29-C28		113.9(5)
C31B-C30-C29		134(2)
C31A-C30-C29		131(3)
(c) Selected bond torsion angles	(1)	(2)
O6-C6-C5-C4	−177.6 (1)	179.7 (3)
O6-C6-N1-C2	177.7 (1)	−180.0 (3)
N1-C6-C5-C4	2.1 (1)	−2.1 (4)
C5-C6-N1-C2	−2.0 (1)	−0.4 (4)
C27-N2-C25-C24		179.2(3)
N2-C27-C28-C29		−180.0(3)
C27-C28-C29-C30		176.3(7)
C28-C29-C30-C31B		−131(2)
C28-C29-C30-C31A		107(3)

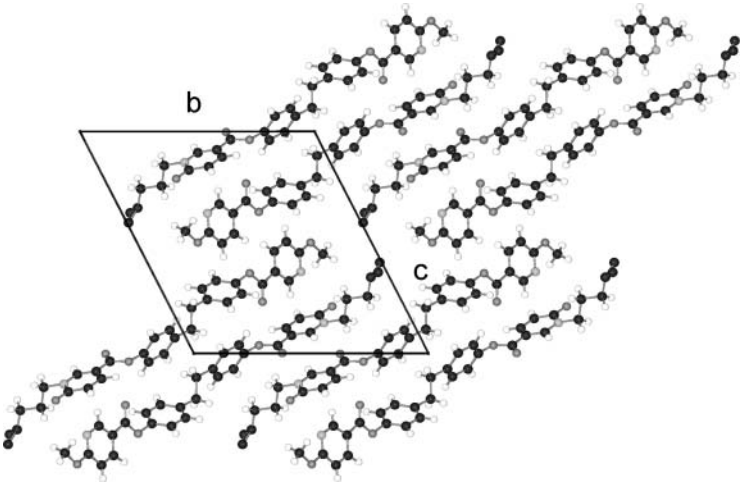


Figure 2. Representation of the arrangement of stables of **1** in [100] direction.

Packing Arrangements

The packing arrangement is dominated by two identical strong polar carbonyl–carbonyl interactions [11] of two antiparallel running molecules with an inversion center in between (Fig. 2). This interaction is regarded to be competitive with hydrogen bonds. The geometry of this interaction is classified as of the perpendicular type and represented for a survey of ketonic (C_2)-C=O structures by Allen et al. [11] in Fig. 3 and the data compared with the investigated ester structure **1**. Due to the inversion center at the origin of the unit cell, dimers are established which can be regarded as the basic unit for the packing arrangement in Fig. 2. The geometry of the two carbonyl–carbonyl dipolar interaction between the antiparallel arranged molecules is identical since the inversion center represents the center of mass of the dimer formed. One geometry is shown in Fig. 4 between C6 = O2 and

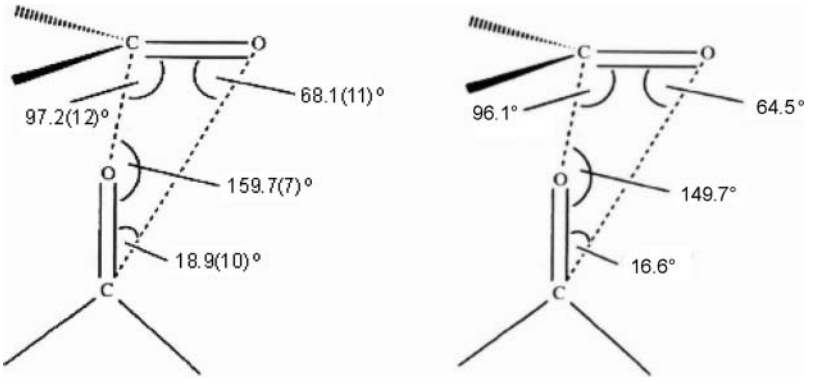


Figure 3. Average geometries for the perpendicular common motif as determined from a database analysis [11]. Standard deviations of the mean ketonic (C_2)-C—O structure are given in brackets (left figure) and comparable data for the investigated compound **1** (right figure) (Figs. adapted from [11] with permission of IUCr).

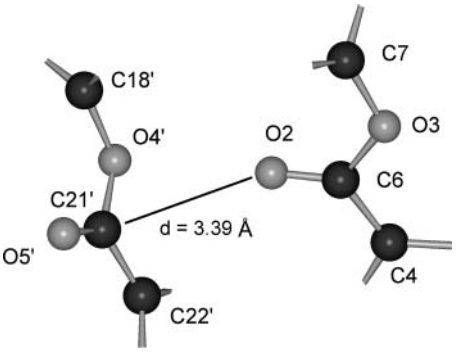


Figure 4. Representation of the geometry of the carbonyl-carbonyl interaction of two parts of symmetry-related molecules of **1**.

C21′ = O5′ (-x, -y, -z), which is identical to C21 = O5 and C6′ = O2′ (-x, -y, -z). The distance between O2 . . . C21′ is $d = 3.39$ Å just above the median value of 3.35 Å [11] but below the cut-off distance of 3.60 Å provided by Allen et al. [11]. The angles (C6 = O2 . . . C21′) = 149.7°, (O2 . . . C21′ = O5′) = 96.1°, (C21′ = O5′ . . . C6) = 64.5°, and (O5′ . . . C6 = O2) = 16.6° are close to the average values established in the survey of Allen et al. for this motif [11].

Conclusions

Single crystal analysis provides the conformation of bibenzyl-4-yl-[5,6-dihydro-6-oxo-1-(4-pentenyl)pyridine-3-carboxylate]-4′-yl-(6-methoxypyridine-3-carboxylate) (Z-EFH) obtained by rearrangement of a pentenyl group at a pyridine ring during synthesis which was not detected by ^{1}H-NMR spectroscopy. Therefore, the decisive step, in which the rearrangement occurs, was not identified, and this transfer will be due to further investigations. The goal of the present paper was primarily to solve the crystal structure of the compound synthesized and to draw conclusions of the molecular und packing arrangements.

The arrangement of the chains is governed by two strong polar carbonyl–carbonyl interactions between two antiparallel chains, which are regarded to have the strength of hydrogen bonds. The formation of a dimer unit is established, which might continue to exist during phase transitions.

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References

[1] Boberg, F., Kußerow, J., Müller, E., & Redding, W. (1993). *J. prakt. Chem.*, *335*, 316.
[2] Kußerow, J., & Boberg, F. (1994). *J. prakt. Chem.*, *336*, 613.
[3] Feder-Holz, E. (1995). *Flüssigkristalline Benzoesäureester und Pyridin-3-carbonsäureester des Bibenzyl-4,4′-diols*. Dissertation, Clausthal University of Technology, Papierflieger: Clausthal-Zellerfeld, Germany.
[4] Fair, C. K. (1990). *MolEN: Crystal Structure Analysis*, Enraf-Nonius: Delft, The Netherlands.

[5] Harms, K. (1993). *XCAD4NV: A Program for Extracting Intensity Data from CAD4 (Enraf-Nonius) Files*, University of Marburg: Marburg, Germany.
[6] Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Burla, M. C., Polidori, G., Camalli, M., & Spagna, R. (1999). *SIR97: A New Tool for Crystal Structure Determination and Refinement*. *J. Appl. Cryst.*, *32*, 115.
[7] Sheldrick, G. M. (1997). *SHELX-97: A Program for Refinement of Single Crystal Diffraction Data*, University of Göttingen: Göttingen, Germany.
[8] Keller, E. (1992). *SCHAKAL-92: A Computer Program for the Graphic Representation of Molecular and Crystallographic Models*, Kristallographisches Institut der Universität Freiburg i. Br.: Freiburg, Germany.
[9] Keller, E. (1999). *SCHAKAL-99: A Computer Program for the Graphic Representation of Molecular and Crystallographic Models*, Kristallographisches Institut der Universität Freiburg i. Br.: Freiburg, Germany.
[10] Yang, H. W., & Craven B. M. (1998). *Acta Cryst.*, *B54*, 912.
[11] Allen, F. H., Baalham, C. A., Lommerse J. P. M., & Raithby, P. R. (1998). *Acta Cryst.*, *B54*, 320.