Crystal Structure of 2,4-Bis(2,5-dipropyloxyphenyl)-6-phenylpyridine

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Z. Naturforsch. **2014**, *69b*, 965 – 968 / DOI: 10.5560/ZNB.2014-4131
Received June 25, 2014

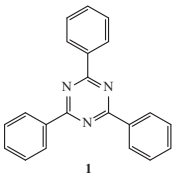
2,4-Bis(2,5-dipropyloxyphenyl)-6-phenylpyridine (**6**), obtained by a one-pot reaction of enone **3**, ketone **4** and ammonium acetate (**5**), is characterized by its molecular structure in the crystalline state, which deviates far from planarity. The interplanar angles of the three benzene rings amount up to 46° in relation to the central pyridine ring.

Key words: 2,4,6-Triarylpyridines, Interplanar Angles, Cross-conjugation

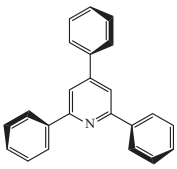
Introduction

2,4,6-Triphenylpyridine and its derivatives find various applications in biomedical and pharmacological studies [1 – 10] and in materials science [11 – 17]. This substructure represents a shape-persistent core for dendrimers and three-star compounds, called hekates [18 – 20]. A great disadvantage of 2,4,6-triphenylpyridine is its low solubility.

In contrast to the fairly planar 2,4,6-triphenyl-1,3,5-triazines (**1**), the 2,4,6-triphenylpyridines (**2**) adopt non-planar conformations with a con- or disrotatory arrangement of the three benzene rings [21, 22].



1

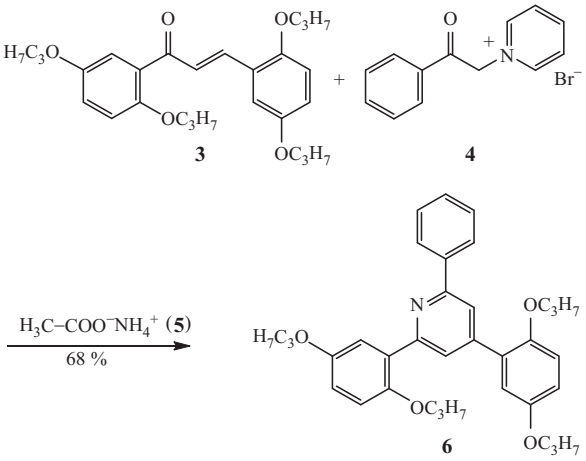


2

The dihedral angles of **2** in solution [21] or in the crystalline state [22] are similar to the torsion angle in biphenyl. The question arises, how solubilizing substituents on the benzene rings change the torsion angles. It can be suspected that *ortho*-substituents particularly enhance the torsion. An exception was found for *o*-hydroxy groups, which can form hydrogen bonds to the N atom of the central pyridine ring [23]. A very strong deviation from planarity would impair the effect of cross conjugation.

Results and Discussion

We synthesized 2,4-bis(2,5-dipropyloxyphenyl)-6-phenylpyridine (**6**) [24] according to a method originally published by Zecher and Kröhnke [25]. Enone **3**, pyridinium bromide **4** and ammonium acetate (**5**) reacted in glacial acetic acid in a one-pot reaction to yield **6** (Scheme 1) [24, 26]. Several improved variants of Kröhnke's method have been published [27 – 34].



Scheme 1.

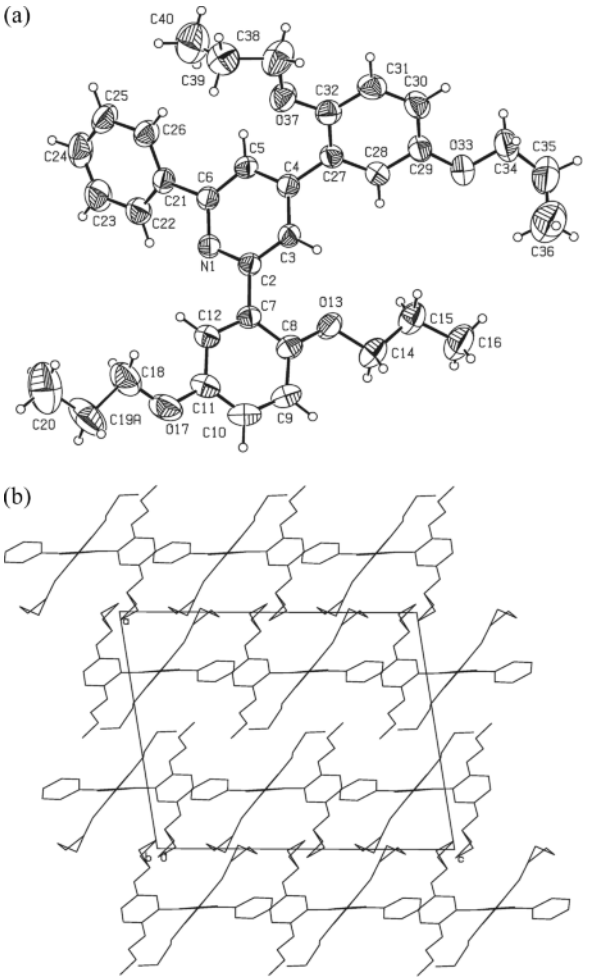


Fig. 1. Crystal and molecular structure of **6**: a) ORTEP plot of the molecular structure with crystallographic numbering scheme adopted; b) unit cell. Atoms C19 and C39 are disordered: C19/C19A 0.7 : 0.3, C39/C39A 0.8 : 0.2. The hydrogen atoms were placed in geometrically calculated positions.

Table 1. Selected bond lengths (pm) of **6** and the parent compound **2**.

	C2–C7	C4–C27	C6–C21
6	149.3(4)	147.7(4)	148.8(4)
2	146.7(7)	147.6(7)	148.8(7)

Table 2. Interplanar angles τ (deg) of the four rings in **6** and **2**.

6	A	B	C	D
A	–	44.4(9)	29.5(1)	46.2(1)
B		–	64.8(1)	43.5(1)
C			–	39.6(1)
D				–
2	A	B	C	D
A	–	36.3(3)	31.1(3)	30.5(3)
B		–	60.2(3)	33.5(3)
C			–	32.8(3)
D				–

Table 3. Details of the crystal structure determination of **6**.

Empirical formula	$C_{35}H_{41}NO_4$
M_r	539.68
Habit	colorless block
Crystal size, mm^3	$0.320 \times 0.512 \times 0.512$
Crystal system	monoclinic
Space group	$P2_1/c$
Cell parameters	
a, Å	15.1545(7)
b, Å	11.2188(6)
c, Å	18.6398(8)
β, deg	99.188(2)
V, Å^3	3127.4(3)
Z	4
$D_{calcd.}$, g cm^{-3}	1.15
Radiation	CuK_α
μ, mm^{-1}	0.6
$F(000)$, e	1160
T, °C	22
θ_{max}, deg	74
No. of reflections	
Measured/unique/R_{int}	6339/6338/–
Observed with $F > 4.0\ \sigma(F)$	3972
Refined parameters	370
R (all data)	0.0884
wR (all data)	0.3240
S	1.083
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.45/ – 0.31

Compound **6** forms colorless monoclinic crystals (monoclinic space group $P2_1/c$ with $Z = 4$). We performed a crystal structure analysis and compared the results to that for the parent compound **2**. The most important structural parameters of **6** and **2** are compiled in Tables 1 and 2. Fig. 1 shows a plot of the obtained molecular structure of **6** and the unit cell. The propyloxy substituents in **6** provoke a lengthening of the bond C2–C7 between the central pyridine ring and a substituted benzene ring. More pronounced is the widening of the interplanar angles of the ring planes in **6** compared to **2**. The substituted benzene rings B and D in **6** are rotated by 44 and 46°, respectively, out of the plane of the central ring A – in comparison to 36 and 30°, obtained for the parent system **2** [22].

The torsions of the benzene rings are disrotatory. Moreover, Fig. 1a shows that the *ortho*-OC_3H_7 groups of the rings B and D avoid steric interaction. The lacking NOE between the OC_3H_7 chains in the ^1H NMR spectra ($CDCl_3$) can be taken as a hint that the corresponding conformer predominates in solution as well.

Conclusion

The crystal structure determination of the 2,4,6-triphenylpyridine **6** revealed enhanced torsions of the propyloxy-substituted benzene rings compared to the parent compound **2**. However, the observed changes do not entail a much decreased cross conjugation. The attenuation factor $\cos^2\tau$ [35] gives a decrease of the resonance from 71 to 59 % for the average increase of τ from 32.6 to 40.1°. This means, that the much better soluble system **6** still conveys a considerable cross conjugation when it is used as core in hekates or dendrimers.

Experimental

2,4-Bis(2,5-dipropyloxyphenyl)-6-phenylpyridine (**6**) was synthesized according to the method described in the literature [25].

Crystal structure analysis

Details of the crystal structure analysis of **6** are summarized in Table 3. The measurement was performed with an Enraf-Nonius CAD-4 diffractometer applying the softwares V5 and COLLECT (Nonius BV, 1997 – 2000). The structure determination was based on the programs SIR-92 [36] and SHELXL-97 [37].

CCDC 1009913 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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