
STRUCTURE
OF ORGANIC COMPOUNDS

Planar Geometry of 4-Substituted-2,2'-bipyridines Synthesized by Sonogashira and Suzuki Cross-Coupling Reactions¹

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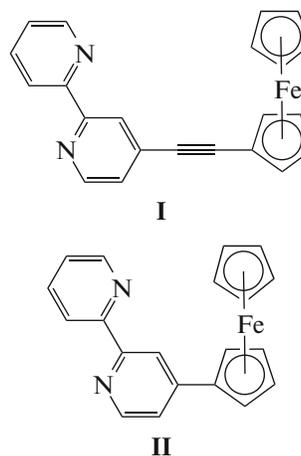
Abstract—Two 4-substituted 2,2'-bipyridines, namely 4-(ferrocenylethynyl)-2,2'-bipyridine (**I**) and 4-ferrocenyl-2,2'-bipyridine (**II**) have been synthesized and fully characterized *via* single-crystal X-ray diffraction and ¹H and ¹³C NMR analyses. The π -conjugated system designed from 2,2'-bipyridine modified with the ferrocenylethynyl and ferrocenyl groups shows the desired planarity. In the crystal packing of **I** and **II**, the molecules arrange themselves in head-to-tail and head-to-head motifs, respectively, resulting in consecutive layers of ferrocene and pyridine moieties.

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INTRODUCTION

The 2,2'-bipyridine is one of the most widely used chelate systems in coordination, supramolecular and macromolecular chemistry [1]. Due to their unique photophysical and photooptical properties, 2,2'-bipyridine derivatives are used in the synthesis of photosensitizers for dye sensitized solar cells (DSSC) [2, 3]. The introduction of different functionalities on the 2,2'-bipyridine moiety is based on the fact that larger delocalization of the π -electrons from the aromatic part of the molecule normally leads to higher extinction coefficients of the metal-to-ligand charge-transfer (MLCT) transitions in their copper(I) complexes [4].

In this paper, we report the synthesis, geometry and molecular arrangement in the crystals of two compounds, namely 4-(ferrocenylethynyl)-2,2'-bipyridine (**I**) and 4-ferrocenyl-2,2'-bipyridine (**II**) which were synthesized by the palladium catalyzed Sonogashira [5, 6] and Suzuki-Miyaura [7, 8] cross-coupling reactions.



EXPERIMENTAL

Synthesis and crystallization. The synthesis of the compound 4-bromo-2,2'-bipyridine was achieved after three steps according to the procedure of Egbe *et al.* [9] with a total yield of 35%. All intermediates were fully characterized by spectroscopic methods.

Procedure for the synthesis of 4-(ferrocenylethynyl)-2,2'-bipyridine (I) by a palladium-catalyzed Sonogashira reaction. Toluene (4.0 mL) was deaerated by exchanging between vacuum and a stream of argon (three times). To this argon saturated solution were

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Experimental details

	I	II
CCDC code	CCDC 1048373	CCDC 1048374
Chemical formula	C ₂₂ H ₁₆ FeN ₂	C ₂₀ H ₁₆ FeN ₂
<i>M_r</i>	364.22	340.20
Crystal system, space group, <i>Z</i>	Monoclinic, <i>Pc</i> , 2	Monoclinic, <i>P2₁/c</i> , 4
<i>a</i> , <i>b</i> , <i>c</i> , Å; β, deg	5.9175(2), 7.5394(3), 18.0598(7); 97.574(4)	18.1271(4), 9.3485(2), 9.1816(2); 92.081(2)
<i>V</i> , Å ³	798.71(6)	1554.89(7)
Crystal size, mm ³	0.40 × 0.15 × 0.10	0.20 × 0.15 × 0.10
<i>T</i> , K	100	100
<i>T_{min}</i> , <i>T_{max}</i>	0.839, 1.000	0.934, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	8431, 3210, 3160,	6225, 3181, 2553,
<i>R_{int}</i>	0.032	0.027
(sinθ/λ) _{max} , Å ⁻¹	0.625	0.625
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.024, 0.056, 1.07	0.038, 0.073, 1.06
No. of reflections, parameters	3210, 226	3181, 272
Δρ _{max} , Δρ _{min} , e Å ⁻³	0.20, -0.26	0.32, -0.33

added 4-bromo-2,2'-bipyridine (59 mg, 0.25 mmol), Pd(PPh₃)₄ (28.5 mg, 0.025 mmol) and CuI (10 mg, 0.050 mmol). To the resulting reaction mixture, a solution of ethynylferrocene (63.0 mg, 0.3 mmol) in argon saturated toluene (1.0 mL) was added dropwise in about 30 minutes. The reaction mixture was heated at 373 K for 4 hours. The reaction mixture turned reddish brown when the cross-coupling completed as indicated by *TLC* (*EtOAc* : *n*-hexane 1 : 4, vol/vol). The reaction mixture was diluted with *EtOAc*, washed with water, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by SiO₂ column chromatography to furnish **I** as a red solid (51 mg, yield 56%). Single crystals of **I** suitable for X-ray diffraction analysis were obtained by recrystallization from *n*-hexane. ¹H NMR (δ p.p.m.; CDCl₃, 500 MHz): 8.71 (1H, *d*, *J* = 4.0 Hz), 8.62 (1H, *d*, *J* = 5.0 Hz), 8.47 (1H, *s*), 8.40 (1H, *d*, *J* = 8.0 Hz), 7.83 (1H, *dt*, *J* = 8.0 Hz and 1.5 Hz), 7.33 (2H, *m*), 4.54 (2H, *m*, ferrocene), 4.30 (2H, *m*, ferrocene), 4.25 (4H, *s*, ferrocene); ¹³C NMR (δ p.p.m.; CDCl₃, 125 MHz): 156.0, 155.7, 149.2, 149.1, 136.9, 133.1, 124.9, 123.9, 122.8, 121.1, 94.2 and 83.8 (C≡C), 71.8, 70.1, 69.4 and 63.7 (C-ferrocene); UV (λ_{max}, nm, in CHCl₃): 367, 455.

Procedure for the synthesis of 4-ferrocene-2,2'-bipyridine (II) by a palladium-catalyzed Suzuki–Miyaura reaction. Toluene (4 mL) was degassed by exchanging between vacuum and a stream of argon (three times). 4-Bromo-2,2'-bipyridine (59 mg, 0.25 mmol) and Pd(Ph₃P)₄ (28.5 mg, 0.025 mmol) were dissolved in this degassed toluene. To the obtained solution, H₂O

(1 mL), K₃PO₄ (67 mg, 0.50 mmol) and ferroceneboronic acid (69 mg, 0.30 mmol) were added. The reaction was vigorously stirred under argon atmosphere at 383 K until *TLC* (100% *n*-hexane) showed the complete consumption of the starting material. The reaction mixture was filtered through celite. The filtrate was washed with H₂O, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by SiO₂ column chromatography (100% *n*-hexane) to give the product as a red solid (66 mg, yield 78%). Single crystals of **II** suitable for X-ray diffraction analysis were obtained by crystallization from chloroform-ethyl acetate (1 : 1 v/v). ¹H NMR (δ p.p.m.; 500 MHz, CDCl₃): 8.72 (1H, *dq*, *J* = 5.0 Hz and 1.0 Hz), 8.54 (1H, *dd*, *J* = 5.0 Hz and 0.5 Hz), 8.45 (1H, *d*, *J* = 1.0 Hz), 8.42 (1H, *dd*, *J* = 8.0 Hz and 1.0 Hz), 7.82 (1H, *dt*, *J* = 8.0 Hz and 2.0 Hz), 7.36 (1H, *dd*, *J* = 5.0 Hz and 1.5 Hz), 7.31 (1H, *m*), 4.86 (2H, *m*, ferrocene), 4.43 (2H, *m*, ferrocene), 4.06 (5H, *s*, ferrocene); ¹³C NMR (δ p.p.m.; 125 MHz, CDCl₃): 156.4, 156.1, 149.7, 149.1, 149.0, 136.8, 123.6, 121.2, 120.6, 117.7, 81.2, 70.2, 69.9 and 67.1 (C-ferrocene); UV (λ_{max}, nm, in CHCl₃): 350, 454.

Structure solution and refinement. The X-ray diffraction data were collected on an Agilent SuperNova diffractometer using mirror-monochromated MoK_α radiation (λ = 0.7107 Å). Using OLEX2 [10] the structures were solved by direct methods using SHELXS [11] and refined by full-matrix least-squares methods based on *F*² using SHELXL [12]. All non-hydrogen atoms were refined anisotropically. For **I** all hydrogen atom parameters were refined, for **II** all hydrogen

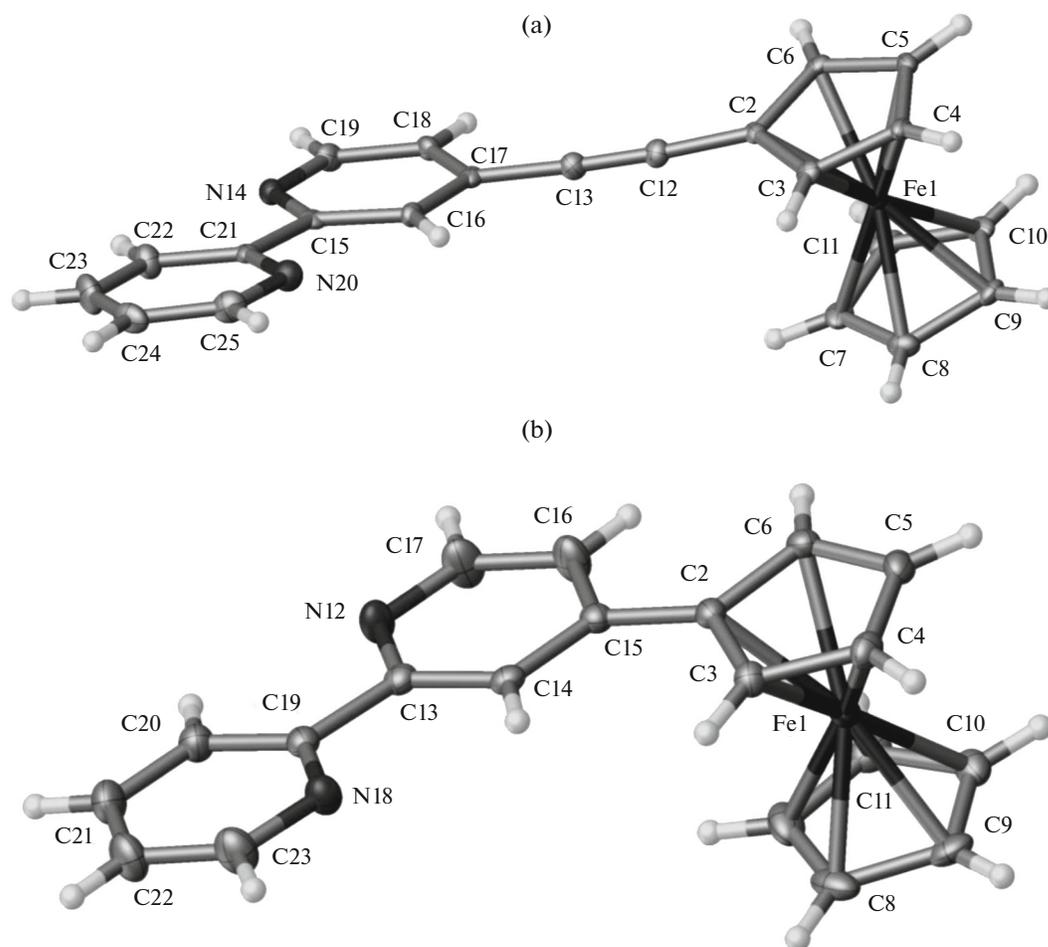


Fig. 1. View of the asymmetric unit in **I** (a) and **II** (b), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level.

atoms were placed in idealised positions and refined in riding mode with U_{iso} assigned the values to be 1.2 times those of their parent atoms with C–H distances of 0.95 Å. Crystal data, data collection and structure refinement details are summarized in the table.

RESULTS AND DISCUSSION

The two 4-substituted 2,2'-bipyridines **I** and **II** were first characterized by ^1H and ^{13}C NMR spectroscopy using d_1 -chloroform as solvent (see Synthesis and crystallization). The ^1H NMR spectra of both compounds show similar chemical shifts and splitting patterns for the 2,2'-bipyridyl protons. In the ^1H NMR spectrum of **I** and **II**, the protons of the ferrocene moiety are easily recognized: the four protons of the substituted cyclopentadienyl give rise to two multiplets at about 4.54–4.86 and 4.30–4.43 p.p.m., while those of the other cyclopentadienyl appear as a singlet at about 4.06–4.25 p.p.m.. The two resonance signals at about 94.2 and 83.8 p.p.m. in the ^{13}C NMR spectrum of **I**

prove the 2,2'-bipyridine and the substituent to be connected by a triple bond, while these signals are not observed in the case of **II** due to direct binding of the two parts. The geometry of the two compounds was further clarified through single-crystal X-ray diffraction analysis.

The molecular structures of **I** and **II** are shown in Fig. 1. The bond lengths and angles are in good agreement with the average values in the Cambridge Structural Database (CSD, Version 5.35, February 2014; [13]). The 2,2'-bipyridyl groups in the two compounds exhibit a *trans* conformation and are co-planar, as indicated by the dihedral angles between the two pyridine rings, viz. 3.47(10)° and 2.78(13)° in **I** and **II**, respectively. The CSD contains currently 18 4-substituted 2,2'-bipyridine structures of which only one structure shows a *cis* conformation (N–C–C–N torsion angle 27.2°; CSD refcode MADCEA; [14]). The other structures occur in the *trans*-conformation with N–C–C–N torsion angles between 152° and 200°. The ferrocenyl groups have a sandwich structure with angles between the two cyclopentadienyl rings of

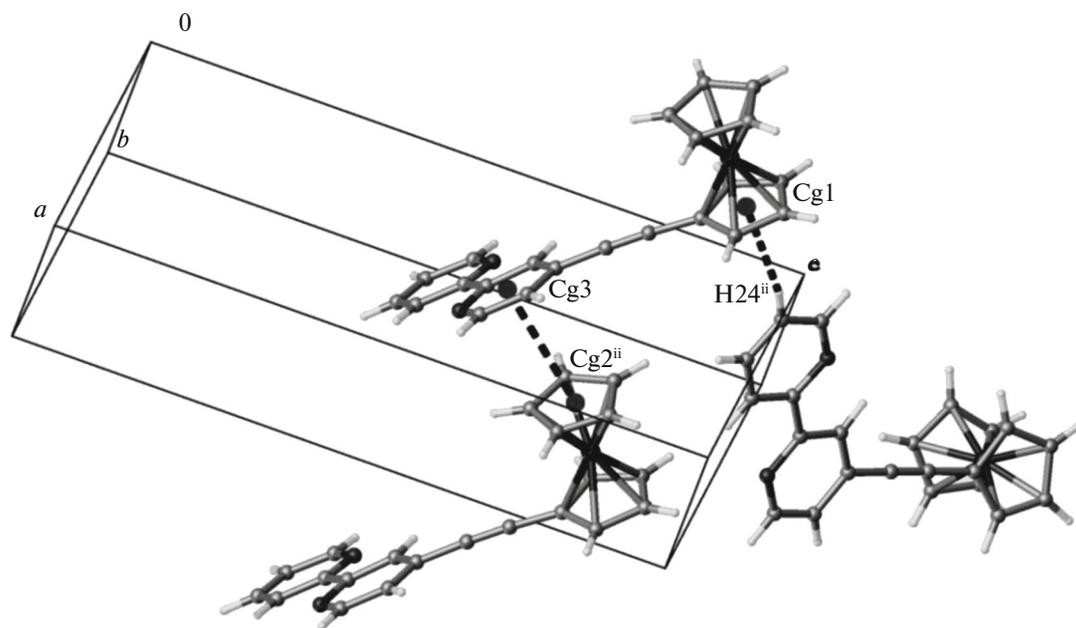


Fig. 2. π - π and C-H \cdots π interactions in **I** [dotted lines; Cg1, Cg2 and Cg3 are centroids of the C2–C6, C7–C11 and N14/C15–C19 rings, respectively; symmetry code: (i) $x + 1, y + 1, z$; (ii) $x, -y + 1, z + 1/2$].

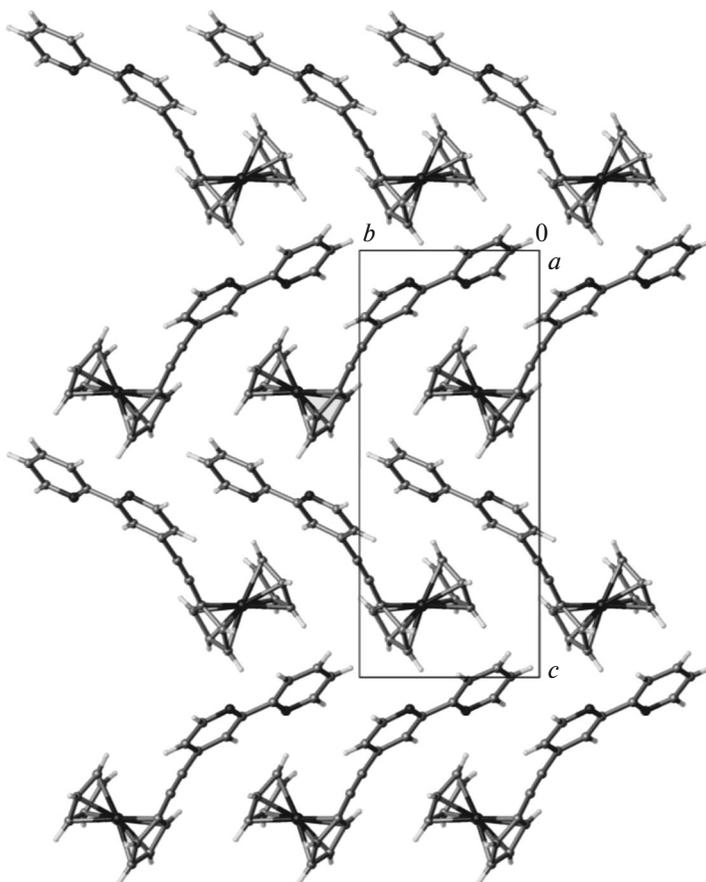


Fig. 3. Head-to-tail arrangement in the crystal packing of **I** showing consecutive layers of ferrocene and bipyridine moieties parallel to the ab plane.

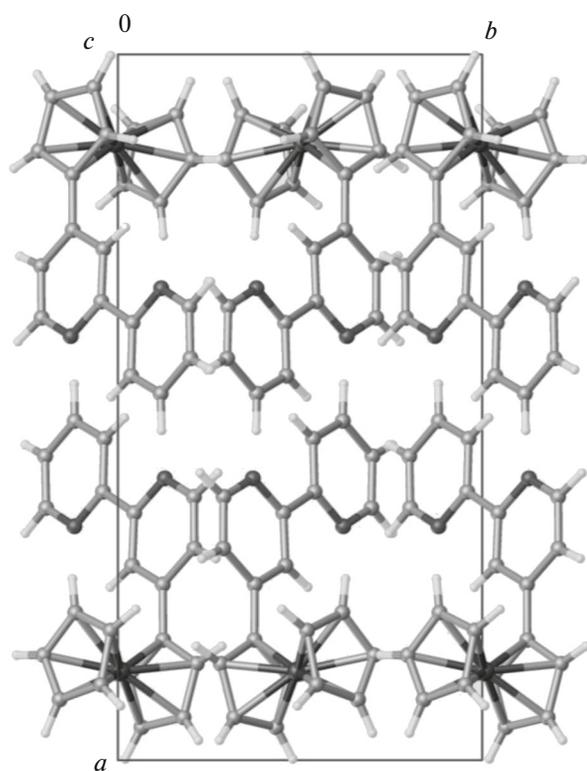


Fig. 4. Head-to-head arrangement in the crystal packing of **II** showing consecutive layers of ferrocene and bipyridine moieties parallel to the *bc* plane.

$1.91(13)^\circ$ in **I** and $0.77(17)^\circ$ in **II**. In both cases, the two cyclopentadienyl rings are almost eclipsed with torsion angles of $C2-Cg1-Cg2-C7 = -9.0(2)^\circ$ in **I** and $-5.6(2)^\circ$ in **II** ($Cg1$ and $Cg2$ are centroids of the $C2-C6$ and $C7-C11$ rings, respectively). The iron(II) cations form with the centroids of the cyclopentadienyl rings angles of $178.51(5)^\circ$ and $179.42(7)^\circ$ in **I** and **II**, respectively.

To achieve higher extinction coefficients of the MLCT transitions of the copper(I) complexes, we aim to enlarge the π -conjugated system of the bipyridine ligand, which is favorable by the planarity of the aromatic moieties. In our previous study, we have showed that the aromatic substituents introduced via an ethylene bridge are planar with the core structure of thieno[3,2-*b*]thiophene [15]. As expected, the molecular geometry of **I**, in which the bipyridine and the cyclopentadienyl moieties are linked by an ethyne bridge, is planar. The ferrocene moiety, however, shows a slightly tilting out of the plane of the 2,2'-bipyridinyl skeleton (the angle between $C2-C6$ and $C7-C11$ rings and the best plane through 2,2'-bipyridine are $22.73(10)^\circ$ and $24.61(10)^\circ$, respectively), which in turn leads to a tilting angle of $4.80(15)^\circ$ of the triple bond linkage $C12-C13$. In contrast to the previous reported structures [15], in which the directly connected substituents showed no co-planarity with the

core structures, the ferrocenyl and the bipyridyl groups in **II** are nearly in the same plane. In fact, the angles between $C2-C6$ and $C7-C11$ rings and the best plane through 2,2'-bipyridine are $8.28(12)^\circ$ and $7.87(13)^\circ$, respectively. This could be due to the absence of the heavy atoms, *viz.* the S and Br atoms as in the cases of 3,6-dibromo-5-alkenyl-2-arylthieno[3,2-*b*]thiophenes [15]. In addition, red shifted absorbance spectra have been observed for both compounds **I** and **II** in which the 2,2'-bipyridine core is in conjugation with the auxochromic phenylethynyl or phenyl group, respectively. Thus, the spectrum of compound **I** shows only a slight shift in the wavelength of maximum absorption for both bands relative to that observed for compound **II** (367 and 455 nm in comparison to 350 and 454 nm), while 2,2'-bipyridine absorbs at 240 and 305 nm [16].

The crystal packing of **I** is characterized by $\pi_{\text{pyridine}} \cdots \pi_{\text{ferrocene}}$ in an offset face-to-face mode and $C_{\text{pyridine}}-H \cdots \pi_{\text{ferrocene}}$ interactions [$Cg3 \cdots Cg2^i = 3.7330(13) \text{ \AA}$; $C24^{ii}-H24^{ii} \cdots Cg1 = 3.527(3) \text{ \AA}$; $Cg1$, $Cg2$ and $Cg3$ are centroids of the $C2-C6$, $C7-C11$ and $N14/C15-C19$ rings, respectively; symmetry code (i) $x + 1, y + 1, z$; (ii) $x, -y + 1, z + 1/2$] (Fig. 2). The molecular arrangement shows consecutive layers parallel to the *ab* plane of ferrocene and bipyridine moieties in a head-to-tail fashion (Fig. 3).

No $\pi \cdots \pi$ or $C-H \cdots \pi$ interactions are observed in the packing of **II**. In stead neighboring bipyridine rings are almost perpendicular to each other resulting in an edge-to-face interaction [see for instance $Cg4 \cdots Cg5^{iii} = 5.0346(15) \text{ \AA}$, the angle between the mean planes is $81.81(13)^\circ$; $Cg4$ and $Cg5$ are centroids of the $N18/C19-C23$ and $N12/C13-C17$ rings, respectively; symmetry code (iii) $x, -y + 3/2, z + 1/2$]. The molecular arrangement shows consecutive layers parallel to the *bc* plane consisting of ferrocene and bipyridine moieties in a head-to-head manner (Fig. 4). The difference in packing between **I** and **II** is a consequence of the slight difference in flexibility of both compounds. The introduction of the ethyne bridge enables **I** to adjust its conformation and to optimize its packing (packing index 73.1 for **I**, 69.2 for **II**).

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