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# Synthesis of new heteroatomic podands from ethyl 2-[(2-aminophenylamino)methylidene]-3-oxoalkanoates and thiophene-2,5-dicarboxaldehyde

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Condensation of two moles of ethyl 2-[(2-aminophenylamino)methylidene]-3-oxo-3-(polyfluoroalkyl)propionates with 2,5-thiophenedicarboxaldehyde results in new heteroatomic podands. X-ray data showed that in the solid state these molecules arrange in two independent chelating fragments of  $\beta$ -amino enone type, thiophene fragment being a spacer.

New podands and their metal complexes have attracted an increasing interest owing to their importance in understanding of the biochemical processes.<sup>1</sup> The design of polydentate ligands is directed to the recognition and transport of specific ions and molecules<sup>2</sup> and, also, to the developing of selective catalysts.<sup>3</sup> Having the ability to self-organization simple binuclear ligands form the complex three-dimensional supramolecular systems with unique properties.<sup>4–9</sup>

Previously, we studied reactions of ethyl 2-[(2-aminophenylamino)methylidene]-3-oxo-3-(polyfluoroalkyl)propionates of type **1** with monoaldehydes<sup>10</sup> and diamines<sup>11,12</sup> leading to symmetrical and nonsymmetrical ligands with one complexation centre. Recently,<sup>13</sup> we described the use of thiophene-2,5dicarboxaldehyde **2** in the synthesis of polydentate ligands.<sup>13</sup> This dialdehyde has a wide application in the synthesis of macrocyclic and acyclic Schiff bases,<sup>14–16</sup> furthermore, sulfur atom can participate in additional coordination with metal ions and, thereby, provide the formation of polyene system. Its condensation with diethyl 2-[(2-aminophenylamino)methylidene]malonate **1a** was found to give tetraethyl 2,2'-[2,5-thienylbis(aminomethylidene-2-iminophenylene)]dimalonate **4a**<sup>13</sup> (Scheme 1) having the single O<sub>2</sub>N<sub>4</sub>S macroacyclic chelating cavity.

The aim of this work was to synthesize similar polydentate geteratomic ligands based on compounds **1b**–**d**<sup>11,12</sup> and thiophene-2,5-dicarboxaldehyde **2**. We anticipated that the compounds thus obtained can find use in access to some binuclear metal complexes or anion receptors.<sup>17</sup> The presence of thiophene ring as a spacer in the molecules of bis-condensation products provides the extensive polyene system that can promote various practically useful properties (*e.g.*, electroconductivity).

We found that the interaction between compounds **1b–d** (2 equiv.) and dialdehyde **2** proceeded regioselectively with the formation of bis-condensation products – bis-azomethines **4b–d** (Scheme 1). The reaction was carried out in benzene in the presence of AcOH with the azeotropic removal of water.

We also changed the starting reactant ratios to get mono-condensation products. However, monoazomethine **3** was obtained in only one case of tetrafluoroethyl-containing compound **1d**. Polyfluoroalkyl-substituted oxo esters seem to be less reactive compared to the non-fluorinated analogues as seen from the lower yields (62–64% for fluoroalkylated products **4c,d** and 75–80% for non-fluorinated podand **4b**).

The structures of compounds **3** and **4b–d** were characterized by IR,  ${}^{1}$ H and  ${}^{19}$ F NMR spectroscopy<sup>†</sup> and elemental analysis



Scheme 1

<sup>†</sup> The <sup>1</sup>H NMR spectrum of azomethine **3** contains two sets of signals since in a  $CDCl_3$  solution this compound exists as a mixture of *Z* and *E* isomers relative to the C=C bond.

According to the <sup>1</sup>H and <sup>19</sup>F NMR data podands **4b–d** in  $CDCl_3$  solutions exist as mixtures of *EE*- and *ZZ*-isomers. *ZZ*-isomers apprearance seems to occur because of the partial isomerisation of crystalline *EE*-isomer under dissolution. The ease of isomerisation of the C=C bonds in compounds **4b–d** is due to their being a push-pull conjugated system in which the rotation barrier around the C=C double bonds is decreased.



Figure 1 X-ray structure of 4b (thermal ellipsoids at 50% probability level, ORTEP drawing).

(see Online Supplementary Materials). X-ray study for products **4b**,**d** was carried out.

In contrast to the previously obtained podand<sup>13</sup> **4a**, compound **4b**<sup> $\ddagger$ </sup> has two independent coordination centres of  $\beta$ -amino enone type, which are connected *via* central thiophene cycle and located in the *trans*-position with respect to each other. The deviation of C(9)C(11)C(13) plane of one phenylene fragment from the C(18)N(3)C(22) plane containing thiophene cycle and another phenylene is 24.8°, that makes the molecule non-planar. In crystal compound **4b** is *s*-*trans*,*s*-*cis*-conformer of *EE*-isomer of bis(amino enone) tautomer (Figure 1).

There are two intramolecular hydrogen bonds (IMHB) in the molecule with the participation of two NH groups of phenylenediamine moiety and two oxygen atoms of acetyl groups: N(1)–H(1)···O(3) and N(4)–H(4)···O(4) (Table 1). Note that carbonyl



Figure 2 The molecular packing of 4b (along the c axis).

<sup>‡</sup> *Crystallographic data for* **4b**: C<sub>32</sub>H<sub>32</sub>N<sub>4</sub>O<sub>6</sub>S, *M* = 600.68, monoclinic, space group *C*2/*c*, *a* = 35.621(4), *b* = 10.5006(13) and *c* = 17.9570(9) Å,  $\beta = 116.539(8)^\circ$ , *V* = 6008.9(10) Å<sup>3</sup>, *Z* = 8, *d*<sub>calc</sub> = 1.328 g cm<sup>-3</sup>,  $\mu$ (MoK $\alpha$ ) = 0.159 cm<sup>-1</sup>, *F*(000) = 2528. A total number of 14 194 reflections were measured on an Xcalibur 3 diffractometer at 295(2) K [ $\omega$ /2 $\theta$ -scanning technique, MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å), graphite monochromator, CCD detector], 5698 independent reflections ( $R_{int} = 0.0501$ ), 2149 reflections with  $F_0 > 4\sigma(F_0)$ . The structure was solved by direct methods and refined by the least-squares method with the use of SHELXL-97<sup>19</sup> program package to  $R_1 = 0.0416$ ,  $wR_2 = 0.0498$  and GOOF = 0.998 [based on reflections with  $I > 2\sigma(I)$ ].

*Crystallographic data for* **4d**: C<sub>34</sub>H<sub>28</sub>F<sub>8</sub>N<sub>4</sub>O<sub>6</sub>S, *M* = 772.66, monoclinic, space group *C*2/*c*, *a* = 65.3010(17), *b* = 5.4738(4) and *c* = 19.2195(13) Å,  $\beta$  = 99.368(5)°, *V* = 6778.3(7) Å<sup>3</sup>, *Z* = 8, *d*<sub>calc</sub> = 1.514 g cm<sup>-3</sup>,  $\mu$ (MoK $\alpha$ ) = 0.192 cm<sup>-1</sup>, *F*(000) = 3168. A total number of 13 122 reflections were measured on an Xcalibur 3 diffractometer at 293(2) K [ $\omega$ /2 $\theta$ -scanning technique, MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å), graphite monochromator, CCD detector], 6707 independent reflections ( $R_{int}$  = 0.0394), 3747 reflections with *F*<sub>0</sub> > 4 $\sigma$ (*F*<sub>0</sub>). The structure was solved by direct methods and refined by the least-squares method with the use of SHELXL-97<sup>19</sup> program package to *R*<sub>1</sub> = 0.0561, *wR*<sub>2</sub> = 0.1434 and GOOF = 1.004 [based on reflections with *I* > 2 $\sigma$ (*I*)].

CCDC 848029 and 800075 contain 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. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

Table 1 Parameters of intramolecular hydrogen bonds in the molecules of compounds 4b,d.

Parameter	N(1)-H(1)····O(3)		$N(4)-H(4)\cdots O(4)$	
	4b	4d	4b	4d
d(N–H)/Å	0.93(2)	0.84(6)	0.85(1)	0.86(8)
$d(H \cdots O)/Å$	1.89(9)	1.99(2)	1.97(4)	1.96(9)
∠NHO/°	131.3(5)	132.6(9)	133.6(1)	136.4(0)
d(N-O)/Å	2.61(0)	2.63(9)	2.63(4)	2.66(6)



Figure 3 X-ray structure of 4d (thermal ellipsoids at 50% probability level, ORTEP drawing)

groups of acetyl fragments take part in the formation of IMHB rather than ethoxycarbonyl groups as in the case of compound **4a**.

The molecular packing (Figure 2) in the unit cell of compound **4b** is organized by the two types of intermolecular hydrogen bonding. The first type includes the interactions between atoms O(4) and H(29A) of acetyl groups [2.66(7) Å] and the second type is realized through the interaction of atoms O(1) and H(31B) of ethoxycarbonyl groups of the adjacent molecules [2.89(9) Å].

To determine the influence of fluoroalkyl substituents on the spatial structure of the molecule the X-ray analysis of  $4d^{\ddagger}$  was carried out. Similarly to 4b, diethyl 2,2'-[2,5-thienylbis(amino-methylidene-2-iminophenylene)]bis(3-oxo-4,4,5,5-tetrafluoropentanoate) 4d in crystal is *s-trans,s-cis*-conformer of *EE*-isomer of bis(amino enone) tautomer (Figure 3) and also has two independent coordination centres. Acceptor properties of the fluoroalkyl group lead to the intramolecular H-bonding between NH groups of phenylenediamine moiety and oxygen atoms of fluoroacyl fragment: N(1)–H(1)···O(3) and N(4)–H(4)···O(4) (Table 1).

The presence of the polyfluoroalkyl groups in the molecule changes the crystal packing so that the orientation of polyfluoroalkyl and hydrocarbon chains as a result of the intermolecular interactions H··F [2.86(1) Å] becomes determinative (Figure 4).<sup>18</sup> Unlike bis-azomethine **4b**, where the intermolecular hydrogen bonding makes the groups naturally equal, in the compound **4d** the interactions between fluorinated ethyl substituent and non-fluorinated one take place. This reason accounts for the different molecule packing.



Figure 4 The molecular packing of 4d (along the c axis).

In summary, perspective approach to the synthesis of openchain macroacyclic heteroatomic polydentate ligands was demonstrated. The ligands obtained are challenging for the further physicochemical research.

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#### **Online Supplementary Materials**

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.09.020.

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