Programmed Construction of Discrete Self-Assembled Cyclic Aggregates

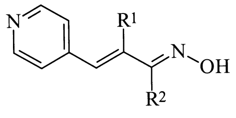
Monika Mazik,*[a] Dieter Bläser,[b] and Roland Boese[b]

Abstract: Examples for programmed self-assembly of α,β-unsaturated ketoximes carrying a terminal pyridine subunit are described. The solid-state structures of a series of pyridinyl α,β-unsaturated ketoximes **1** were investigated by X-ray structural analysis; this demonstrated that molecules **3**–**5** predictably form discrete cyclic aggregates stabilized by a network of hydrogen bonds and aromatic interactions.

Keywords: crystal engineering · hydrogen bonding · molecular recognition · self-assembly · supramolecular chemistry

Introduction

Programmed self-assembly of small building blocks through noncovalent interactions is a promising alternative to covalent synthesis for the development of functional materials. The advantages of this strategy are the simplified synthesis of small subunits, the economy in construction of structures with nanometer dimensions and the reversible formation of complex structures. In addition, controlled self-assembly of small building blocks provides insight into the molecular recognition phenomena; small molecular assemblies can provide models for macromolecular aggregates involved in a large number of biological processes. The design of molecular subunits that self-assemble into well-defined, discrete structures in the solid state or in solution is a contemporary challenge in supramolecular chemistry.[1, 2] One potential method for forming discrete aggregates involves hydrogen-bond-mediated cyclic aggregation. So far, only a few examples can be found in the literature of discrete, hydrogen-bonded cyclic assemblies, which contain 3–15 subunits, in the solid state and/or in solution.[3–13]



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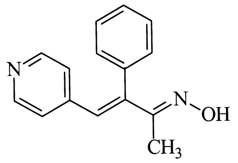

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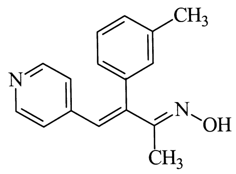

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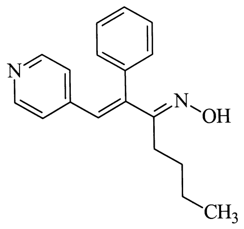

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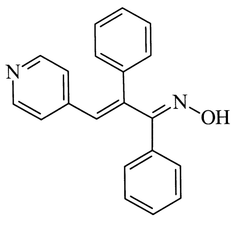

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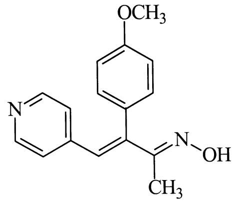

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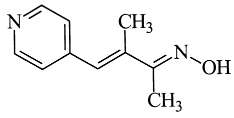

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In this study the aggregation behaviour of compounds of type **1**, which contain a pyridine and an α,β-unsaturated ketoxime subunit, is described. The crystal packing was analyzed as a function of the residues R^1 and R^2 in order to explore the scope of controling the formation of well-defined cyclic structures in the solid state. Our design is based on the observation that in the crystalline state four molecules of 3-phenyl-4-pyridin-4′-yl-3-buten-2-onoxime (**2**; $R^1 = C_6H_5$, $R^2 = CH_3$) form discrete cyclic tetramers stabilized by a network of eight hydrogen bonds (including four OH···N and four CH···N interactions) as well as aromatic interactions.[14] The analysis of the factors directing the formation of the supermacrocycle of **2** allowed the following predictions. i) All

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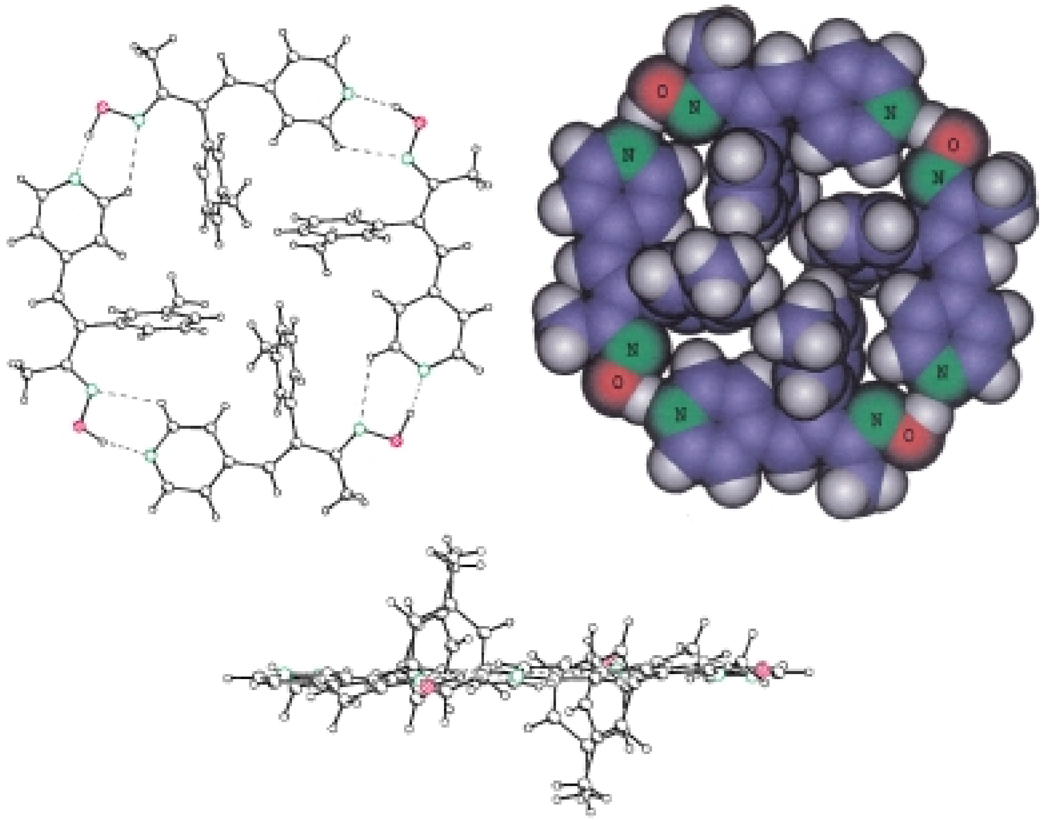

Figure 1. The tetragonal motif of **3** in the crystal (top and side view).

compounds of type **1** carrying a suitably sized aromatic (not heteroaromatic) group as R^1 subunit would be expected to form discrete cyclic aggregates; thus, a derivative possessing, for example, a *meta*-substituted phenyl group should also form similar tetramers, whereas *para*-substituted phenyl groups as R^1 should not (steric hindrance). ii) The replacement of an aromatic residue (R^1) by aliphatic groups probably should not lead to the supramolecular cyclic structure owing to the absence of edge-to-face interactions between aromatic groups projected into the cavity of the supermacrocycle. iii) Both aliphatic and aromatic groups as R^2 residue (R^1 = aryl, R^2 = alkyl or aryl) should allow the formation of discrete cyclic assemblies. iv) As a consistent feature of the solid-state structures of compounds of type **1**, the formation of OH···N-pyr hydrogen bonds between oxime hydroxyl and pyridine nitrogen atom would be expected. In order to verify these hypotheses and the generality of the presented supramolecular motif, compounds **3**–**7** were synthesized and their crystal structure was analyzed by X-ray diffraction.

Abstract in German: *Beispiele für die programmierte Selbstorganisation von α,β-ungesättigten Ketoximen, die eine terminale Pyridinyl-Einheit beinhalten, werden beschrieben. Die Festkörperstrukturen einer Serie von Pyridinyl-α,β-ungesättigten Ketoximen **1** wurden mittels Röntgenstrukturanalyse bestimmt. Diese Untersuchungen zeigen, daß die Moleküle **3**–**5** vorhersagbare diskrete cyclische Aggregate bilden, die durch ein Netz von Wasserstoffbrücken und aromatische Wechselwirkungen stabilisiert sind.*

In these compounds the terminal pyridine unit as molecular recognition element (pyridine nitrogen atom as a hydrogen bond acceptor) was kept constant, and the residues R^1 and R^2 were varied. Compounds **3** and **6** served to test the first hypothesis, the crystal structures of compounds **4**, **5** and **7** should confirm the second and third predictions.

Results and Discussion

Compounds **3**–**7** were obtained by condensation of pyridine-4-carbaldehyde with 1-(3-methyl-phenyl)-2-propanone, 1-phenyl-2-hexanone, 1,2-diphenylethanone, 1-(4-methoxyphenyl)-2-propanone and 2-butanone, respectively, followed by oxime formation of the resulting pyridinyl α,β-unsaturated ketones. Crystals of compounds **3**–**7** were grown by slow evaporation of the solvent from ethanolic solutions of the compounds. The X-ray analyses of **3**–**7** indeed confirmed the generality of the motif based on hydrogen bonding and aromatic interactions.

Compounds **3** (R^1 = 3-CH_3-C_6H_4, R^2 = CH_3) and **4** (R^1 = C_6H_5, R^2 = $CH_2CH_2CH_2CH_3$) form a cyclic structure closely related to that of compound **2**. As expected, incorporation of an additional substituent in the *meta*-position of the phenyl ring (as in **3**) or replacement of the methyl by an *n*-butyl group (as in **4**) does not change the general packing mode. The crystal structures show an arrangement in which each molecule participates in two OH···N and two CH···N hydrogen bonds[15] to two neighbouring residues (Figures 1 and 2, Scheme 1). The resulting tetrameric ring structure

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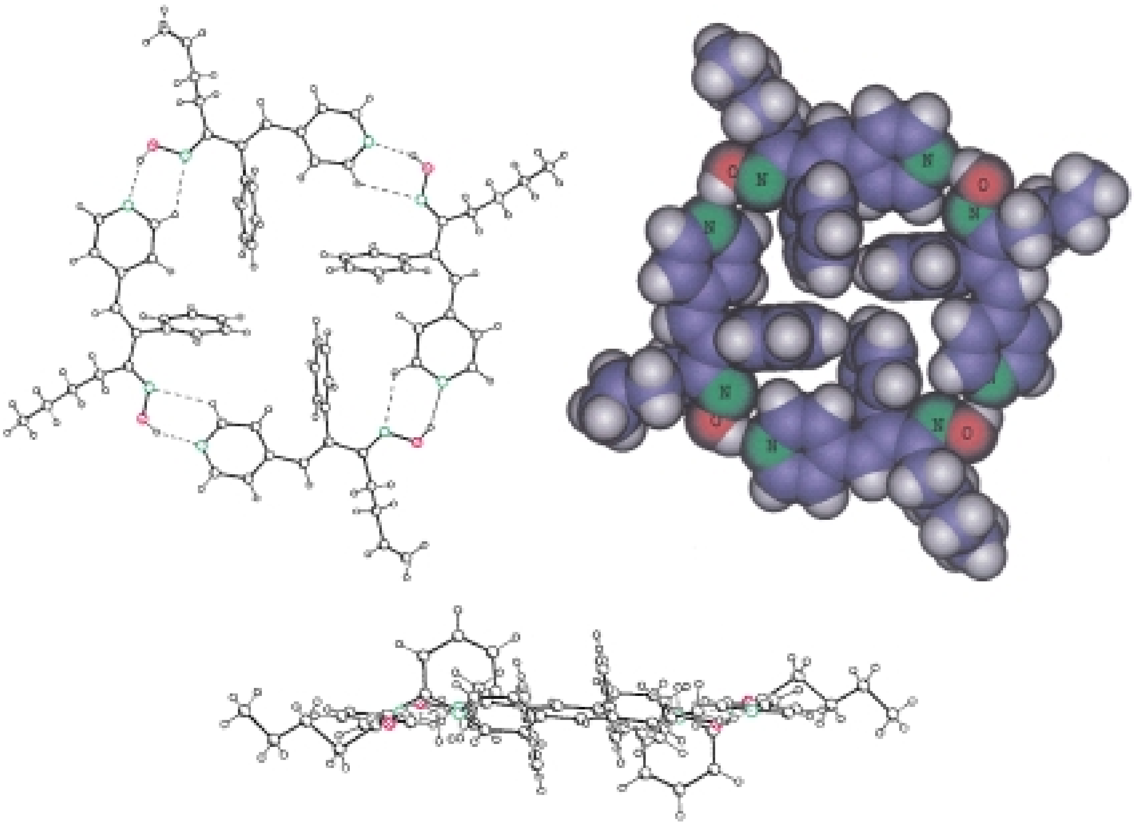

Figure 2. The tetragonal motif of **4** in the crystal (top and side view).

consists of a backbone established by four oxime moieties and is "filled" by four phenyl groups. The pyridine and the phenyl rings of the neighbouring molecules show edge-to-face orientations in which the H atoms on the pyridine ring interact with negatively charged regions on the phenyl residue. In addition, phenyl–phenyl interactions can be recognized (phenyl rings adopt a herringbone arrangement).[16] The four pyridine rings form a nearly planar structure and the "inner" phenyl rings are substantially twisted out of this plane. The planes of the opposite phenyl rings are arranged coplanar, and the planes of adjacent phenyl rings are nearly orthogonally oriented (interplanar angles of 95.8° and 90.3° for tetramers of **3** and **4**, respectively).

The OH···N and CH···N bond lengths in two pairs of hydrogen bonds on opposite sides of the tetramer of **3** are 1.80 Å (O···N distance, 2.79 Å; O-H···N angle, 156°) and 2.50 Å (C···N distance, 3.20 Å; C-H···N angle, 124°), respectively, and the OH···N and CH···N bond lengths in the two remaining opposite pairs of hydrogen bonds are 1.65 Å (O···N distance, 2.77 Å; O-H···N angle, 172°) and 2.57 Å (C···N distance, 3.25 Å; C-H···N angle, 120°; Scheme 1). The OH···N hydrogen bonds in the tetramer of **4** have alternating bond lengths of 1.94 Å (O···N distance, 2.71 Å; O-H···N angle, 149°) and 1.98 Å (O···N distance, 2.78 Å; O-H···N angle, 155°). For CH···N contacts distances of 2.49 Å (C···N distance, 3.19 Å; C-H···N angle, 122°) and 2.83 Å (C···N distance, 3.41 Å; C-H···N angle, 114°; Scheme 1) were observed.

The distances between the pyridine hydrogen atoms (C–H adjacent to the pyridine nitrogen) and the centre of the phenyl rings of the neighbouring molecules in the supermacrocycle of **3** alternate between 2.86 and 2.95 Å. The interplanar angles between the pyridine and phenyl rings of adjacent molecules alternate between 69° and 78°. In the tetramer of **4** the closest pyridine-H···phenyl centroid (phenyl of the neighbouring residue) contacts amount to 2.92 and 4.16 Å, and the interplanar angles between the pyridine and phenyl rings of the neighbouring molecules alternate between 75° and 81°. The methyl or butyl groups in both type of aggregates are located on the outside of the cavities. Figures 3 and 4 show the packing of discrete supramolecular aggregates of **3** and **4** in the crystal.

The crystal structure of **5** ($R^1 = R^2 = C_6H_5$) is closely related to those of **3** and **4**. Once again the supramolecular, cyclic structure is stabilized by hydrogen bonds and aromatic interactions. However, in this case ethanol molecules are incorporated in the aggregate, which consists of four molecules of **5** and four molecules of ethanol (Scheme 1, Figure 5).

As a result of the presence of the second phenyl group in the molecular structure **5**, the $-C{=}C{-}C{=}N-$ unit loses the planarity. The C3-C2-C1-N10 torsion angle is 164° (Figure 5); in contrast, these torsion angles for **3** and **4** amount to 179 and 176°, respectively. The lengths of oxime-OH···O-ethanol hydrogen bonds amount to 1.69 Å (O···O distance, 2.65 Å; OH···O angle, 179°). The intermolecular Et-OH···N-pyr hydrogen bonds have a length of 1.85 Å (O···N distance, 2.74 Å; OH···N angle, 169°, Scheme 1). The aryl–aryl interactions observed in the supermacrocycle of **5** are similar as those found in tetramers of **3** and **4**. The four phenyl groups (R^1) project into the central cavity of the macrocycle and

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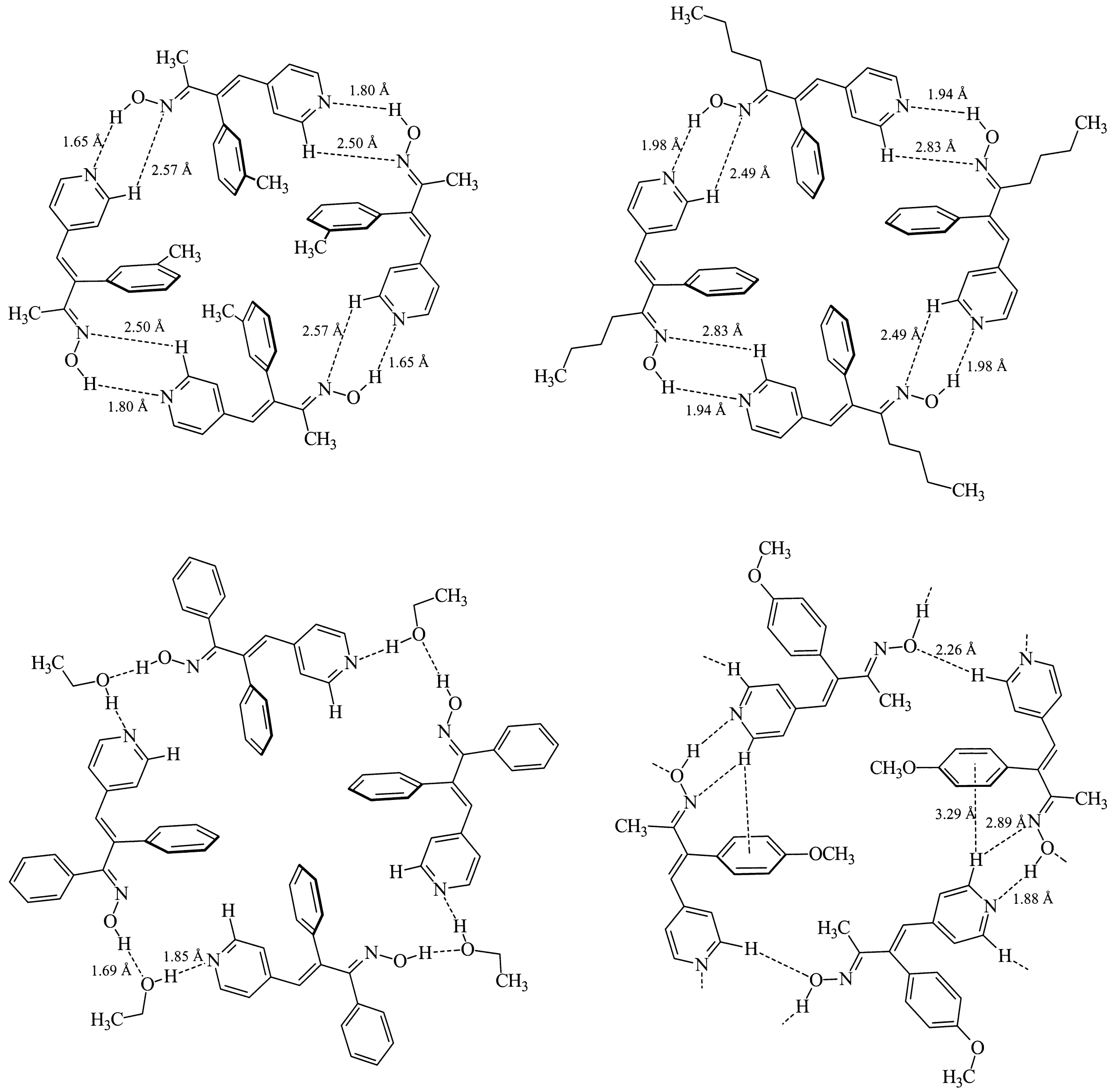


Scheme 1. Schematic structure of the tetrameric aggregates of **3** (top left) and **4** (top right), the cyclic aggregate of **5** (bottom left) and the tetramer of **6** (bottom right).

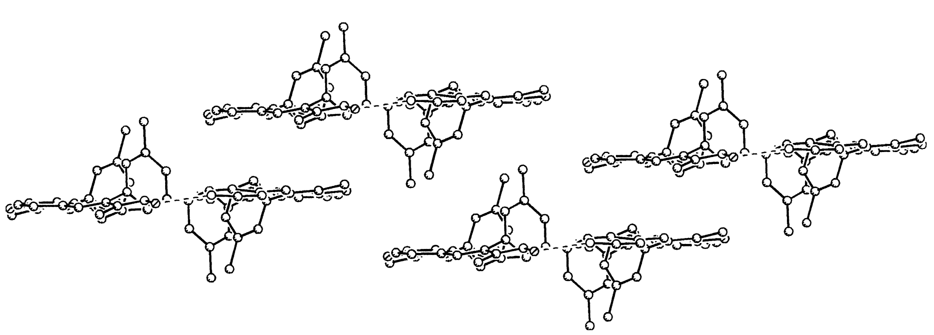


Figure 3. Packing of the supramolecular ring-shaped structures of **3**.

participate in edge-to-face interactions. The planes of the opposite phenyl rings are coplanar, and the planes of adjacent phenyl rings are oriented nearly orthogonal (interplanar angles of 87.7° and 92.3°). The distances of pyridine H atoms (C–H adjacent to the pyridine nitrogen) to the centre of the phenyl rings of the neighbouring molecules amount to 2.62 Å. The interplanar angles between pyridine and phenyl rings of the neighbouring molecules are 63°. In order to form such similar aromatic interactions as those of tetramers of **3** and **4**, the backbone of the supermacrocycle of **5**, established by four oxime moieties and four ethanol molecules, adopts no planar geometry. Figure 6 show the stacking of discrete supramolecular aggregates of **5** in the crystal.

The X-ray structure of 3-(*p*-methoxy-phenyl)-4-pyridin-4′-yl-3-buten-2-onoxime (**6**) provides a further example of the present type of control of molecular self-assembly through

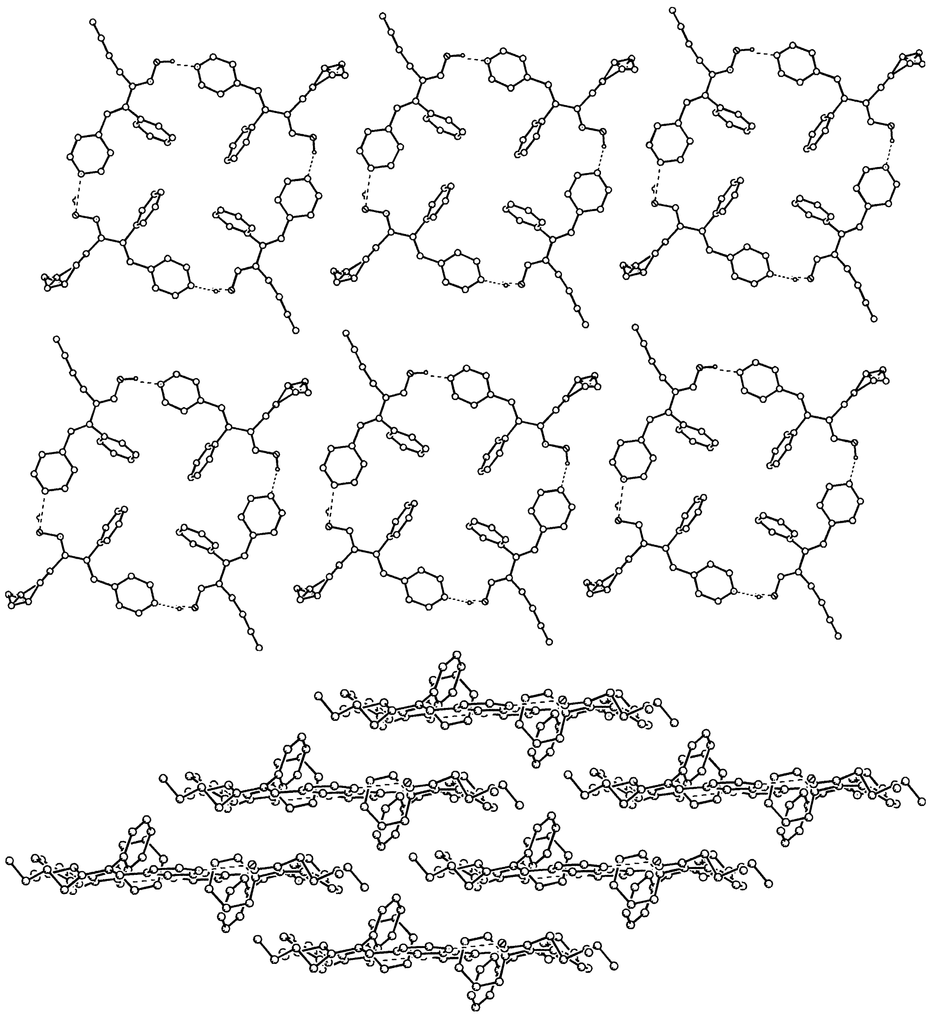
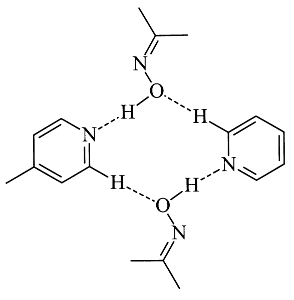


Figure 4. Packing of the supramolecular ring-shaped structures of **4**.

hydrogen bonding and aromatic interactions. However, as expected, the cyclic tetrameric aggregates are not discrete (Scheme 1), but joint via hydrogen-bond patterns corresponding to the motif **6a**. This is very likely due to the steric demand



6a

of the methoxyphenyl groups allowing only two aromatic groups to point into the central cavity of the macrocyclic structure (Figure 7). The crystal structure displays an infinite sheet arrangment in which the individual molecules are involved in four hydrogen bonds to four neighbouring residues (Figure 8); this leads to cycles formed by four oxime molecules. The backbone of the tetramer is held together by two strong intermolecular OH$\cdots$N and two weaker CH$\cdots$O hydrogen bonds[17] with distances of 1.88 (O$\cdots$N distance, 2.68 Å; O-H$\cdots$N angle, 157°) and 2.26 Å (C$\cdots$O distance, 3.30 Å; C-H$\cdots$O angle, 161°) respectively. The oxime hydroxyl group forms cooperative hydrogen bonds through simultaneous participation as donor and acceptor of hydrogen bonds. The pyridine nitrogen acts as an acceptor and the aromatic CH group that is adjacent to the nitrogen atom acts as a hydrogen bond donor. The four pyridine rings form a nearly planar structure. The inner phenyl rings are in a coplanar arrangement. The distances between the pyridine atoms and the centre of the phenyl rings of the adjacent molecules are 3.29 Å (Scheme 1). The methyl groups participate in CH$\cdots\pi$ interactions with the phenyl rings (Figure 7).[18]

It turns out that the presence of the aromatic ring (substituent R^1) in structure **1** is essential for the creation of cyclic aggregates. Evidence for this provided by the crystal structure of **7**. As supposed, compound **7** ($R^1 = CH_3$, $R^2 = CH_3$) does not form a cyclic arrangement, but prefers a linear motif in the solid state (Figure 9).

Clearly, these results show that the presence of phenyl groups has a stabilizing effect for the formation of cyclic arrangements. The pyridine nitrogen atom and the oxime hydroxyl group of each molecule are used for hydrogen bonding. Each molecule of **7** is involved in two OH$\cdots$N hydrogen bonds with lengths of 1.79 Å (O$\cdots$N distance, 2.75 Å; OH$\cdots$N angle, 165°). Additionally, short pyr-CH$\cdots$N-oxime contacts between molecules of neighbouring chains are found (CH$\cdots$N distance, 2.70 Å).

Conclusion

In the present work we have demonstrated that the combination of pyridine and α,β-unsaturated ketoxime subunits forms versatile components for the self-assembly in the solid state and represents a robust and simple building block for crystal engineering. The molecular self-assembly of these molecules is controlled by both hydrogen bonding and aromatic interactions. In each case a consistent feature of

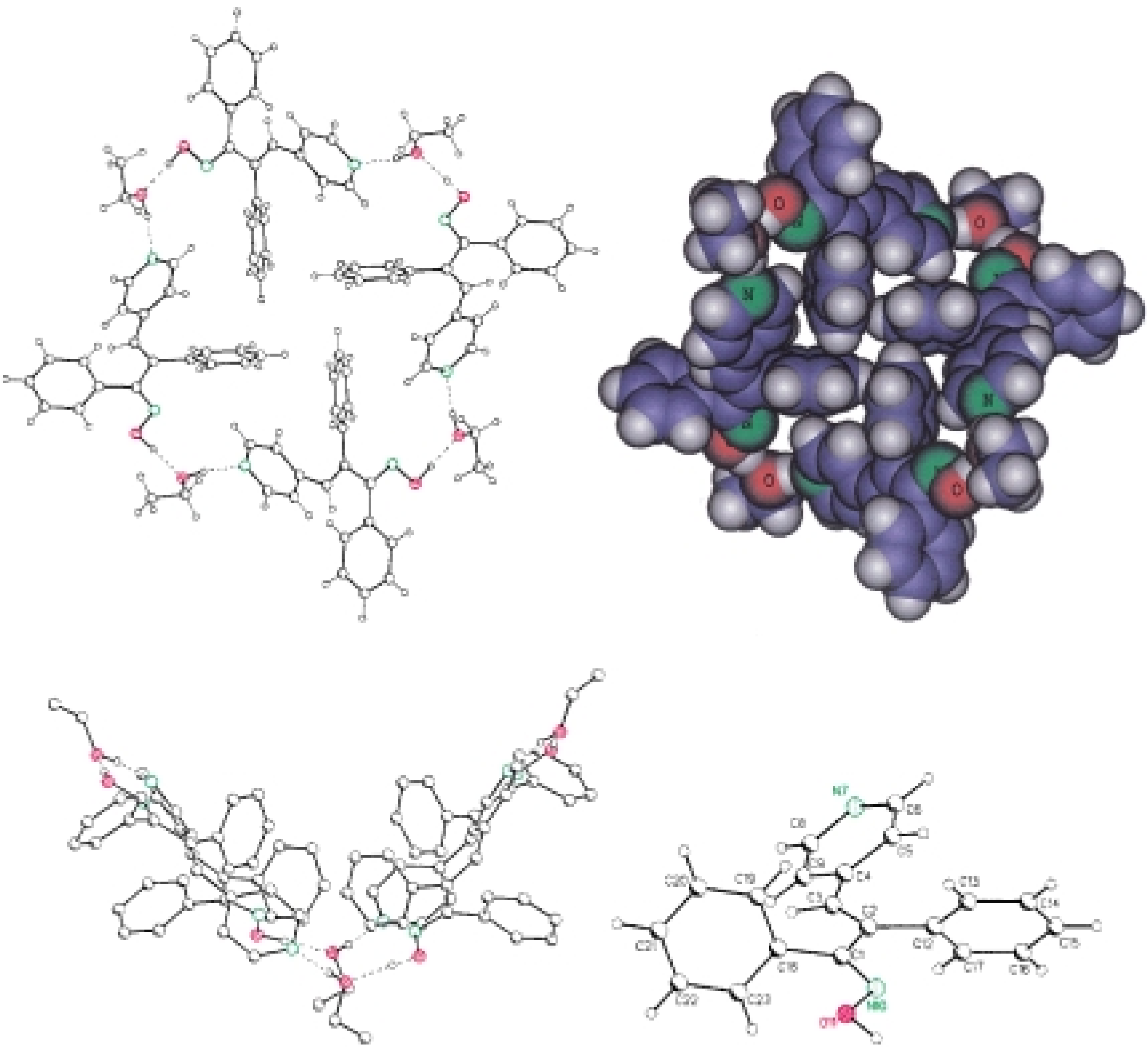


Figure 5. The cyclic motif of **5** (top and side view) and the monomeric unit in the crystal.

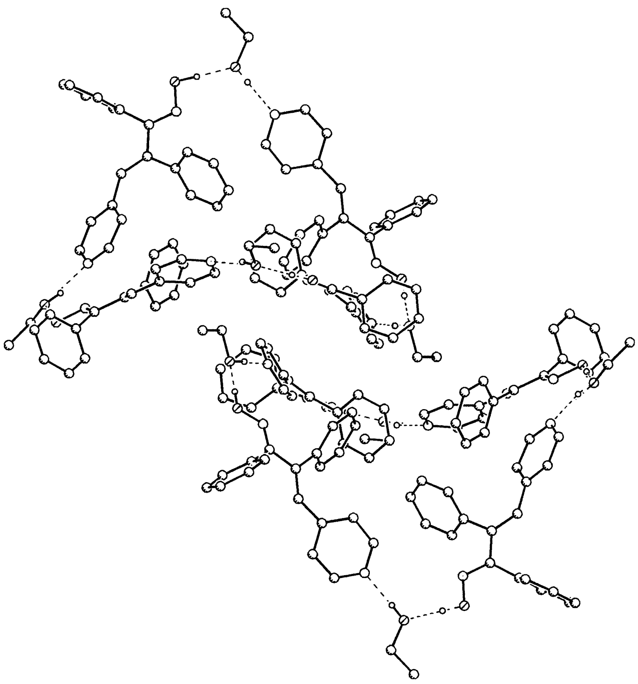


Figure 6. Packing of the cyclic aggregates of **5**.

the solid state structures is the formation of OH···N-pyr hydrogen bonds.

As expected, the cyclic aggregates were only observed for compounds carrying an aromatic group as R^1 substituent (compounds **3**–**6**). The formation of cyclic aggregates is further governed by the steric demand of the aromatic substituent R^1. If steric hindrance is present, as in the case of compound **6**, the cyclic assemblies are formed. These, however, are not discrete entities, but linked through hydrogen bonds.

X-ray structure analyses of **4** and **5** confirmed that the variation of the R^2 residue does not prevent the formation of discrete cyclic aggregates, as demonstrated by the replacement of a methyl by a *n*-butyl subunit (**4**) or a phenyl ring (as in **5**). A major difference between the supermacrocycles of compounds **3** and **4** and those of compound **5** lies in the incorporation of ethanol molecules in the supramolecular structure of **5**.

In all of the above supermacrocycles the edge-to-face stacking interactions between pyridine and the phenyl rings of the neighbouring molecules can be recognized. Furthermore, the phenyl–phenyl interactions appear to be of importance for the stabilization of the cyclic aggregates.

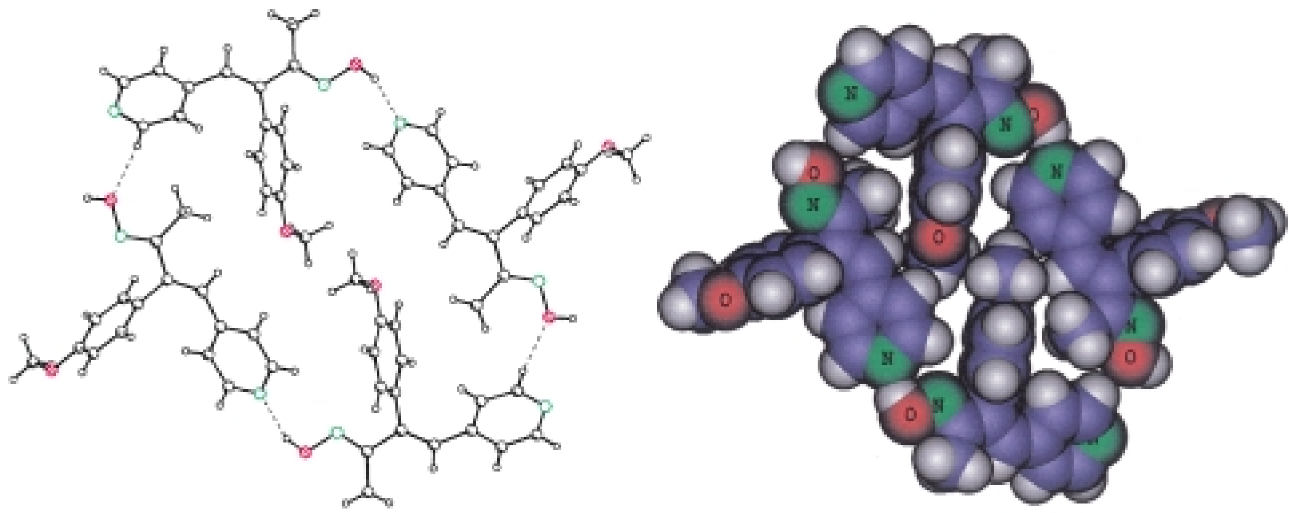


Figure 7. The tetragonal motif of **6** in the crystal.

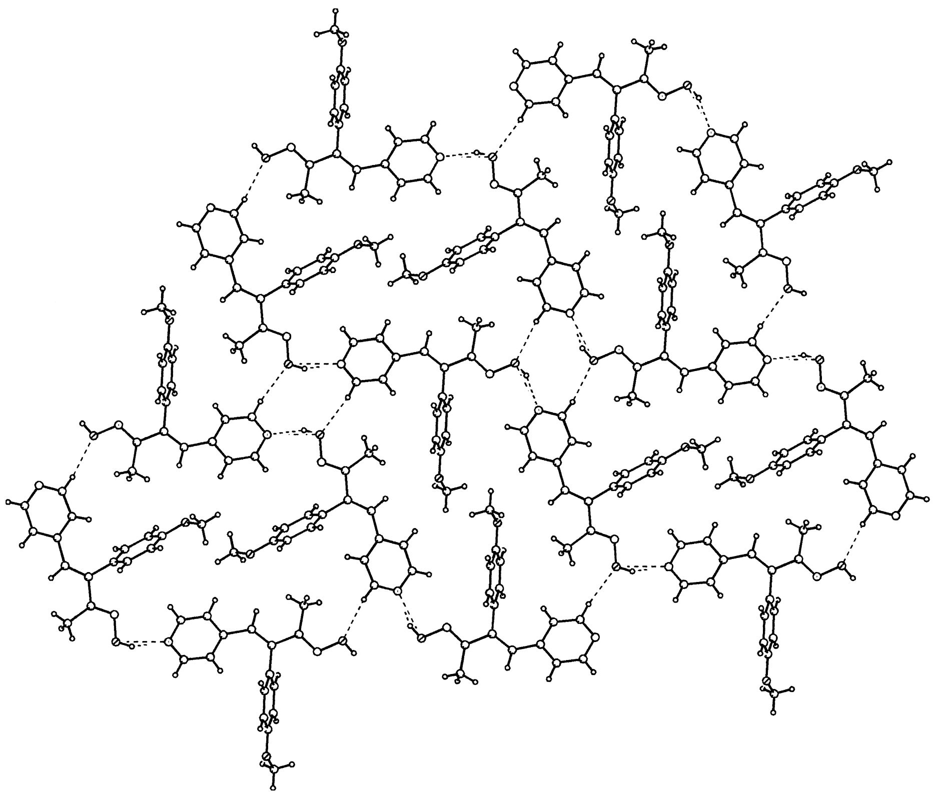


Figure 8. Packing of the tetramers of **6**.

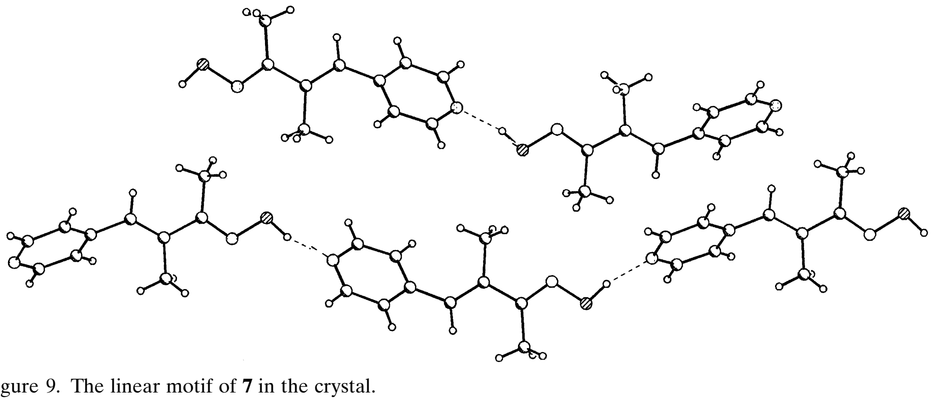


Figure 9. The linear motif of **7** in the crystal.

The formation of discrete cyclic tetrameric aggregates of **3**–**5** is an example for the creation of predictable, well-defined supramolecular structures.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer; chemical shifts are reported in ppm downfield from TMS as internal standard (solvent $CDCl_3$). Mass spectra were measured with a Fisons VG Prospec3000 and a Hewlett Packard HP5971A MSD spectrometer. Analytical TLC were carried out on Merck Kieselgel 60 F_{254} plates by employing a methanol/chloroform 1:7 (v/v) or benzene/ethyl acetate mixture 3:1 (v/v) as the mobile phase.

General procedure for the synthesis of 3–7: A mixture of pyridine-4-carbaldehyde (5.35 g, 0.05 mol) and ketone (0.1 mol) in chloroform (150 mL) was saturated with gaseous hydrogen chloride (0.1 mol) at 0–5 °C. Then the reaction mixture was kept at 25 °C for 48 h. Chloroform was evaporated, and the residue was washed several times with diethyl ether. The residual product was dried under vacuum. The crude hydrochlorides of pyridinyl α,β-unsaturated ketones were used for the oximation reactions without further purification. The mixture of pyridinyl α,β-unsaturated ketone hydrochloride (0.05 mol), hydroxylamine hydrochloride (0.15 mol) and sodium hydroxide (0.10 mol) in aqueous ethanol (200 mL) was heated under reflux for 4 h and then poured into water (300 mL). The oxime formed was filtered off and crystallized from ethanol. Additionally, the

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water solution (after evaporation of ethanol) was extracted with chloroform. After the chloroform separation the residual product was crystallized from ethanol.

3-(3-Methylphenyl)-4-(pyridin-4′-yl)-3-buten-2-onoxime (3): Yield 80%; m.p. 148–151 °C; ^{1}H NMR (500 MHz): $\delta = \delta = 2.11$ (s, 3H; CH_3), 2.29 (s, 3H; CH_3), 6.73–6.74 ($2\,H_{arom}$), 6.81 (s, 1H; =CH), 6.88–6.91 ($2\,H_{arom}$), 7.14–7.15 ($1\,H_{arom}$), 7.21–7.22 ($1\,H_{arom}$), 8.30–8.32 ($2\,H_{arom}$), 8.34 (s, 1H; NOH, shift strongly concentration dependent); ^{13}C NMR (125 MHz): $\delta = 158.64$ (C=N), 149.45, 143.83, 143.75, 138.45, 136.55, 129.85, 128.88, 128.64, 127.89, 126.42, 123.91, 21.37 (CH_3), 11.26 (CH_3); MS: m/z (%): 252 (83) $[M]^+$, 236 (100), 221 (8), 210 (11), 195 (20), 183 (3), 174 (11), 165 (14), 152 (12), 144 (5), 136 (11), 122 (28), 108 (12), 91 (11), 78 (17), 63 (10), 51 (25), 43 (11), 28 (10); $C_{16}H_{16}N_2O$: calcd 252.1263 found 252.1245; $R_f = 0.53$ (methanol/chloroform 1:7 v/v).

2-Phenyl-1-(pyridin-4′-yl)-1-hepten-3-onoxime (4): Yield 75%; m.p. 139–143 °C; ^{1}H NMR (500 MHz): $\delta = 0.92$ (t, $J = 7.6$ Hz, 3H; CH_3), 1.38 (m, 2H; CH_2,), 1.50 (m, 2H; CH_2), 2.56 (t, $J = 7.9$ Hz, 2H; CH_2), 6.72–6.73 ($2\,H_{arom}$), 6.79 (s, 1H; =CH), 7.09–7.10 ($2\,H_{arom}$), 7.32–7.33 ($3\,H_{arom}$), 8.30–8.31 ($2\,H_{arom}$), 8.34 (s, 1H; NOH, shift strongly concentration dependent); ^{13}C NMR (125 MHz): $\delta = 162.35$ (C=N), 149.42, 143.82, 142.99, 136.77, 129.36, 128.75, 128.05, 127.85, 123.95, 28.51 (CH_2), 24.71 (CH_2), 22.83 (CH_2), 13.81 (CH_3); MS: m/z (%): 280 (65) $[M]^+$, 279 (100), 263 (56), 236 (32), 221 (26), 219 (28), 207 (35), 180 (28), 152 (23), 130 (10), 106 (10), 77 (10), 41 (11); $C_{18}H_{20}N_2O$: calcd 280.1576; found 280.1563; $R_f = 0.51$ (methanol/chloroform 1:7 v/v).

1,2-Diphenyl-3-(pyridin-4′-yl)-2-propen-1-onoxime (5): Yield 40%; m.p. 205–208 °C; ^{1}H NMR (500 MHz): $\delta = 6.34$ (s, 1H; =CH), 6.57–6.58 ($2\,H_{arom}$), 7.16–7.42 ($10\,H_{arom}$), 8.14–8.15 ($2\,H_{arom}$), 8.80 (s, 1H; NOH, shift strongly concentration dependent); ^{13}C NMR (125 MHz): $\delta = 160.91$ (C=N), 149.05, 144.30, 143.92, 136.67, 132.04, 131.98, 129.55, 128.95, 128.87, 128.74, 128.41, 128.08, 123.89; MS: m/z (%): 300 (100) $[M]^+$, 299 (68), 283 (94), 256 (5), 223 (33), 206 (24), 193 (35), 152 (34), 141 (10), 127 (13), 105 (43), 89 (12), 77 (37), 51 (25); $C_{20}H_{16}N_2O$: calcd 300.1263; found 300.1268; $R_f = 0.55$ (methanol/chloroform 1:7 v/v).

3-(4-Methoxyphenyl)-4-(pyridin-4′-yl)-3-buten-2-onoxime (6): Yield 88%; m.p. 172–174 °C; ^{1}H NMR (500 MHz): $\delta = 2.04$ (s, 3H; CH_3), 3.76 (s, 3H; OCH_3), 6.72–6.73 (3H; $2\,H_{arom}$, =CH), 6.80–6.82 ($2\,H_{arom}$), 6.95–6.97 ($2\,H_{arom}$), 8.26–8.28 ($2\,H_{arom}$), 8.31 (s, 1H; NOH, shift concentration dependent); ^{13}C NMR (125 MHz): $\delta = 159.80$ (C=N), 159.04, 149.89, 144.44, 143.73, 131.14, 128.98, 128.19, 124.36, 114.67, 55.63 (OCH_3), 11.88 (CH_3); MS: m/z (%): 268 (100) $[M]^+$, 251 (100), 236 (17), 210 (30), 195 (12), 167 (20), 139 (12), 121 (7); $C_{16}H_{16}N_2O_2$: calcd 268.1212; found 268.1203; $R_f = 0.26$ (benzene/ethyl acetate mixture 3:1 v/v).

3-Methyl-4-(pyridin-4′-yl)-3-buten-2-onoxime (7):[19] Yield 85%; m.p. 139–140 °C; ^{1}H NMR (500 MHz): $\delta = 2.10$ (d, $J = 1.2$ Hz, 3H; $CH{=}CCH_3$), 2.17 (s, 3H; $COCH_3$), 6.78 (1H; =CH), 7.14–7.26 ($2\,H_{arom}$), 8.52–8.65 ($2\,H_{arom}$), 9.50 (s, 1H; NOH, shift strongly concentration dependent); ^{13}C NMR (125 MHz): $\delta = 157.04$ (C=N), 149.35, 145.47, 138.86, 127.32, 123.99, 14.35 (CH_3), 10.26 (CH_3); MS: m/z (%): 176 (18) $[M]^+$, 175 (56), 158 (15), 144 (8), 131 (4), 118 (12), 117 (23), 106 (12), 91 (85), 77 (25), 72 (100), 65 (38), 51 (34): $C_{10}H_{12}N_2O$: calcd 176.0901; found 176.0906; $R_f = 0.10$ (benzene/ethyl acetate mixture 3:1 v/v).

X-ray crystallographic analysis: The data of the crystals of **3**–**7** were obtained with a Siemens SMART-CCD three circle diffractometer ($Mo_{K\alpha}$ radiation, graphite monochromator) at 293 K. The structures were solved using direct methods and refined on F^2 using SHELXTL (Version 5.03). All non-H atoms were anisotropically refined and aromatic and methyl H atoms were treated as riding groups with the 1.2-fold U value (1.5 for methyl hydrogens) of the corresponding C atoms, hydroxy hydrogen atoms were located in a difference Fourier map and then treated as riding atoms. The mentioned distances to H atoms are based on normalized C–H bond lengths ($d_{C-H} = 1.08$ Å).

Crystal data for compound 3: $C_{16}H_{16}N_2O$, $M = 252.31$, crystal dimensions $0.21 \times 0.13 \times 0.07$ Å^3, crystal system triclinic, space group $P\bar{1}$, $a = 10.5015(11)$, $b = 10.9308(12)$, $c = 13.910(2)$ Å, $\alpha = 79.893$, $\beta = 73.947$, $\gamma = 66.899°$, $V = 1407.4(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.191\ g\,cm^{-3}$, wavelength 0.71073 Å, 17012 reflections collected (full sphere, θ range 2.03–25.00°), 4957 independent reflections ($R_{int} = 0.0656$), 2315 observed $[F_o \geq 4\sigma(F_o)]$, 343 parameters, $R1 = 0.0693$, $wR2 = 0.1543$, residual electron density 0.316 e Å^{-3}, $\mu = 0.076\ mm^{-1}$, empirical absorption correction, max/min transmission 1.00/0.667.

Crystal data for comopund 4: $C_{18}H_{20}N_2O$, $M = 280.36$, crystal dimensions $0.41 \times 0.32 \times 0.11$ Å^3, crystal system triclinic, space group $P\bar{1}$, $a = 9.0940(13)$, $b = 9.654(2)$, $c = 19.026(3)$ Å, $\alpha = 82.338(3)$, $\beta = 85.545(3)$, $\gamma = 87.530(3)°$, $V = 1649.5(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.129\ g\,cm^{-3}$, wavelength 0.71073 Å, 10160 reflections collected (full sphere, θ range 2.42–28.29°), 6216 independent reflections ($R_{int} = 0.0317$), 2668 observed $[F_o \geq 4\sigma(F_o)]$, 397 parameters, $R1 = 0.0703$, $wR2 = 0.1705$, residual electron density 0.585 e Å^{-3}, $\mu = 0.071\ mm^{-1}$, empirical absorption correction, max/min transmission 1.00/0.78.

Crystal data for compound 5: $C_{20}H_{16}N_2O \cdot C_2H_5OH$, $M = 346.42$, crystal dimensions $0.32 \times 0.29 \times 0.24$ Å^3, crystal system tetragonal, space group $I4_1a$, $a = 26.3378(12)$, $b = 26.3378(12)$, $c = 10.8514(7)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 7527.4(7)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.223\ g\,cm^{-3}$, wavelength 0.71073 Å, 31908 reflections collected (full sphere, θ range 2.03–28.52°), 4615 independent reflections ($R_{int} = 0.0676$), 2856 observed $[F_o \geq 4\sigma(F_o)]$, 235 parameters, $R1 = 0.0661$, $wR2 = 0.1424$, residual electron density 0.335 e Å^{-3}, $\mu = 0.079\ mm^{-1}$, empirical absorption correction, max/min transmission 1.00/0.50.

Crystal data for compound 6: $C_{16}H_{16}N_2O_2$, $M = 268.31$, crystal dimensions $0.25 \times 0.21 \times 0.08$ Å^3, crystal system monoclinic, space group $P2_1c$, $a = 7.3559(5)$, $b = 19.5451(12)$, $c = 10.4586(6)$ Å, $\alpha = 90$, $\beta = 99.1990$, $\gamma = 90°$, $V = 1484.3(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.201\ g\,cm^{-3}$, wavelength 0.71073 Å, 5730 reflections collected (full sphere, θ range 2.23–22.49°), 1792 independent reflections ($R_{int} = 0.0486$), 1274 observed $[F_o \geq 4\sigma(F_o)]$, 181 parameters, $R1 = 0.0566$, $wR2 = 0.1339$, residual electron density 0.188 e Å^{-3}, $\mu = 0.080\ mm^{-1}$, empirical absorption correction, max/min transmission 1.00/0.48.

Crystal data for compound 7: $C_{10}H_{12}N_2O$, $M = 176.22$, crystal dimensions $0.16 \times 0.13 \times 0.07$ Å^3, crystal system monoclinic, space group $P2_1c$, $a = 7.6070(2)$, $b = 9.9609(3)$, $c = 13.0772(4)$ Å, $\alpha = 90$, $\beta = 101.3960$, $\gamma = 90°$, $V = 971.36(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.205\ g\,cm^{-3}$, wavelength 0.71073 Å, 8271 reflections collected (full sphere, θ range 2.59–28.33°), 1978 independent reflections ($R_{int} = 0.0427$, empirical absorption correction), 1434 observed $[F_o \geq 4\sigma(F_o)]$, 118 parameters, $R1 = 0.0620$, $wR2 = 0.1646$, residual electron density 0.311 e Å^{-3}, $\mu = 0.080\ mm^{-1}$, empirical absorption correction, max/min transmission 1.00/0.60.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-13504 (**3**), 135005 (**4**), 135006 (**5**), 135008 (**6**) and 135007 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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