

Supramolecular Synthesis of Solid-State Tapes Through Molecular Facial Self-Recognition

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Four heterocyclic compounds are presented which exhibit specific self-recognition of identical Donor–Acceptor (D–A) H-bonding arrays, resulting in solid-state tapes with the same, but anti-parallel functional-group distribution on opposite sides. A detailed X-ray-crystallographic analysis of these supramolecular structures is described.

Introduction. – Solid-state structures such as molecular tapes and sheets [1] (*Fig. 1*) which are maintained through H-bonding and π – π stacking interactions have attracted much interest in the field of supramolecular chemistry [2]. Such well-ordered materials have the potential to exhibit unique electronic and optical properties for example, due to the precise integration of the respective active components into the crystal lattice [3]. As the relationship between molecular and crystalline structure becomes better understood, predictable supramolecular synthetic methodologies can be developed to prepare these advanced materials with tunable properties.

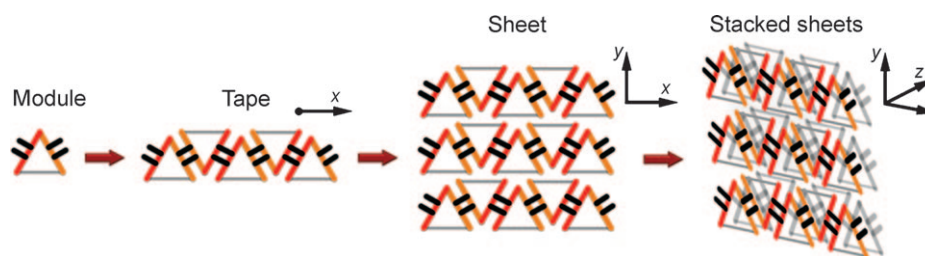


Fig. 1. *Solid-state organization of a module into a three-dimensional solid consisting of stacked sheets.* Each of the self-complementary compound **1–4** forms H-bonds to the identical A–D array (represented by one colored side of the triangle) on the adjacent monomer.

Many solid-state tapes have been constructed from either a *single* self-complementary molecule or *two* different molecules that are complementary to each other [1]. It is quite common for the organic compounds used in these supramolecular structures to possess rigid cores and strong directional H-bonding capabilities in order to limit their orientations in the solid state.

In this report, two monocyclic (2,4-diamino-6-methoxy-5-(prop-2-en-1-yl)pyridine-3-carbonitrile (**1**) and 4-chloro-2-(methylamino)-6-(prop-2-en-1-ylamino)pyrimidine-5-carbaldehyde (**2**)) and two bicyclic (4-(benzyloxy)-2,7-bis(prop-2-en-1-ylamino)pyrido[2,3-*d*]pyrimidine-6-carbonitrile (**3**) and (7*E*)-4-chloro-7-imino-8-(prop-2-en-1-yl)-2-(prop-2-en-1-ylamino)-7,8-dihydropyrido[2,3-*d*]pyrimidine-6-carbonitrile (**4**)) intermediate self-complementary molecules illustrated in Fig. 2 were investigated¹). In addition to being highly functionalized (*i.e.* allyl, benzyl, chloro, methylamino, methoxy), each of these aromatic compounds contains two or more H-bond acceptor and donor atoms that can potentially participate in intermolecular H-bonding interactions to generate a variety of crystal-packed structures. Herein, we describe the X-ray crystallographic details of each of these heterocyclic compounds **1–4**, noting in particular, the facially-selective self-recognition process that occurs during the course of the tape formation.

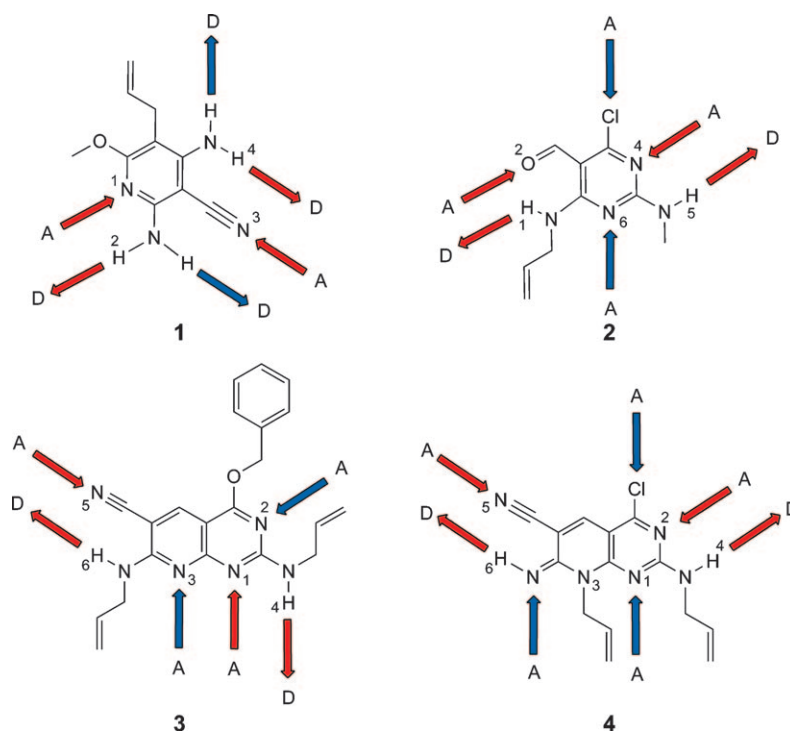


Fig. 2. Subset of potential H-bond acceptor ('A') and H-bond donor ('D') atoms for **1–4**. Red arrows indicate atoms involved in tape formation.

Results and Discussion. – Crystals suitable for single-crystal X-ray diffraction analysis were obtained from **1–4** using operationally simple conditions, by dissolving each of the compounds in AcOEt/hexane (**1** and **2**, 1:1 mixture; **4**, 10:1 mixture) or

¹) The detailed synthesis of **1**, **3**, and **4** will be published elsewhere. For the synthesis of **2**, see [4b].

CH_2Cl_2 (**3**) at room temperature, followed by slow evaporation of the solvents. Results of these crystal studies, which are illustrated in *Figs. 3–6*, show that despite their ability to associate in a variety of ways (due to the presence of multiple acceptor–donor pairs), each self-complementary compound **1–4** forms sheets consisting of well-organized tapes that are then stacked to form the three-dimensional solids²⁾. For each of these tapes, the self-complementary subunits are held together by H-bonds with $\text{N}\cdots\text{N}$ or $\text{N}\cdots\text{O}$ distances ranging from 2.97–3.21 Å (*Table 1*). Compound **2** contains a bifurcated H-atom which participates in intramolecular H-bonding ($\text{N}(1)\text{–H}\cdots\text{O}(2)$) in addition to intermolecular H-bonding (*Fig. 4,a*). The most interesting aspect of all four tapes, however, is the facial recognition exhibited by **1–4** during the course of intermolecular H-bond formation. More specifically, each pair of acceptor–donor atoms (*i.e.* for compound **1**, $\text{N}(1)$ and $\text{H}\text{–}\text{N}(2)$ are one pair and $\text{N}(3)$ and $\text{H}\text{–}\text{N}(4)$ are a second pair), which is represented by one colored side of the triangle in *Fig. 1*,

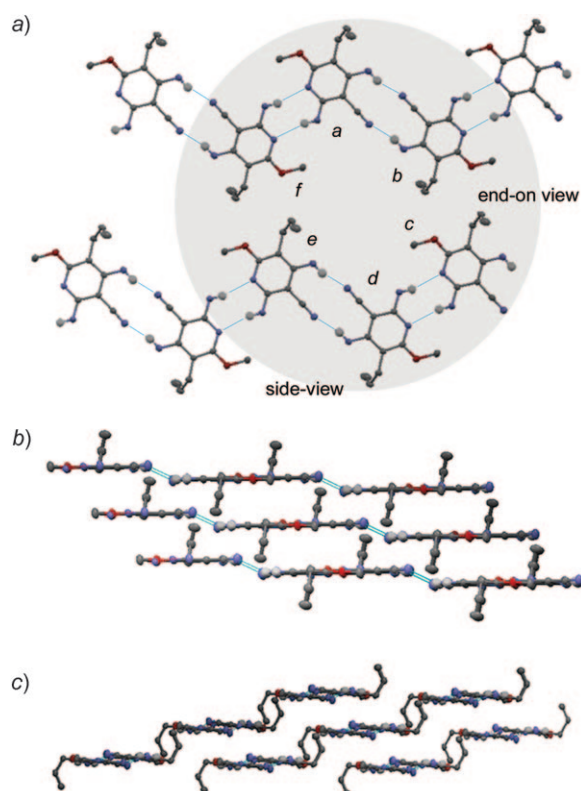


Fig. 3. *Crystal-structure analysis of 1.* a) Two zig-zag tapes in sheet formation. b) Side view of sheets in stacking formation. c) End-on view of sheets in stacking formation down the long axes direction.

²⁾ CCDC-672257, -672258, -639262, and -672259 for **1–4**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

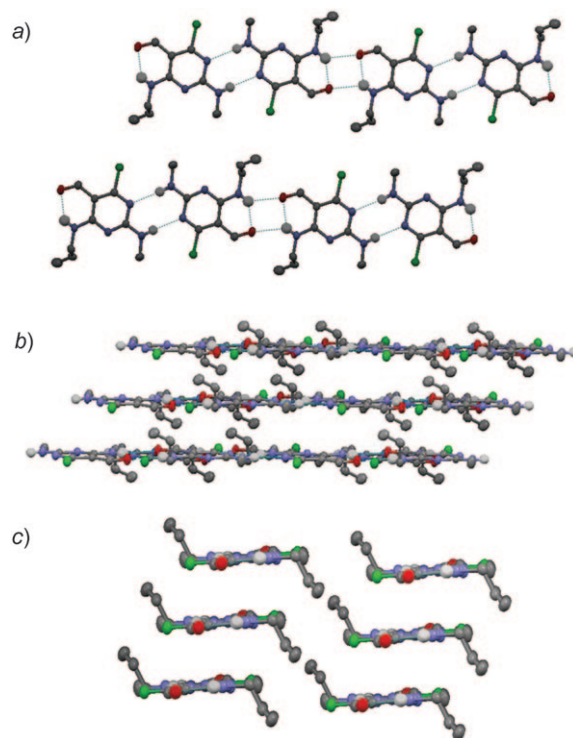


Fig. 4. *Crystal-structure analysis of 2.* a) Two nearly linear tapes in sheet formation. b) Side view of sheets in stacking formation. c) End-on view of sheets in stacking formation down the long axes direction.

recognizes the same acceptor–donor pair on the adjacent molecule (orange H-bonds to orange and red H-bonds to red). The result of these exclusive H-bonding interactions are molecular tapes which feature identical and anti-parallel functional-group distribution on opposite sides.

It is also important to note the different H-bonding arrays in the tapes generated from **3** and **4** (*i.e.* $N(1)\cdots H-N(4)$ vs. $N(2)\cdots H-N(4)$, resp.) even though these compounds are alike in structure. Such differences can be accounted for by considering a combination of steric and electronic factors. In compound **3** for example, although both $N(1)$ and $N(2)$ experience similar resonance contributions from the electron-donating O-atom, the inductive effect of this electronegative atom renders $N(1)$ a better H-bond acceptor than $N(2)$. In compound **4** alternatively, the allyl substituent covalently bonded to $N(3)$ may prevent this electronically more favorable $N(1)\cdots H-N(4)$ H-bonding pattern for steric reasons. This latter steric argument may also explain the H-bonding pattern for the structurally similar compound **2**, which is even further enforced by the ‘locking’ of $N(1)-H$ into position through the intramolecular $N(1)-H\cdots O(2)$ H-bond.

As noted above, each of the tapes that are generated from **1–4** are aligned with their long axis in a parallel fashion to form sheets (*Figs. 3–6, a*). A close examination of

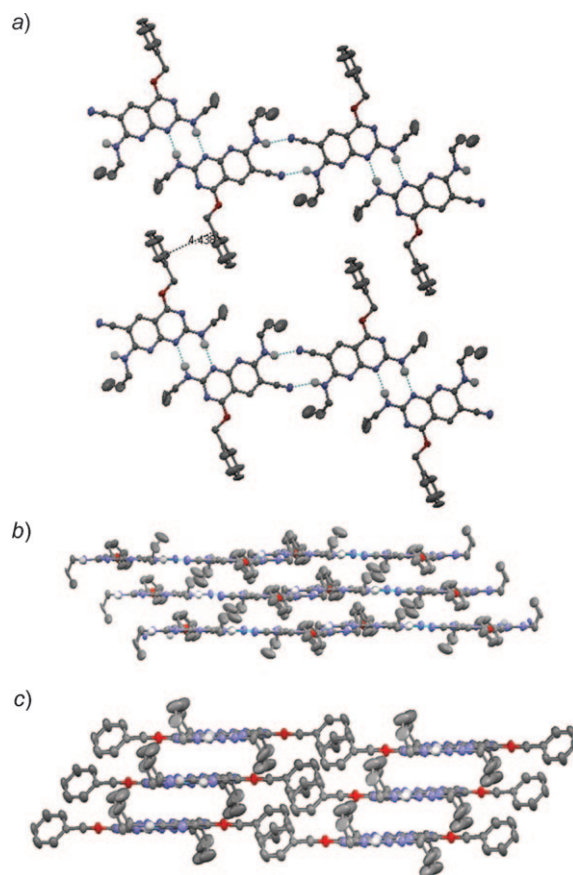


Fig. 5. *Crystal-structure analysis of 3.* a) Two crinkled tapes in sheet formation. b) Side view of sheets in stacking formation. c) End-on view of sheets in stacking formation down the long axes direction.

these sheets constructed from compounds **1**, **2**, and **4** reveals that alternating tapes are out-of-register from each other. In compound **1**, highlighted in *Fig. 3, a*, the two parallel zig-zag tapes create a hexameric rosette-like [4] arrangement between molecules *a–f*, which may offer further insight for engineering molecules that are capable of self-assembling into porous solids. In this arrangement, the allyl groups of **1** in adjacent tapes (e.g. molecule '*e*' and '*f*') are oriented in opposite directions relative to the plane of the sheet. In the case of compound **2**, the allyl groups from one linear tape are positioned near the chlorine and methylamine groups of neighboring molecules of the adjacent tape (*Fig. 4, a*). Lastly, for bicyclic compound **4** (*Fig. 6, a*), the two oppositely oriented allyl groups of each molecule flank each other between tapes in an interlocking fashion.

Compound **3**, on the other hand, is unique amongst the others in that alternating crinkled tapes are less displaced as shown in *Fig. 5, a*, which positions two benzyl groups from adjacent tapes in close proximity to each other (*i.e.* interplanar distance = 4.4 Å).

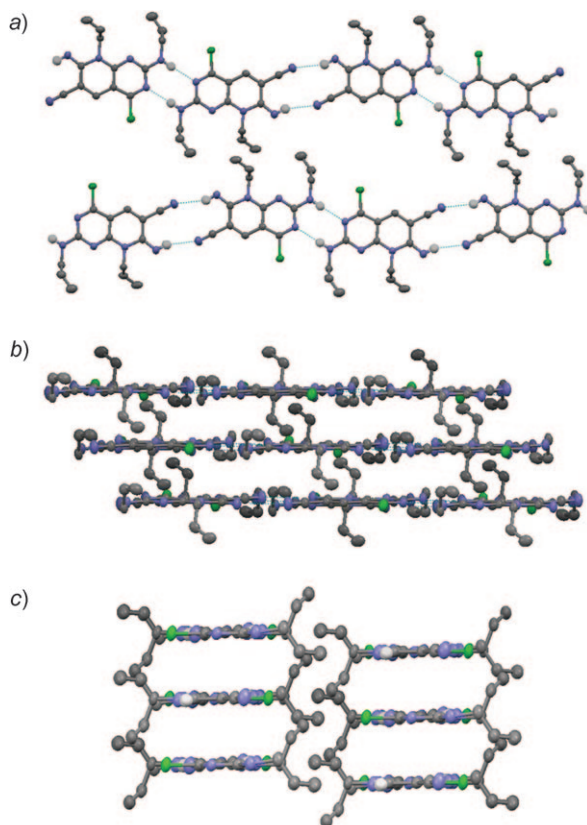


Fig. 6. *Crystal-structure analysis of 4.* a) Two nearly linear tapes in sheet formation. b) Side view of sheets in stacking formation. c) End-on view of sheets in stacking formation down the long axes direction.

In order to determine whether $\pi-\pi$ stacking interactions [5] of the Ph rings contribute to the assembly of the tapes into sheets, quantum-chemical calculations were carried out with electron correlation using the second-order *Møller–Plesset* perturbation theory (MP2) in conjunction with cc-pVDZ basis set [6]. Interaction energies were corrected for the basis set superposition error by the *Boys–Bernardi* counterpoise correction [7]. As illustrated in *Fig. 7,a*, dimer **3** obtained from the X-ray crystal data was compared to the dimer shown in *Fig. 7,b*, which has H-atoms in place of the Ph groups. The calculated interaction energies of -3.3 kcal/mol and 0.1 kcal/mol for *a* and *b*, respectively, suggest that the $\pi-\pi$ interactions may indeed contribute to the supramolecular arrangement of **3** in the solid state.

When the sheets are stacked to form the three-dimensional solid, the opposite face of the pyridyl ring of compound **1** is blocked by the allyl group of the adjacent molecule related by the crystallographic inversion center ($1/2, 1/2, 1/2$) (*Fig. 3,b*). In compounds **2** (*Fig. 4,b*), **3** (*Fig. 5,b*), and **4** (*Fig. 6,b*), adjacent allyl groups between the planes of the sheets are directed in an alternating up and down sequence. Whereas the end-on

Table 1. *H-Bonding Distances*

D–H...A	D–H [Å]	H...A [Å]	D...A [Å]	<D–H...A [°]
1				
N2–H2...N1 ^{a)}	0.88	2.33	3.1875(14)	164
N4–H4...N3 ^{b)}	0.88	2.28	3.0650(14)	148
2				
N1–H1...O2	0.83	2.09	2.726(2)	133
N1–H1...O2 ^{b)}	0.83	2.35	3.018(2)	138
N5–H5...N4 ^{c)}	0.86	2.21	3.063(2)	175
3				
N4–H4...N1 ^{d)}	0.88	2.10	2.973(3)	173
N6–H6...N5 ^{e)}	0.88	2.22	3.032(3)	153
4				
N4–H4...N2 ^{b)}	0.88	2.18	3.055(2)	171
N6–H6...N5 ^{f)}	0.88	2.37	3.208(2)	160

a) At 1–x, y, z. b) At x, 1–y, z. c) At 2–x, 1–y, 1–z. d) At 1–x, 1–y, z. e) At –1–x, 2–y, z. f) At 1–x, –1–y, z.

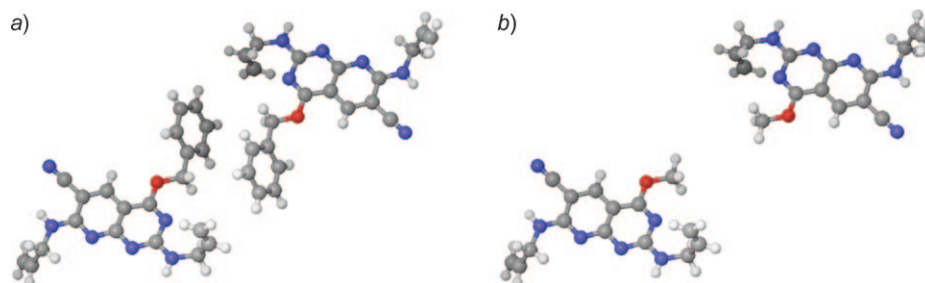
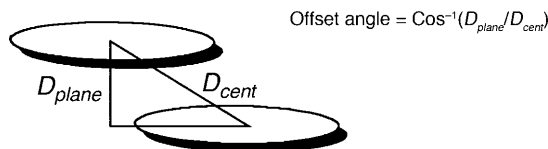


Fig. 7. a) Dimer of **3** obtained from the X-ray crystal data. b) Modeling of **3** with H-atoms substituted for the Ph groups.

packing view down the long axes direction for **2** (Fig. 4, c) and **3** (Fig. 5, c) are similar (with the exception of the benzyl groups in **3**), packed sheets of **4** (Fig. 6, c) appear as stacked hexagonal rings. The offset stacking angles were calculated for the four compounds using the distance between planes of nearest neighbor (D_{plane}) and the distance between centroids of nearest neighbor ‘stacked ring’ (D_{cent}) as shown in Table 2. In all cases, the stacking distance parameters are within the normal range (3.3–3.5 Å) [8], which indicates that π – π stacking interactions are important in the layering of the sheets into the three-dimensional solid.

In summary, we have demonstrated four examples of functionalized self-complementary heterocycles **1**–**4** that 1) form crystals at room temperature suitable for X-ray-diffraction analysis using standard and operationally simple conditions; 2) despite having multiple acceptor/donor atoms, all four molecules formed well-organized three-dimensional solids comprised of tapes/sheets; and 3) during tape formation, adjacent molecules self-assembled in a very specific, facially-selective manner, resulting in the same but anti-parallel functional distribution on opposite sides of the tapes.

Table 2. Ring Stacking Distances and Angles



	1	2	3	4
D_{plane} [Å]	3.50	3.40	3.36	3.39
D_{cent} [Å]	3.54	4.68	3.66	3.69
Offset angle [°]	8.62	43.46	23.60	23.17

Experimental Part

X-Ray Crystal-Structure Analysis for 1 (CCDC-672257). $C_{10}H_{12}N_4O$, $M_r = 204.24$, $0.60 \times 0.36 \times 0.11$ mm³, triclinic, $P\bar{1}$ (No. 2), $a = 6.8698(8)$ Å, $b = 9.3787(11)$ Å, $c = 9.6440(11)$ Å, $\alpha = 107.8121(15)^\circ$, $\beta = 108.2296(15)^\circ$, $\gamma = 104.2314(16)^\circ$, $V = 520.27(10)$ Å³, $Z = 2$, $\rho_{calc.} = 1.304$ g/cm³, $\mu = 0.090$ mm⁻¹, graphite-monochromated MoK_α (0.71073) radiation (λ [Å]), $T = -80^\circ$, 2θ limit = 55.02° , independent reflections (R_{int}): 2357 (0.0105), $R_1 [F_o^2 \geq 2\sigma(F_o^2)] = 0.0426$, $wR_2 [F_o^2 \geq -3\sigma(F_o^2)] = 0.1263$, observed reflections [$F_o^2 \geq 2\sigma(F_o^2)$]: 2044, largest difference peak and hole: 0.369 and -0.171 e Å⁻³, structure solution method [9]: direct methods (SHELXS-97), refinement method [9]: full-matrix least-squares on F^2 (SHELXL-97), Bruker PLATFORM/SMART 1000 CCD diffractometer³⁾, absorption correction: Gaussian integration (face-indexed). H-Atoms generated from idealized sp² or sp³ geometries of parent N- or C-atoms, with thermal parameters 120% of U_{eq} for parent atoms.

X-Ray Crystal-Structure Analysis for 2 (CCDC-672258). $C_9H_{11}ClN_4O$, $M_r = 226.67$, $0.38 \times 0.22 \times 0.19$ mm³, triclinic, $P\bar{1}$ (No. 2), $a = 4.6792(3)$ Å, $b = 9.9242(8)$ Å, $c = 11.8051(10)$ Å, $\alpha = 103.193(4)^\circ$, $\beta = 90.083(5)^\circ$, $\gamma = 93.332(5)^\circ$, $V = 532.76(13)$ Å³, $Z = 2$, $\rho_{calc.} = 1.413$ g/cm³, $\mu = 0.335$ mm⁻¹, graphite-monochromated MoK_α (0.71073) radiation (λ [Å]), $T = -80^\circ$, 2θ limit = 54.87° , independent reflections (R_{int}): 2361 (0.049), $R_1 [F_o^2 \geq 2\sigma(F_o^2)] = 0.0448$, $wR_2 [F_o^2 \geq -3\sigma(F_o^2)] = 0.1219$, observed reflections [$F_o^2 \geq 2\sigma(F_o^2)$]: 1787, largest difference peak and hole: 0.231 and -0.372 e Å⁻³, structure solution method [9]: direct methods (SHELXS-97), refinement method [9]: full-matrix least-squares on F^2 (SHELXL-97), Nonius KappaCCD diffractometer, empirical absorption correction [10]. H-Atoms attached to C-atoms generated from idealized sp² or sp³ geometries of parent atoms, with thermal parameters 130% of U_{eq} for parent atoms. H-Atoms attached to N-atoms were located and freely refined.

X-Ray Crystal-Structure Analysis for 3 (CCDC-639262). $C_{21.25}H_{20.50}Cl_{0.50}N_6O$, $M_r = 393.66$, $0.50 \times 0.24 \times 0.06$ mm³, triclinic, $P\bar{1}$ (No. 2), $a = 4.9574(9)$ Å, $b = 13.970(3)$ Å, $c = 16.201(3)$ Å, $\alpha = 64.549(3)^\circ$, $\beta = 87.731(3)^\circ$, $\gamma = 89.433(3)^\circ$, $V = 1012.3(3)$ Å³, $Z = 2$, $\rho_{calc.} = 1.291$ g/cm³, $\mu = 0.147$ mm⁻¹, graphite-monochromated MoK_α (0.71073) radiation (λ [Å]), $T = -80^\circ$, 2θ limit = 52.98° , independent reflections (R_{int}): 4165 (0.0362), $R_1 [F_o^2 \geq 2\sigma(F_o^2)] = 0.0693$, $wR_2 [F_o^2 \geq -3\sigma(F_o^2)] = 0.2051$, observed reflections [$F_o^2 \geq 2\sigma(F_o^2)$]: 2495, largest difference peak and hole: 0.295 and -0.241 e Å⁻³, structure solution method [9]: direct methods (SHELXS-97), refinement method [9]: full-matrix least-squares on F^2 (SHELXL-97), Bruker PLATFORM/SMART 1000 CCD diffractometer³⁾, absorption correction: Gaussian integration (face-indexed). The disordered Ph ring of the benzyloxy group of **3** was constrained to be an idealized hexagon with a C–C distance of 1.39 Å and the geometries of the disordered allyl groups were restrained to be the same during refinement. H-Atoms generated from idealized sp² or sp³ geometries of parent N- or C-atoms, with thermal parameters 120% of U_{eq} for parent atoms. Attempts to refine peaks of residual electron density as CH₂Cl₂ solvent atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure [11] as

³⁾ Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.

implemented in PLATON [12]. A total solvent-accessible void volume of 69.4 \AA^3 with total electron count of 18 consistent with a half-occupancy molecule of CH_2Cl_2 solvent (or 0.25 molecules for each molecule of compound **3**) was found in the unit cell.

X-Ray Crystal-Structure Analysis for 4 (CCDC-672259). $\text{C}_{14}\text{H}_{13}\text{ClN}_6$, $M_r = 300.75$, $0.73 \times 0.27 \times 0.18 \text{ mm}^3$, triclinic, $P\bar{1}$ (No. 2), $a = 8.1907(13) \text{ \AA}$, $b = 8.3489(13) \text{ \AA}$, $c = 11.0476(18) \text{ \AA}$, $\alpha = 94.570(2)^\circ$, $\beta = 110.014(2)^\circ$, $\gamma = 99.129(2)^\circ$, $V = 693.51(19) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc.}} = 1.440 \text{ g/cm}^3$, $\mu = 0.278 \text{ mm}^{-1}$, graphite-monochromated MoK_α (0.71073) radiation (λ [Å]), $T = -80^\circ$, 2θ limit = 52.00° , independent reflections (R_{int}): 2690 (0.0120), R_1 [$F_o^2 \geq 2\sigma(F_o^2)$] = 0.0397, wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$] = 0.1116, observed reflections [$F_o^2 \geq 2\sigma(F_o^2)$]: 2169, largest difference peak and hole: 0.286 and $-0.181 \text{ e \AA}^{-3}$, structure solution method [9]: direct methods (SHELXS-97), refinement method [9]: full-matrix least-squares on F^2 (SHELXL-97), Bruker PLATFOM/SMART 1000 CCD diffractometer³), absorption correction: Gaussian integration (face-indexed). H-Atoms generated from idealized sp^2 or sp^3 geometries of parent N- (except N6) or C-atoms, with thermal parameters 120% of U_{eq} for parent atoms. For N6 (the C=NH group), the H-atom (H6N) was located from a difference Fourier map; during refinement, H6N was given a thermal parameter 120% of $U_{\text{eq}}(\text{N6})$ and the N6–H6N distance was fixed at 0.88 \AA (but the C6–H6–H6N angle was unconstrained).

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