**Supplementary materials**

Within stereoatomic model[12] an atom or a molecule are characterized by such descriptors as:

$^{0}\mathbf{d}_{min}$ and $^{0}\mathbf{d}_{max}$ – the shortest and the longest distances between the atoms of neighboring molecules.

$^{0}D_{AZ}$ and $^{>1}D_{AZ}$ - Relative contributions (in per cents) of a given type of non-valence interactions A/Z to the total area of molecular surface ($^{0}\mathbf{S}$) or the area of VDP faces internal to the molecular surface ($^{>1}\mathbf{S}$).

$^{>1}f_{AZ}$ – The module of difference between the number of faces of a given A/Z type and RC value for two molecular VDPs. $^{>1}F$ - the sum of $^{>1}\phi_{AZ}$ for all theoretically possible types of intramolecular A/Z ineractions for one molecule.

$\mathbf{G}_3$ – dimensionless second moment of inertia of a VDP (either atomic and molecular).

$^{0}\mathbf{k}$ and $^{>1}\mathbf{k}$ – as the number of inter- and intramolecular contacts per one molecule; calculated as the number of pyramids with a vertex situated in the atomic position and the base in a VDP face with corresponding RC (0 and >1).

**MMVDP** – the method of representation of a crystal space by the molecular Voronoi-Dirichlet polyhedra.

**RC** – Rank of interatomic contact, the number of chemical bonds in the shortest chain connecting the A and B atoms in the crystal structure. Rank = 1 for valence bonds, Rank > 1 for intramolecular non-valence interactions and the Rank of intermolecular contacts is set to zero.

$^{0}\mathbf{S}$ and $^{>1}\mathbf{S}$ – Total areas of VDP faces with RC = 0 and >1.The former denotes the area of a molecular surface and the latter is the area of intramolecular contacts.

$\mathbf{v}_{ij}$ – and a volume of a pyramid with a vertex in a position of $A_i$ or $A_j$ atom and the base in the VDP face common for the $A_i$ and $A_j$, atoms. Upon the latter descriptor, a total volume of pyramids based on the faces with RC = 0 and with the vertexes in the atomic positions interior to the molecular surface ($^{0}\mathbf{V}$) can be calculated.

**VDP** – Voronoi-Dirichlet polyhedron of a point represents a convex polyhedron of minimum volume, containing this point, and bounded by perpendicular planes, which pass through middle points of segments, connecting this point with all other points.

Full set of molecular descriptors for **1 – 5** is listed in Table 1S.

Table 1S. Some characteristics of non-valence interactions in the crystals of polymorphs 1 – 5 obtained within the MMVDP[a]

| Polymorph number | Reference code Allen, 2002 | Reference | Space group | $V_{mol}$, Å$^3$ | $T_e$, K | Intermolecular interactions | | | | | Intramolecular interactions | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $^0k$ | $^0d_{min}$,Å | $^0d_{max}$, Å | $^0S$, Å$^2$ | $^0V$, Å$^3$ | $^{>1}k$ | $^{>1}d_{min}$, Å | $^{>1}d_{max}$, Å | $^{>1}S$, Å$^2$ | $^{>1}V$, Å$^3$ |
| Polymorphs of $C_{13}H_{11}NO$ (**1**) | | | | | | | | | | | | | | | |
| **1**-1A | SALCAN01 | Arod *et al.*, 2005 | $P2_12_12_1$ | 255.8 | 120 | 268 | 2.55 | 4.11 | 281.5 | 146.6 | 49 | 1.72 | 3.35 | 100.3 | 38.4 |
| **1**-2B | SALCAN03 | Arod *et al.*, 2007 | P $bc2_1$ | 256.8 | 120 | 264 | 2.57 | 4.36 | 282.2 | 148.3 | 41 | 1.79 | 2.92 | 97.8 | 36.7 |
| **1**-3C [b] | SALCAN04 | Arod *et al.*, 2007 | P 1 | 271.3 | 120 | 258 | 2.56 | 4.60 | 293.6 | 157.6 | 53 | 1.83 | 3.46 | 103.8 | 40.8 |
| Polymorphs of $C_{13}H_{11}N_3O_4$ (**2**) | | | | | | | | | | | | | | | |
| **2**-1A | RIGHUK01 | Scherl *et al.*, 1996 | P $2_1/c$ | 320.3 | 296 | 282 | 2.43 | 4.49 | 324.3 | 170.9 | 72 | 1.55 | 3.83 | 181.5 | 69.3 |
| **2**-2A | RIGHUK05 | Naumov & Sakurai, 2005 | P $2_1/c$ | 322.9 | 316 | 284 | 2.49 | 4.59 | 325.0 | 172.9 | 71 | 1.56 | 3.85 | 185.4 | 70.0 |
| **2**-3A | RIGHUK06 | Naumov & Sakurai, 2005 | P $2_1/c$ | 322.8 | 319.7 | 282 | 2.49 | 4.59 | 325.3 | 172.7 | 72 | 1.45 | 3.90 | 183.8 | 69.6 |
| **2**-4A | RIGHUK07 | Naumov & Sakurai, 2005 | P $2_1/c$ | 323.2 | 324 | 282 | 2.50 | 4.59 | 324.9 | 173.0 | 72 | 1.56 | 3.90 | 185.4 | 70.1 |
| **2**-5B | RIGHUK08 | Naumov & Sakurai, 2005 | P $2_1/c$ | 325.7 | 328.9 | 284 | 2.52 | 4.59 | 327.2 | 176.2 | 71 | 1.56 | 3.80 | 179.1 | 67.8 |
| **2**-6B | RIGHUK09 | Naumov & Sakurai, 2005 | P $2_1/c$ | 329.4 | 337.5 | 284 | 2.53 | 4.60 | 329.5 | 178.2 | 72 | 1.56 | 3.81 | 180.9 | 68.6 |
| **2**-7B | RIGHUK | Eichen *et al.*, 1997 | P $2_1/c$ | 327.6 | 343 | 286 | 2.53 | 4.54 | 327.6 | 176.2 | 78 | 1.31 | 4.44 | 177.3 | 67.4 |
| **2**-8C | RIGHUK04 | Schmidt *et al.*, 1999 | C c | 313.8 | 293 | 283 | 2.26 | 4.47 | 322.5 | 169.8 | 75 | 1.34 | 3.77 | 169.4 | 63.4 |
| Polymorphs of $C_{17}H_{12}N_4O_4$ (**3**) | | | | | | | | | | | | | | | |

Formatted Table

Formatted Table

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** -1A | ZOGQAN04 | Naumov & Ohashi, 2004 | P n a 21 | 377.8 | 78 | 358 | 2.39 | 4.74 | 387.1 | 202.4 | 87.5 | 1.60 | 3.75 | 171.8 | 68.9 |
| **3** -2A | ZOGQAN02 | Scherl *et al*., 1996 | P n a 21 | 380.7 | 173 | 353 | 2.36 | 4.79 | 386.5 | 204.0 | 91.5 | 1.57 | 3.76 | 180.2 | 71.6 |
| **3** -3B | ZOGQAN03 | Scherl *et al*., 1996 | P 21/c | 382.5 | 173 | 374 | 2.40 | 4.59 | 387.9 | 204.2 | 80 | 1.72 | 3.79 | 173.8 | 70.2 |
| **3** -4C | ZOGQAN05 | Naumov & Ohashi, 2004 | P 21/c | 375.1 | 78 | 346 | 2.51 | 4.61 | 379.8 | 198.8 | 90 | 1.50 | 3.93 | 176.1 | 70.9 |
| | | | Polymorphs of $C_{39}H_{46}N_2O_2$ (**4**) | | | | | | | | | | | | |
| **4** -1A | ATIWOP | Taneda *et al*., 2004 | P 21/n | 878.3 | 296 | 596 | 2.20 | 5.00 | 772.2 | 409.8 | 300 | 1.36 | 4.60 | 750.0 | 281.2 |
| **4** -2B | ATIWOP01 | Taneda *et al*., 2004 | C 2/c | 856.8 | 296 | 628 | 2.20 | 4.91 | 796.6 | 408.2 | 293 | 1.47 | 4.30 | 621.6 | 241.4 |
| | | | Polymorphs of $C_{22}H_{27}NO_3$ (**5**) | | | | | | | | | | | | |
| **5** -1A | MOPNAH | Johmoto et al., 2009 | P $2_1$/n | 497.1 | 295 | 416 | 1.85 | 5.15 | 471.8 | 246.1 | 161 | 1.57 | 3.91 | 389.7 | 140.6 |
| **5** -2B | MOPNAH01 | Johmoto et al., 2009 | P $2_1$/c | 511.0 | 293 | 406 | 1.82 | 5.05 | 488.4 | 257.2 | 166 | 1.57 | 3.59 | 405.3 | 145.2 |
| **5** -3C | MOPNAH02 | Johmoto et al., 2009 | C 2/c | 502.5 | 295 | 412 | 2.42 | 5.01 | 459.4 | 244.7 | 161.5 | 1.57 | 3.57 | 402.9 | 143.2 |

a $T_e$ – the temperature of the X-ray diffraction experiment. b The Characteristics of non-valence interactions are given for a major orientation of a molecule in a twinning crystal.

Table 2S. Relative contributions of inter- ($^{0}\Delta$) and intramolecular ($^{>1}\Delta$) non-valence contacts A/Z into the area of molecular surface of polymorphs **1, 3, 4, 5**[a]

| The polymorph number | Relative contribution, % | The type of a non-valence interaction A/Z | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | O/O | N/O | C/O | H/O | N/N | C/N | H/N | C/C | H/C | H/H |
| Polymorphs of $C_{13}H_{11}NO$ (**1**) | | | | | | | | | | | |
| **1**-1A | $^{0}\Delta$ | - | - | 0.8 | 9.5 | - | 0.2 | 3.4 | 1.2 | 38.0 | 46.9 |
| | $^{>1}\Delta$ | - | - | - | 5.7 | - | - | 19.5 | 0.6 | 15.8 | 58.3 |
| **1**-2B | $^{0}\Delta$ | - | - | 0.5 | 9.3 | - | 0.2 | 4.5 | 1.1 | 41.6 | 42.9 |
| | $^{>1}\Delta$ | - | - | - | 4.3 | - | - | 19.8 | 0.5 | 14.0 | 61.4 |
| **1**-3C | $^{0}\Delta$ | - | - | 0.6 | 8.6 | - | - | 3.8 | 0.5 | 40.2 | 46.3 |
| | $^{>1}\Delta$ | - | - | - | 4.7 | - | - | 21.3 | 0.5 | 17.0 | 56.5 |
| Polymorphs of $C_{17}H_{12}N_4O_4$ (**3**) | | | | | | | | | | | |
| **3**-1A | $^{0}\Delta$ | 4.4 | 1.5 | 5.1 | 26.4 | - | 1.9 | 8.9 | 4.0 | 21.8 | 25.9 |
| | $^{>1}\Delta$ | 3.2 | 1.1 | 2.4 | 23.4 | 2.3 | 4.0 | 13.3 | 2.8 | 14.5 | 33.0 |
| **3**-2A | $^{0}\Delta$ | 4.7 | 1.6 | 5.4 | 25.8 | - | 2.0 | 8.9 | 4.0 | 21.0 | 26.6 |
| | $^{>1}\Delta$ | 2.9 | 1.3 | 2.6 | 23.3 | 2.0 | 3.9 | 13.3 | 3.1 | 17.3 | 30.4 |
| **3**-3B | $^{0}\Delta$ | 2.6 | 2.1 | 2.4 | 32.2 | 1.2 | 2.3 | 6.8 | 6.0 | 18.9 | 25.5 |
| | $^{>1}\Delta$ | 2.8 | - | 6.0 | 22.5 | - | 2.4 | 17.8 | 2.6 | 12.4 | 33.4 |
| **3**-4C | $^{0}\Delta$ | 5.0 | 2.1 | 5.3 | 25.3 | - | 1.5 | 8.8 | 3.7 | 22.9 | 25.3 |
| | $^{>1}\Delta$ | 1.8 | 1.3 | 4.2 | 23.5 | 2.2 | 3.9 | 13.3 | 2.1 | 12.9 | 34.8 |
| Polymorphs of $C_{39}H_{46}N_2O_2$ (**4**) | | | | | | | | | | | |
| **4**-1A | $^{0}\Delta$ | - | - | 0.1 | 7.2 | - | - | 0.4 | 0.1 | 24.0 | 68.2 |
| | $^{>1}\Delta$ | - | - | <0.1 | 1.3 | - | 0.1 | 6.7 | 0.6 | 24.6 | 66.6 |
| **4**-2B | $^{0}\Delta$ | - | - | 0.4 | 6.6 | - | - | 0.4 | 0.1 | 25.1 | 67.4 |
| | $^{>1}\Delta$ | - | - | <0.1 | 1.2 | - | <0.1 | 3.9 | 1.2 | 26.0 | 67.8 |
| Polymorphs of $C_{22}H_{27}NO_3$ (**5**) | | | | | | | | | | | |
| **5**-1A | $^{0}\Delta$ | 0.2 | - | 0.9 | 14.4 | - | <0.1 | 2.2 | 0.6 | 22.2 | 59.6 |
| | $^{>1}\Delta$ | - | - | 0.2 | 9.5 | - | - | 5.3 | 1.1 | 20.5 | 63.4 |
| **5**-2B | $^{0}\Delta$ | 0.6 | - | 0.2 | 15.5 | - | <0.1 | 2.1 | 0.8 | 22.1 | 58.6 |
| | $^{>1}\Delta$ | - | - | 0.1 | 10.0 | - | - | 4.6 | 0.9 | 18.4 | 65.9 |
| **5**-3C | $^{0}\Delta$ | - | - | <0.1 | 12.2 | - | 0.6 | 1.8 | 4.2 | 16.7 | 64.5 |
| | $^{>1}\Delta$ | - | - | 0.1 | 8.4 | - | - | 5.3 | 0.8 | 17.9 | 67.4 |

a The values of $^{0}\Delta$ and $^{>1}\Delta$ are round to one decimal place and calculated in respect to $^{0}S$ and $^{>1}S$, correspondingly. The absence of some type of intermolecular interactions in the crystal is denoted with hephen.


Allen, F. (2002) *Acta Crystallogr., B***58,** 380–388.
Arod, F., Gardon, M., Pattison, P., Chapuis, G. (2005) *Acta Crystallogr., C***61**, o317–o320.
Arod, F., Pattison, P., Schenk, K. J., Chapuis, G. (2007*) Crystal Growth & Des.*, **7**, 1679–1685.
Eichen, Y., Botoshansky, M., Peskin, U., Scherl, M., Haarer, D., Khatib, S. (1997) *J. Amer. Chem. Soc.*, **119**, 7167–7168.
Johmoto, K., Sekine, A., Uekusa, H., Ohashi, Y. (2009) *Bull.Chem.Soc.Jpn*, **82**, 50–57.
Naumov, P., Ohashi, Y. (2004) *Acta Crystallogr., B***60**, 343–349.
Naumov, P. & Sakurai, K. (2005) *Crystal Growth & Des.*, **5**, 1699–1701.
Scherl, M., Haarer, D., Fischer, J., DeCian, A., Lehn, J.-M., Eichen, Y. (1996) *J.Phys.Chem.* **100**, 16175–16186.
Schmidt, A., Kababya, S., Appel, M., Khatib, S., Botoshansky, M., Eichen, Y. (1999) *J.Amer.Chem.Soc.*, **121**, 11291–11299.
Taneda, M., Amimoto, K., Koyama, H., Kawato, T. (2004*) Org. Biomol. Chem.*, **2**, 499–504.


Field Code Changed
Formatted: German (Germany)