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**Electronic Supporting Information**

**For paper**

# Hydrogen bonding *vs* stacking interaction in the crystals of the simplest coumarin derivatives: study from the energetic viewpoint

Svitlana V. Shishkina, Irina S. Konovalova, Sergiy M. Kovalenko, Pavlo V. Trostianko, Anna O. Geleverya, Natalya D. Bunyatyan

**Table S1**. Pairwise interaction energies (kcal mol$^{-1}$) of the basic molecule with neighbouring ones in crystal of (**I**)**.**

| Dimer | Symmetry operation | $E_{int}$, kcal mol$^{-1}$ | Contribution to the total interaction energy, % | Interaction type |
|---|---|---|---|---|
| **I_d1** | -x,1-y,1-z | -12.85 | 19.3 | N–H···O (2) |
| **I_d2** | 1+x,y,z | -10.06 | 15.1 | stacking |
| **I_d3** | -1+x,y,z | -10.06 | 15.1 | stacking |
| **I_d4** | x,1/2-y,1/2+z | -4.02 | 6.0 | C–H···O1 |
| **I_d5** | x,1/2-y,-1/2+z | -4.02 | 6.0 | C–H···O1 |
| **I_d6** | 1+x,1/2-y,-1/2+z | -3.49 | 5.2 | C–H···O3 |
| **I_d7** | -1+x,1/2-y,1/2+z | -3.49 | 5.2 | C–H···O3 |
| **I_d8** | 1-x,1-y,1-z | -3.13 | 4.7 | Stacking C=O |
| **I_d9** | 2-x,1/2+y,1/2-z | -2.52 | 3.8 | C-H…O |
| **I_d10** | 2-x,-1/2+y,1/2-z | -2.52 | 3.8 | C-H…O |
| **I_d11** | 1+x,1/2-y,1/2+z | -2.48 | 3.7 | non-specific |
| **I_d12** | -1+x,1/2-y,-1/2+z | -2.48 | 3.7 | non-specific |
| **I_d13** | 2-x,-y,1-z | -2.02 | 3.0 | non-specific |
| **I_d14** | 1-x,1/2+y,1/2-z | -1.62 | 2.4 | non-specific |
| **I_d15** | 1-x,-1/2+y,1/2-z | -1.62 | 2.4 | non-specific |
| **I_d16** | 3-x,-y,1-z | -0.22 | 0.3 | non-specific |
| Total energy is -66.58 kcal mol$^{-1}$ | | | | |

**Table S2**. Pairwise interaction energies (kcal $mol^{-1}$) of the basic molecule with neighbouring ones in crystal of (**II**).

| Dimer | Symmetry operation | $E_{int}$, kcal $mol^{-1}$ | Contribution to the total interaction energy, % | Interaction type |
|---|---|---|---|---|
| **II_d1** | -x,1-y,1-z | -12.39 | 19.2 | N–H···O (2) |
| **II_d2** | 1+x,y,z | -10.19 | 15.8 | stacking |
| **II_d3** | -1+x,y,z | -10.19 | 15.8 | stacking |
| **II_d4** | x,1/2-y,1/2+z | -3.54 | 5.5 | C–H···O1 |
| **II_d5** | x,1/2-y,-1/2+z | -3.54 | 5.5 | C–H···O1 |
| **II_d6** | 1+x,1/2-y,-1/2+z | -3.53 | 5.5 | C–H···O3 |
| **II_d7** | -1+x,1/2-y,1/2+z | -3.53 | 5.5 | C–H···O3 |
| **II_d8** | 2-x,1/2+y,1/2-z | -2.54 | 3.9 | C-H…N |
| **II_d9** | 2-x,-1/2+y,1/2-z | -2.54 | 3.9 | C-H…N |
| **II_d10** | 1-x,1-y,1-z | -2.40 | 3.7 | Stacking C=O |
| **II_d11** | 2-x,-y,1-z | -2.06 | 3.2 | non-specific |
| **II_d12** | 1+x,1/2-y,1/2+z | -1.92 | 3.0 | non-specific |
| **II_d13** | -1+x,1/2-y,-1/2+z | -1.92 | 3.0 | non-specific |
| **II_d14** | 1-x,1/2+y,1/2-z | -1.86 | 2.9 | non-specific |
| **II_d15** | 1-x,-1/2+y,1/2-z | -1.86 | 2.9 | non-specific |
| **II_d16** | 3-x,-y,1-z | -0.37 | 0.6 | non-specific |
| Total energy is -64.40 kcal $mol^{-1}$ | | | | |

**Table S3**. Pairwise interaction energies (kcal $mol^{-1}$) of the basic molecule with neighbouring ones in crystal of (**III**).

| Dimer | Symmetry operation | $E_{int}$, kcal $mol^{-1}$ | Contribution to the total interaction energy, % | Interaction type |
|---|---|---|---|---|
| **III_d1** | 1-x,1-y,2-z | -10.98 | 15.7 | N–H···S (2) |
| **III_d2** | 1-x,1-y,1-z | -10.13 | 14.4 | stacking |
| **III_d3** | 1/2-x,1/2+y,3/2-z | -9.48 | 13.5 | C–H···S |
| **III_d4** | 1/2-x,-1/2+y,3/2-z | -9.48 | 13.5 | C–H···S |
| **III_d5** | 1-x,-y,1-z | -6.03 | 8.6 | C–H···O (2) |
| **III_d6** | x,1+y,z | -5.37 | 7.7 | Non-specific |
| **III_d7** | x,-1+y,z | -5.37 | 7.7 | Non-specific |
| **III_d8** | 1/2+x,1/2-y,1/2+z | -3.50 | 5.0 | N-H…π |
| **III_d9** | -1/2+x,1/2-y,-1/2+z | -3.50 | 5.0 | N-H…π |
| **III_d10** | 1/2+x,3/2-y,1/2+z | -2.50 | 3.6 | non-specific |
| **III_d11** | -1/2+x,3/2-y,-1/2+z | -2.50 | 3.6 | non-specific |
| **III_d12** | 1/2-x,1/2+y,1/2-z | -0.64 | 0.9 | non-specific |
| **III_d13** | 1/2-x,-1/2+y,1/2-z | -0.64 | 0.6 | non-specific |
| Total energy is -70.10 kcal $mol^{-1}$ | | | | |

**Table S4**. Pairwise interaction energies (kcal $mol^{-1}$) of the basic molecule with neighbouring ones in crystal of (**IV**)**.**

| Dimer | Symmetry operation | $E_{int}$, kcal $mol^{-1}$ | Contribution to the total interaction energy, % | Interaction type |
|---|---|---|---|---|
| **IV_d1** | 2-x,1-y,1-z | -15.63 | 24.5 | stacking |
| **IV_d2** | 1-x,1-y,1-z | -14.62 | 22.9 | stacking |
| **IV_d3** | 1-x,-y,2-z | -10.42 | 16.3 | N–H···S (2) |
| **IV_d4** | 2-x,-y,1-z | -6.67 | 10.4 | C–H···S (2) |
| **IV_d5** | x,1+y,z | -3.18 | 5.0 | non-specific |
| **IV_d6** | x,-1+y,z | -3.18 | 5.0 | non-specific |
| **IV_d7** | 1-x,2-y,1-z | -3.00 | 4.7 | non-specific |
| **IV_d8** | 1-x,1-y,2-z | -2.15 | 3.4 | non-specific |
| **IV_d9** | 2-x,1-y,-z | -1.95 | 3.1 | non-specific |
| **IV_d10** | 1+x,y,-1+z | -1.58 | 2.5 | C-H…N |
| **IV_d11** | -1+x,y,1+z | -1.58 | 2.5 | C-H…N |
| **IV_d12** | 2-x,2-y,-z | 0.08 | -0.1 | non-specific |
| Total energy is -63.87 kcal $mol^{-1}$ | | | | |

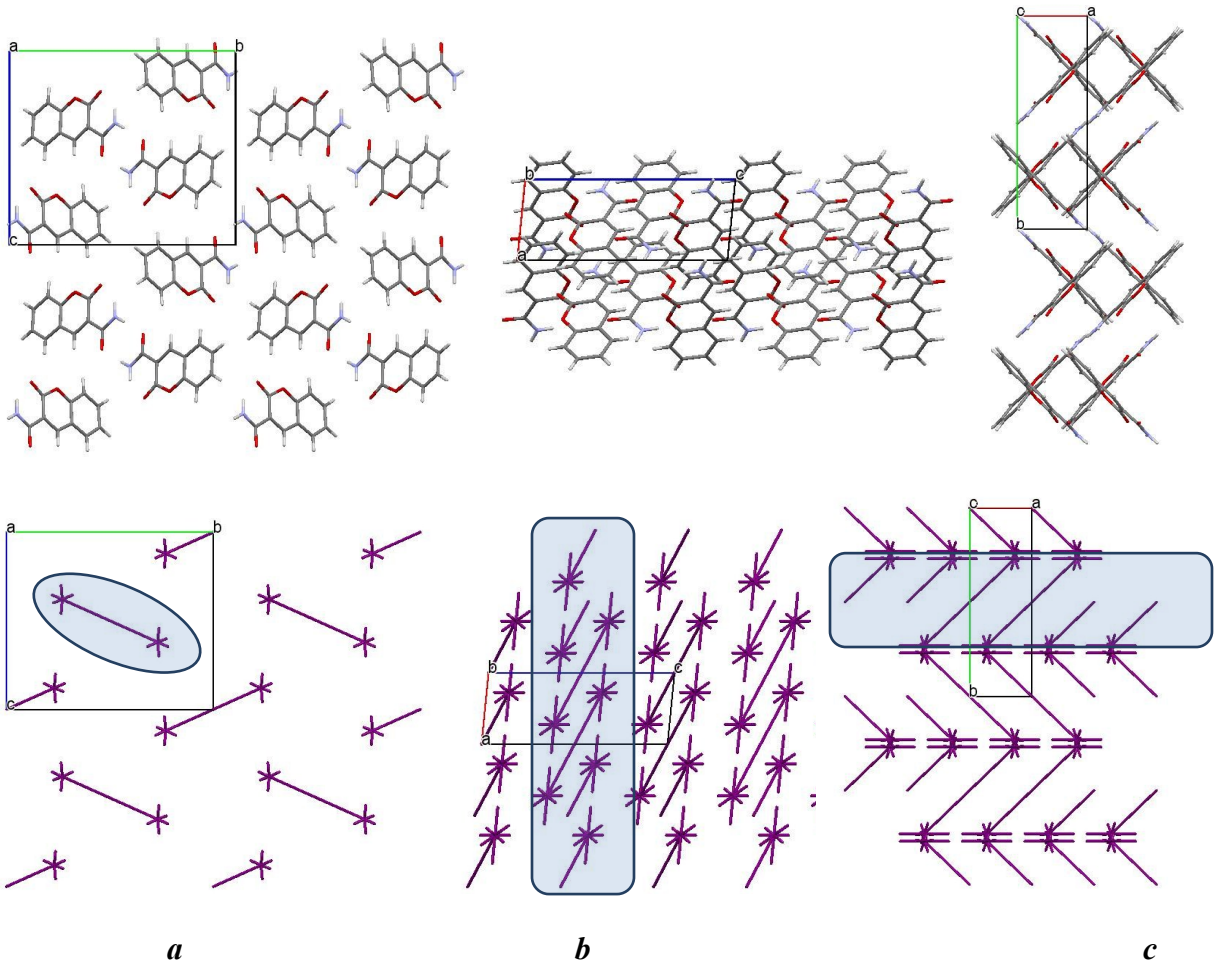


Figure S1. Packing of molecules (top) and energy-vector diagram (bottom) in the crystals (**I**). The projections along *a*, *b* and crystallographic direction are presented. The chains/columns are highlighted by different in blue.

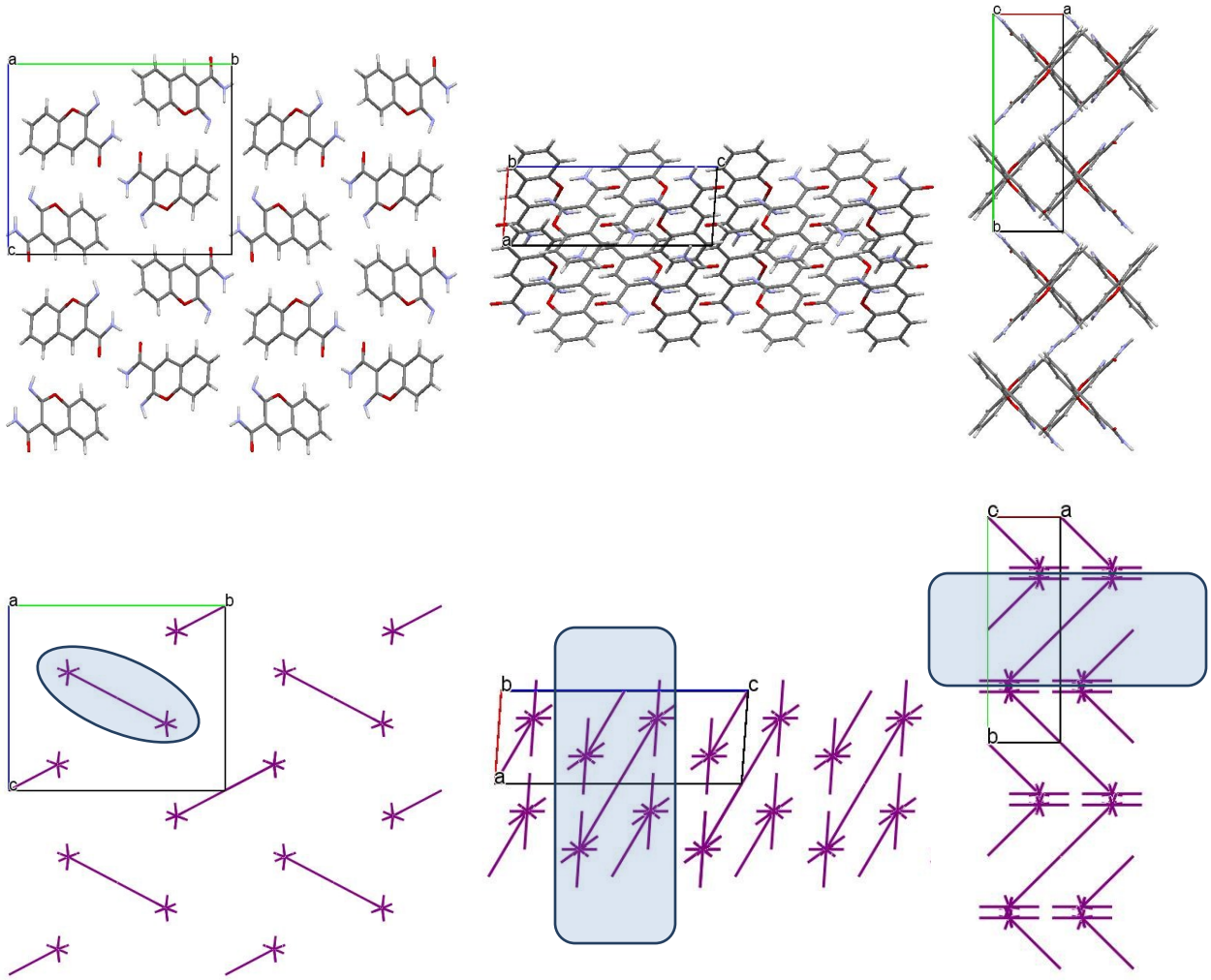


Figure S2. Packing of molecules (top) and energy-vector diagram (bottom) in the crystals (**II**). The projections along *a*, *b* and crystallographic direction are presented. The chains/columns are highlighted by different in blue.

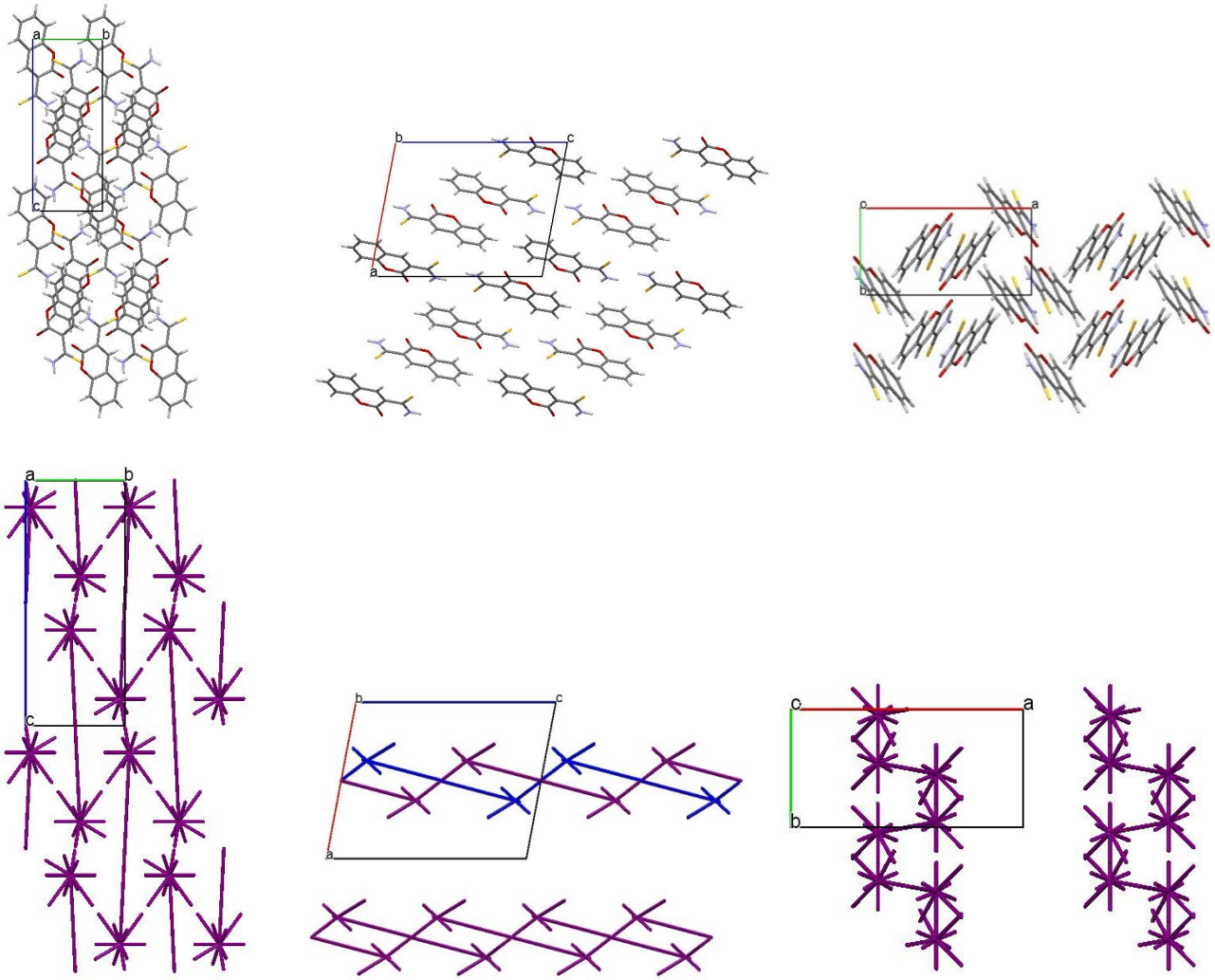


Figure S3. Packing of molecules (top) and energy-vector diagram (bottom) in the crystals (**III**). The projections along *a*, *b* and crystallographic direction are presented.

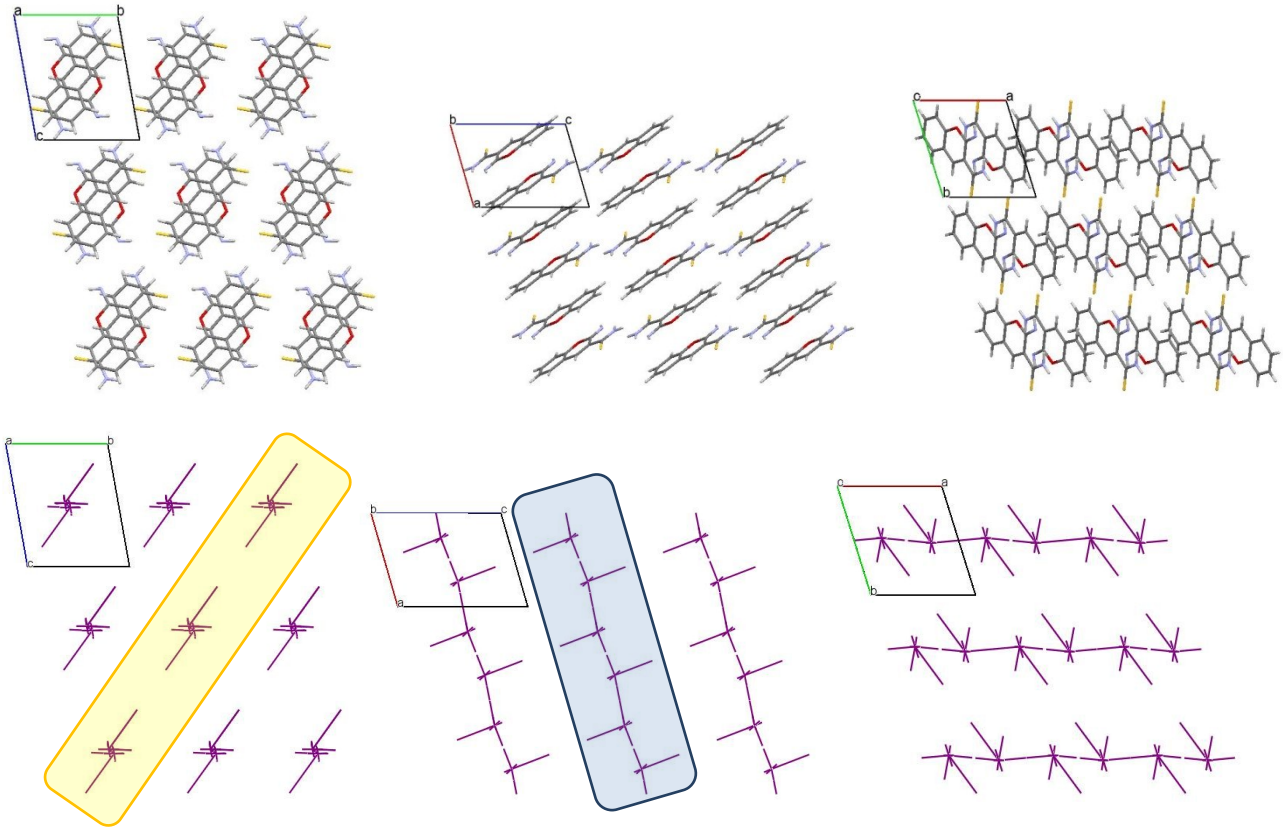

Figure S4. Packing of molecules (top) and energy-vector diagram (bottom) in the crystals (**IV**). The projections along *a*, *b* and crystallographic direction are presented. The stacked column is highlighted in blue. The layer is highlighted in yellow.