**SUPPORTING INFORMATION**

**CONFORMATION BEHAVIOR OF THE N1-(DIPHENYLPHOSPHORYL)ACETYL-N4-PHENYL-THIOSEMICARBASIDE IN VARIOUS CRYSTAL ENVIRONMENT**

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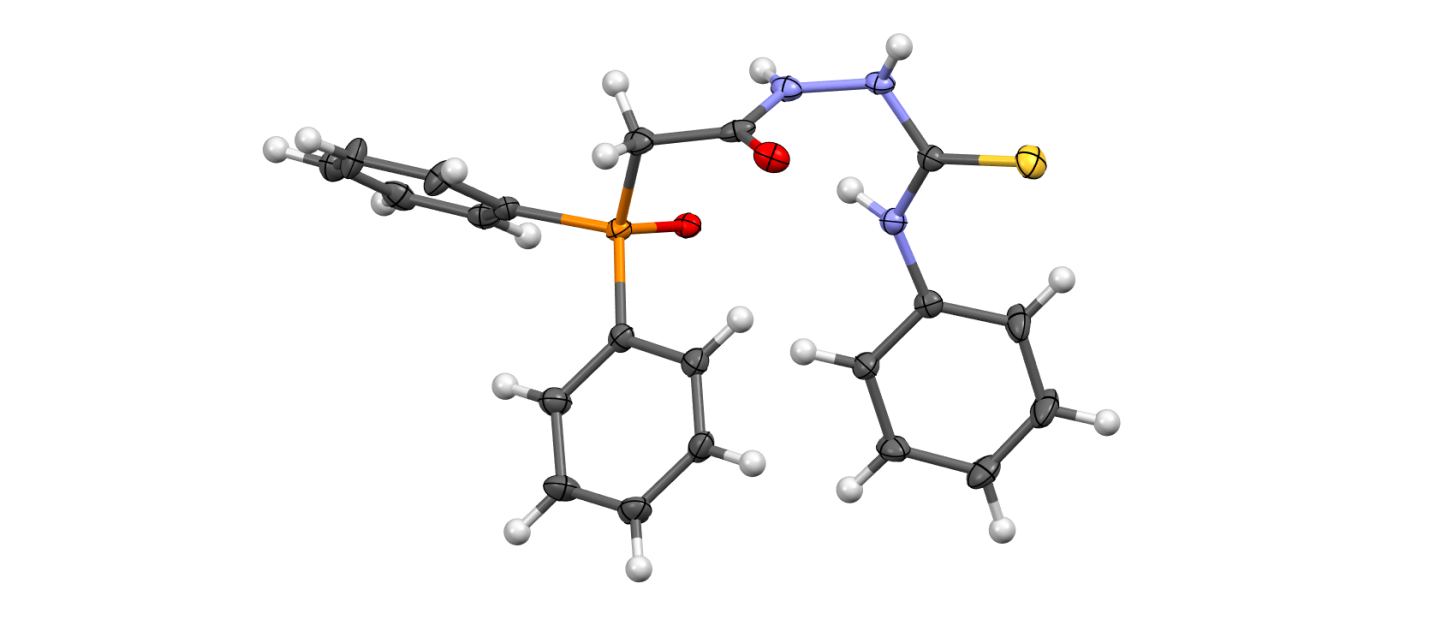
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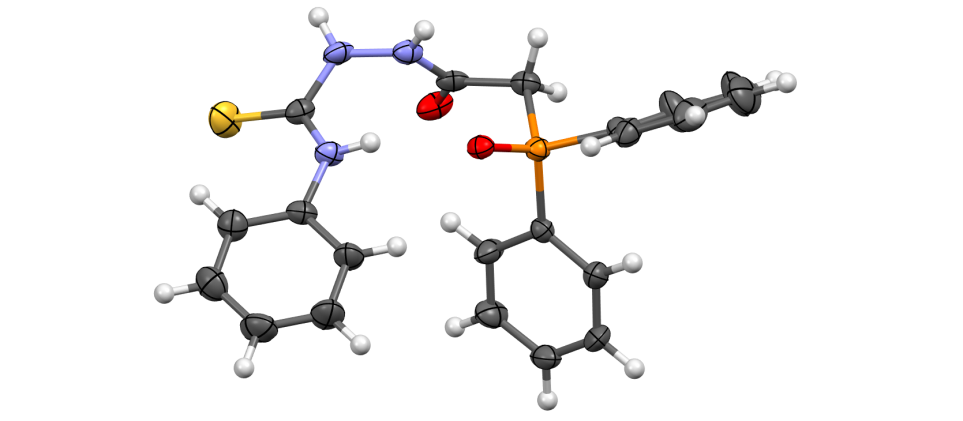
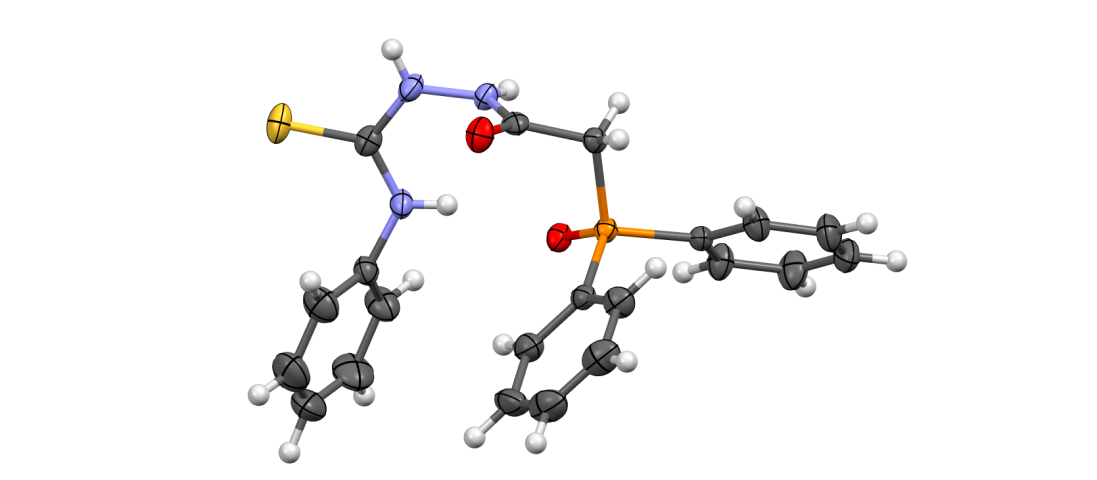
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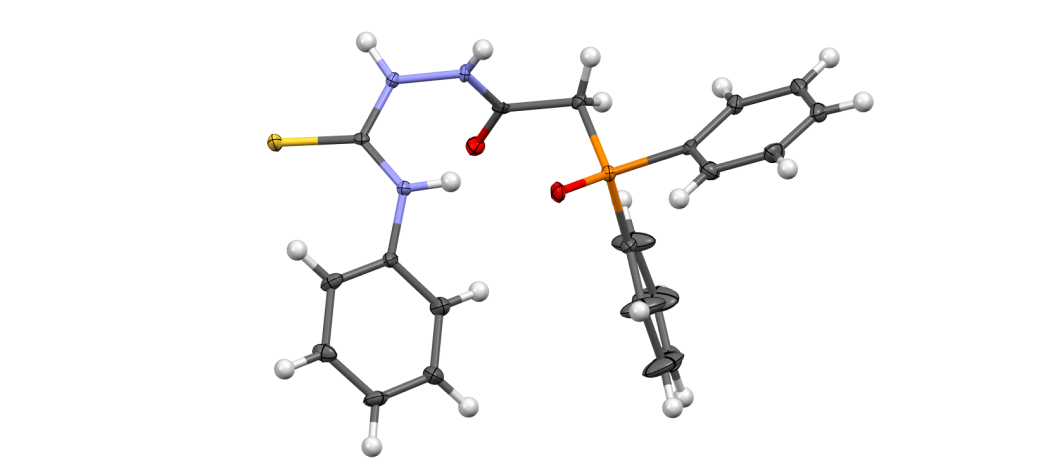
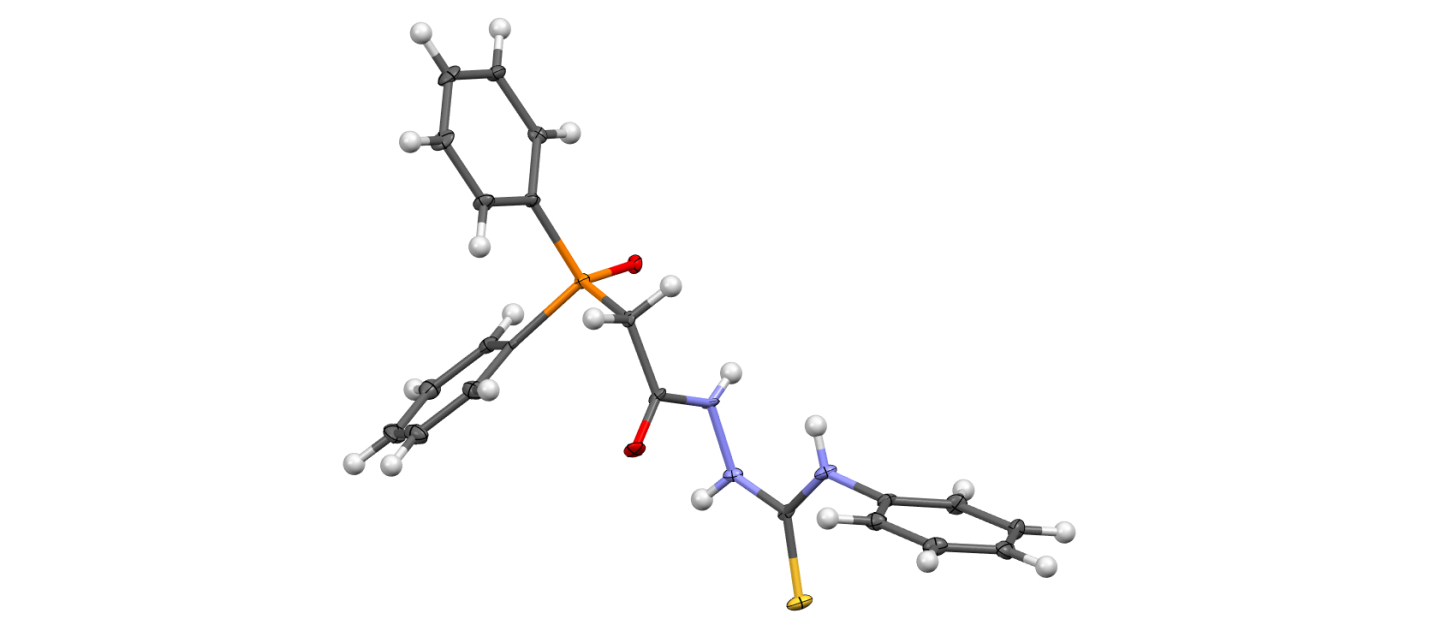
**Figure S1.** Molecule of compound **1**.

(a) (b)

**Figure S2.** Molecules (a) *A*and (b) *B* of compound **2**.

(a) (b)

**Figure S3.** Molecules (a) *A* and (b) *B* of compound **3**.

**Scheme S1.** Molecular fragments used for the search for thiosemicarbazide derivatives similar in structure to compounds **1**–**3**. Variable interatomic bonds are showed with dashed lines.

**Table S1.** Compounds from CSD with a thiosemicarbazide fragment according to scheme S1

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Code | Solvate | *d*(H…O), Å | Acceptor | ∠(*X*–O…H), deg | ∠(N–H…O), deg |
| 1 | REWVIP | DMSO | 2.19 | –P=O | 123.11 | 165.39 |
| 2 | CEFWOC | CH3CN | 2.086 | –C=O | 137.874 | 155.362 |
| CEFWOC | 2.093 | –C=O | 140.89 | 160.491 |
| CEFWOC | 2.107 | –C=O | 143.398 | 159.662 |
| CEFWOC | 2.109 | –C=O | 140.452 | 157.73 |
| CEFWOC | 2.142 | –C=O | 139.718 | 159.042 |
| CEFWOC | 2.159 | –C=O | 142.653 | 153.255 |
| 3 | CICZEW | H2O | 2.328 | –C=O | 121.674 | 164.718 |
| 4 | CUNJOM | DMF | 2.139 | –C=O | 151.914 | 158.764 |
| 2.177 | –C=O | 149.205 | 148.169 |
| 5 | CUNJUS | CH3OH | 2.272 | –C=O | 127.376 | 163.476 |
| 6 | CUNJUS01 | CH3OH | 2.277 | –C=O | 127.538 | 163.095 |
| 7 | CUNKAZ | DMF | 2.223 | –C=O | 133.728 | 151.343 |
| **8** | **DAHZIW** | **–** | **6.502** | **–OCH3** | **21.323** | **126.318** |
| 9 | GAXKEY | – | 2.377 | –SO2 | 135.541 | 174.429 |
| ***–*** | **4.223** | –SO2 | **52.458** | **149.974** |
| 10 | GAXKIC | – | 2.267 | –SO2 | 133.239 | 168.593 |
| **–** | **4.094** | –SO2 | **52.134** | **154.641** |
| 11 | GEDFUT | DMSO | 2.157 | –C=O | 115.418 | 156.414 |
| DMSO | 2.1 | –C=O | 115.897 | 158.034 |
| 12 | GEDGAA | DMSO | 2.048 | –C=O | 113.808 | 155.609 |
| 2.244 | –C=O | 123.821 | 161.856 |
| GEDGAA | 2.233 | –C=O | 123.137 | 160.542 |
| 2.131 | –C=O | 117.656 | 156.787 |
| **13** | **GURHOR** | **–** | **9.277** | **–OCH3** | **34.923** | **94.89** |
| 14 | IXONIU | – | 2.276 | –C=O | 126.286 | 159.298 |
| 15 | KAYTOU | C2H5OH | 2.317 | –OH | 134.438 | 147.628 |
| 16 | KEQTOS | CH3CN | 2.113 | –C=O | 141.353 | 157.521 |
| **17** | **KIKSON** | **–** | **6.943** | **–OCH3** | **65.718** | **51.92** |
| 18 | MATBOB | DMF | 2.229 | –C=O | 136.486 | 158.701 |
| 19 | MATBOB02 | DMF | 2.229 | –C=O | 136.083 | 159.013 |
| 20 | MATJOJ | DMF | 2.214 | –C=O | 136.964 | 159.899 |
| 21 | MATJOJ02 | DMF | 2.217 | –C=O | 136.19 | 160.342 |
| 22 | NOBJOG | – | 2.352 | –SO2 | 144.232 | 152.928 |
| **–** | **4.436** | –SO2 | **46.968** | **131.705** |
| **23** | **NUCXIU** | **–** | **6.386** | –C=O | **76.528** | **129.428** |
| 24 | OREWAL | – | 2.315 | –C=O | 125.05 | 162.041 |
| 25 | OREWAL02 | – | 2.321 | –C=O | 124.376 | 162.599 |
| **26** | **POBWUB** | **H2O** | **6.423** | **–OH** | **63.568** | **122.855** |
| 27 | QAPPAB | DMF | 2.146 | –C=O | 137.506 | 156.471 |
| 28 | QAPPAB02 | DMF | 2.148 | –C=O | 136.818 | 157.597 |
| **28** | **RIGCIU** | **–** | **5.518** | **–OCH3** | **66.188** | **176.574** |
| **–** | **7.51** | **–OCH3** | **15.606** | **137.493** |
| **30** | **SOLMUC** | **H2O** | **6.288** | **–COOCH3** | **60.136** | **106.987** |
| 31 | UYACUU | – | 2.286 | –C=O | 126.198 | 157.932 |
| 32 | ZINDOR | – | 2.403 | –C=O | 117.277 | 152.928 |

Compound CEFWOC contains six independent molecules in the unit cell. Molecules in CUNJOM, GEDFUT, and GEDGAA contain two thiosemicarbazide fragments per independent molecule. As we can see from Table S1, for seven compounds (highlighted in bold), large O…H distances and interaction angles less than 90° can be noted. This indicates the absence of intramolecular interaction of the type under consideration. In this case, this is due to the fact that the atoms of the main skeleton of the molecule are part of cyclic fragments, which blocks the possibility of free rotation and arrangement of atoms in space.

RESULTS OF DFT OPTIMIZATION

Gas-phase optimization of independent molecules was performed for compound **2** and **3** bythe B3LYP method with the 6-31G(d,p) basic set using Gaussian09. The geometry of molecules in crystals was used as a starting model.

(a) (b)



**Figure S4.** (a) Molecule *A* of compound **2** in the crystal and (b) the optimized one. Total DFT Energy = –1866.590050. Zero-corrected energy = –1866.213251.

(a) (b)

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**Figure S5.** (a) Molecule *B* of compound **2** in the crystal and (b) the optimized one. Total DFT Energy = –1866.590050. Zero-corrected energy = –1866.213251.

(a) (b)

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**Figure S6.** (a) Molecule *A* of compound **3** in the crystal and (b) the optimized one. Total DFT Energy = –1866.590050. Zero-corrected energy = –1866.213250.

(a) (b)

** **

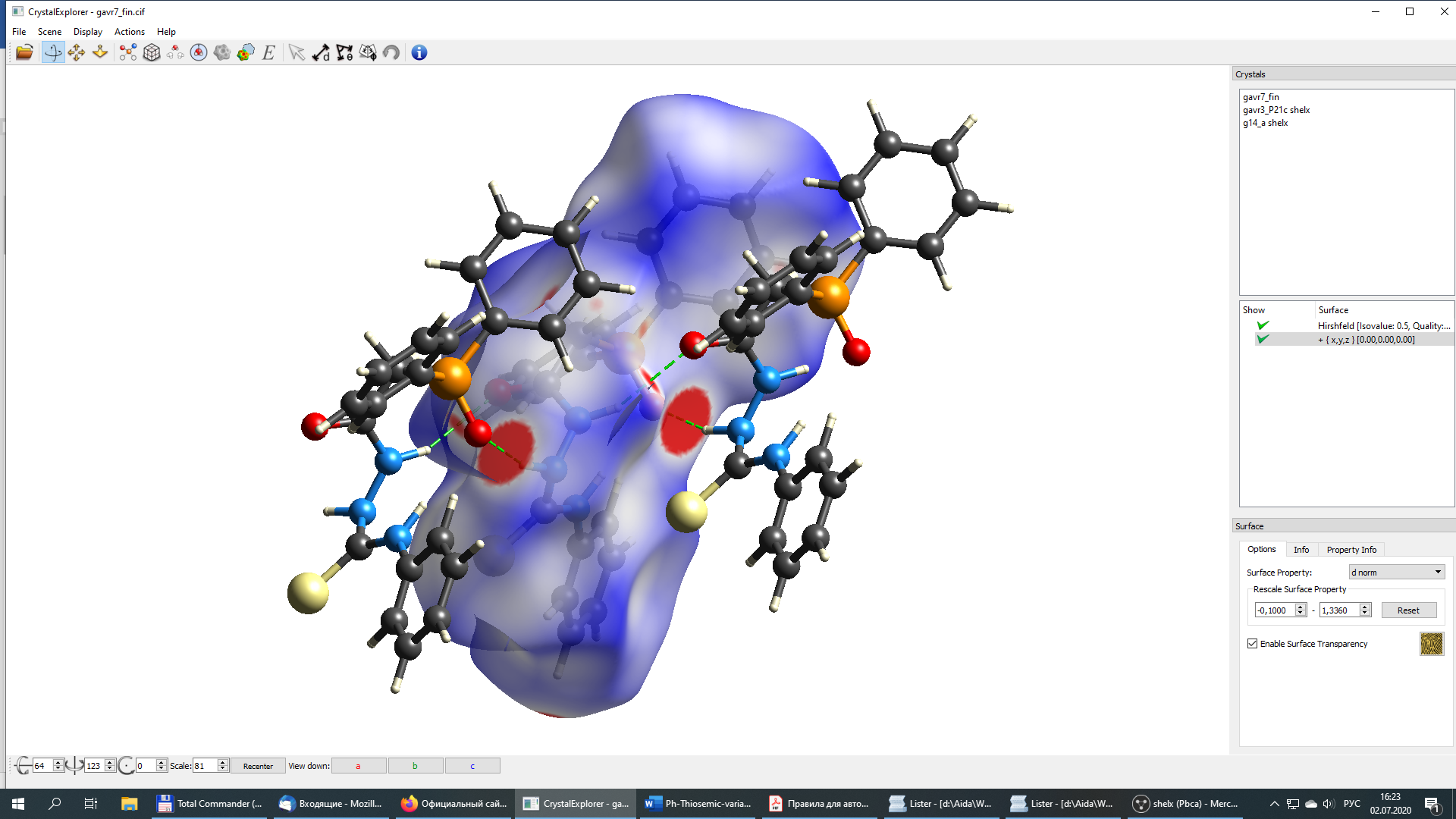
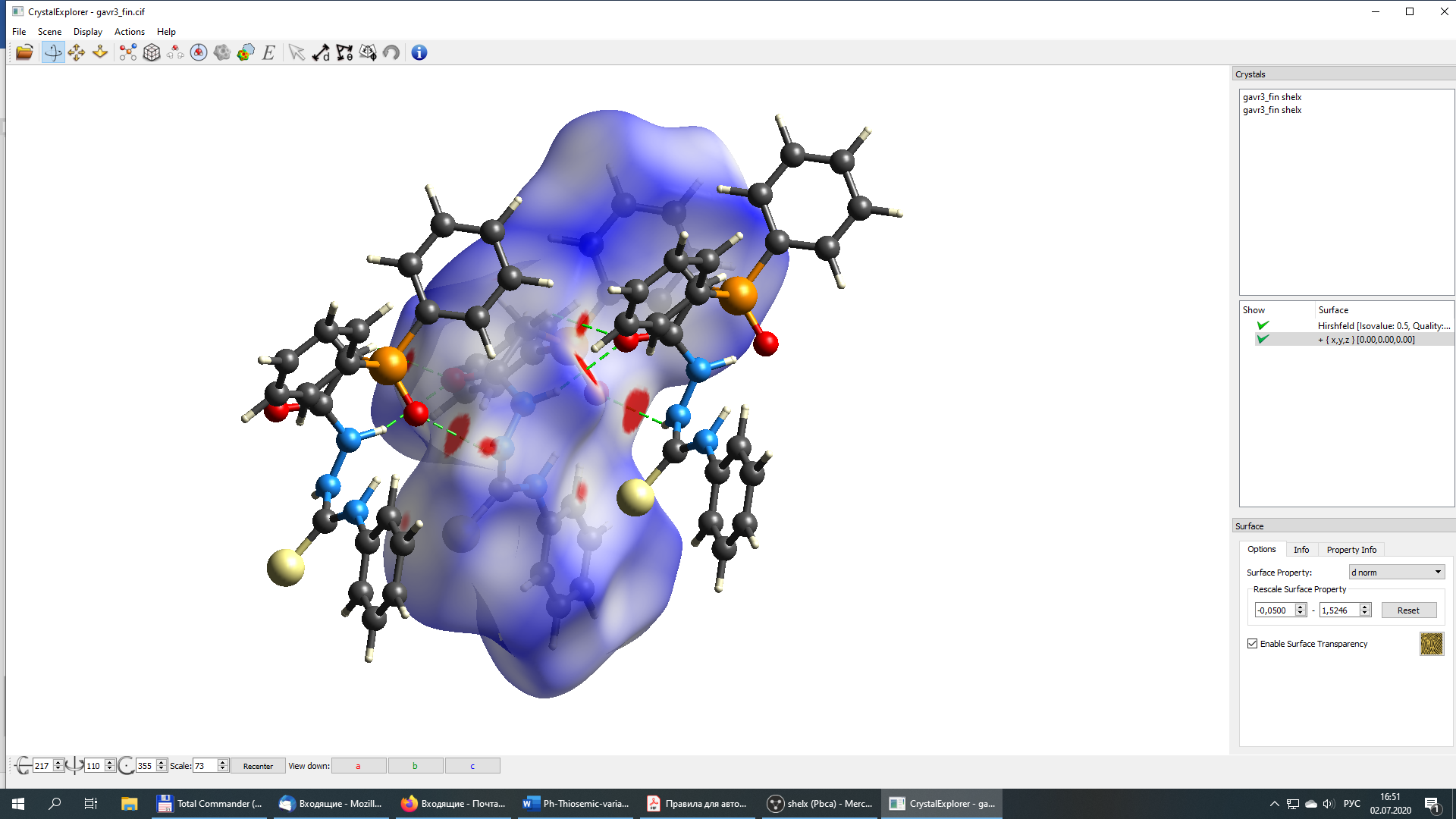
**Figure S7.** (a) Molecule *B* of compound **3** in the crystal and (b) the optimized one. Total DFT Energy = –1866.587085. Zero-corrected energy = –1866.210962.

ANALYSIS OF HIRSHFELD'S SURFACES FOR COMPOUND **1–3**

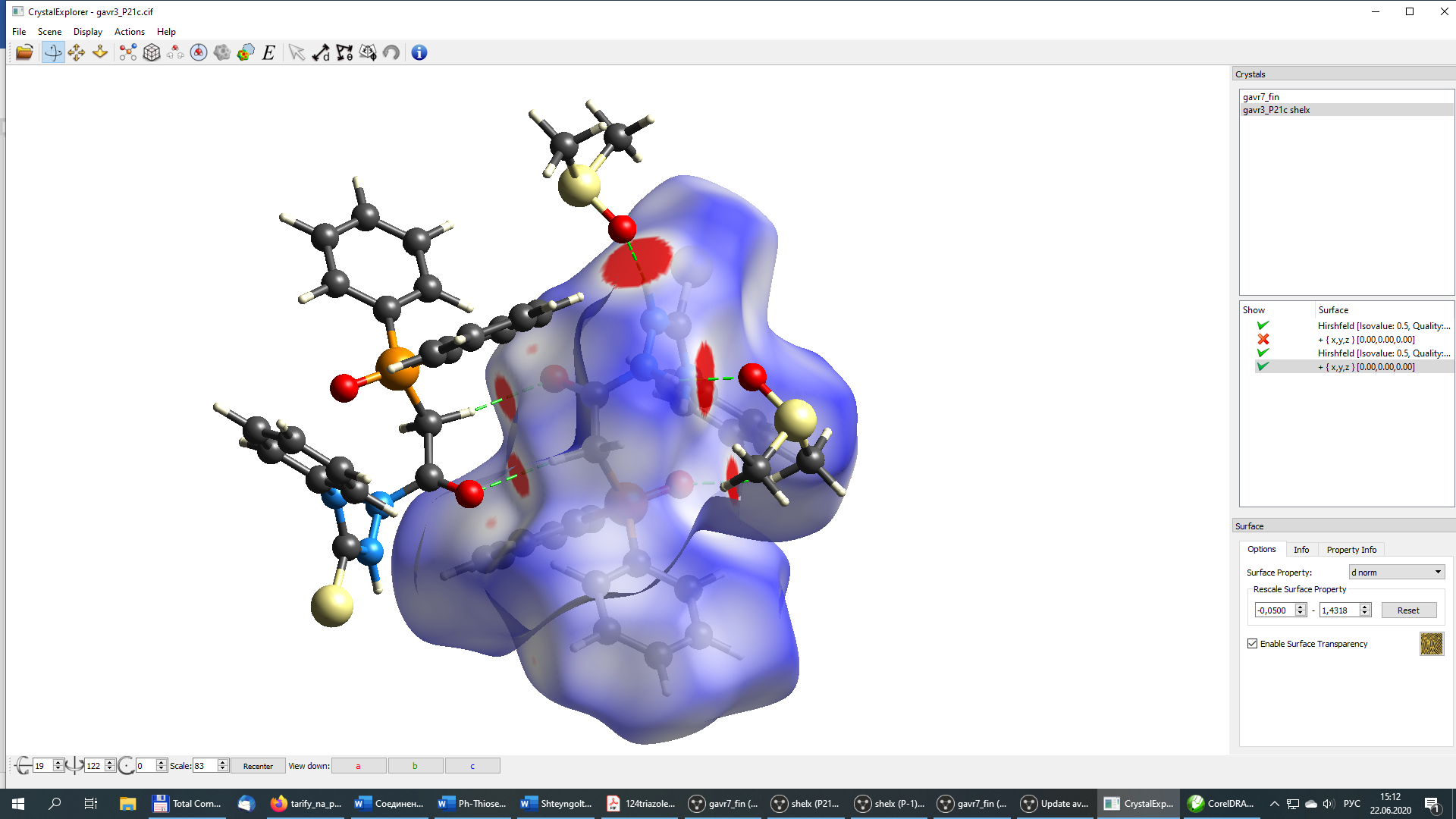
Colors on the Hirshfeld surfaces corresponding to intermolecular contacts or their absence are defined by the *d*norm value, and also range from red (), when the distance between the contacting pair of atoms is less than the sum of their van der Waals radii, through white () to blue ().

In compound **1**, the N2–H2…O13 interaction is the main crystal-forming one and is characterized by bigger larger concentric red zone corresponding to a shorter Н…О distance, while N1–H1⋅⋅⋅O11 can be considered as a forced contact (Fig. S8a). In crystal 2, both interactions (N1*А*–H1*А*⋅⋅⋅O11*А* and N2*А*–H2*А*⋅⋅⋅O13*А*) are equal in the area of red concentric zones. This can explain the increasing in the unit cell parameter of compound **2**, which corresponds to the axis along which the supramolecular structure is oriented.

(a) (b)

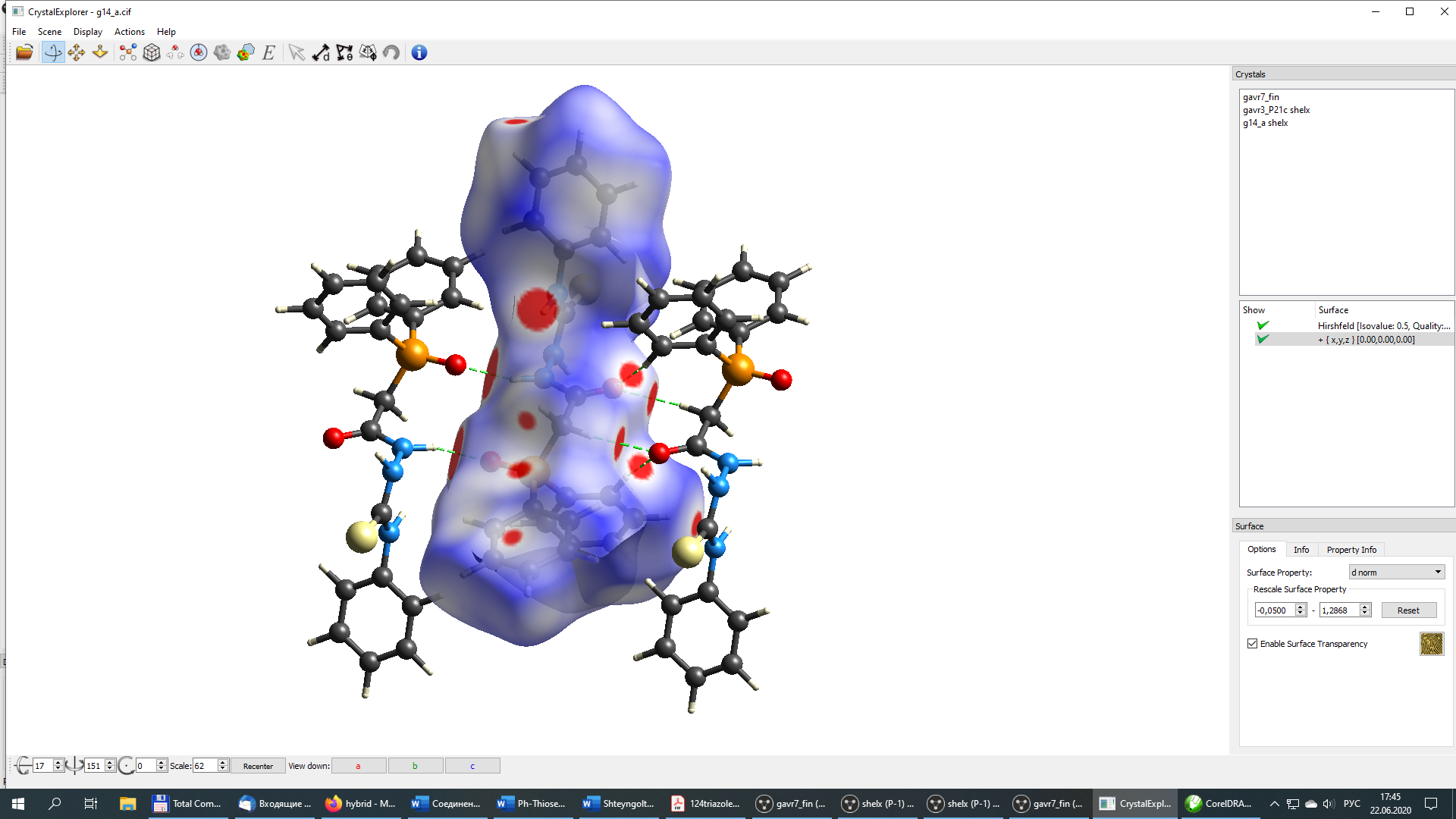
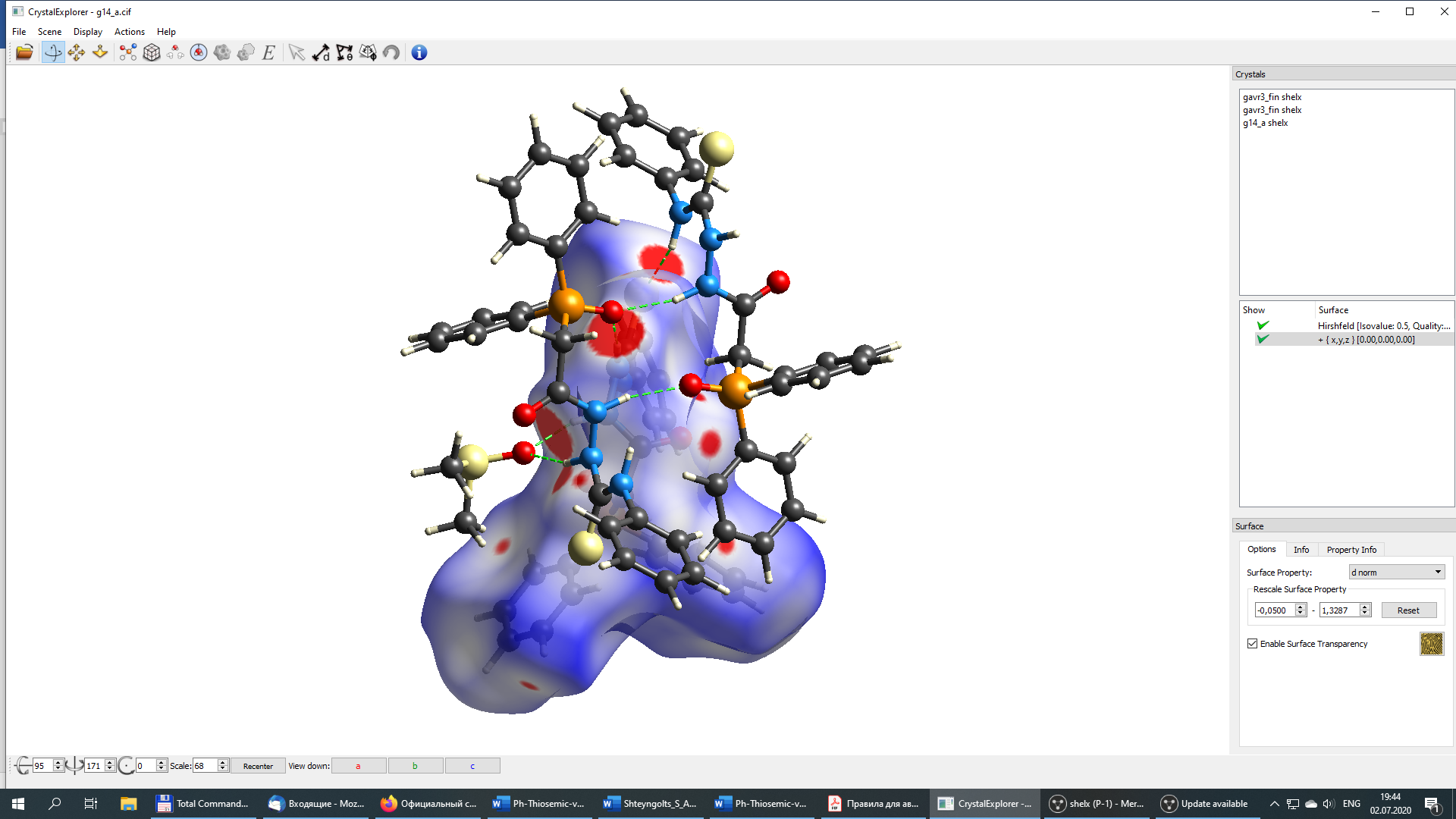
 

**Figure S8.** Hirshfeld surfaces for (a) molecules of compound **1** and (b) molecule *A*of compound **2**. The color scale corresponding to the value is taken from blue (1.5246) to red (–0.0500). Intermolecular interactions are shown with dashed lines.



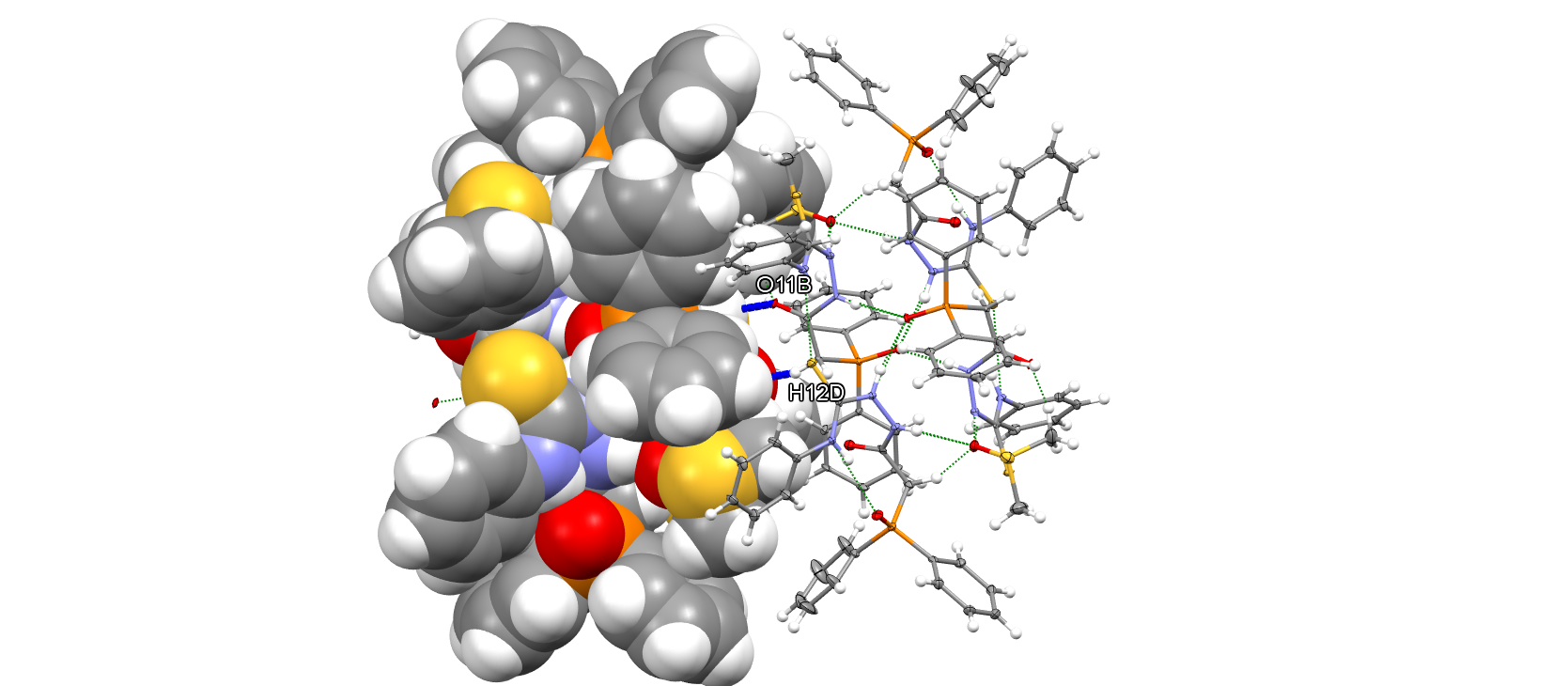
**Figure S9.** Hirshfeld surfaces for *B* molecules of compound **2**. The color scale corresponding to the value is taken from blue (1.5246) to red (–0.0500). Intermolecular interactions are shown with dashed lines.

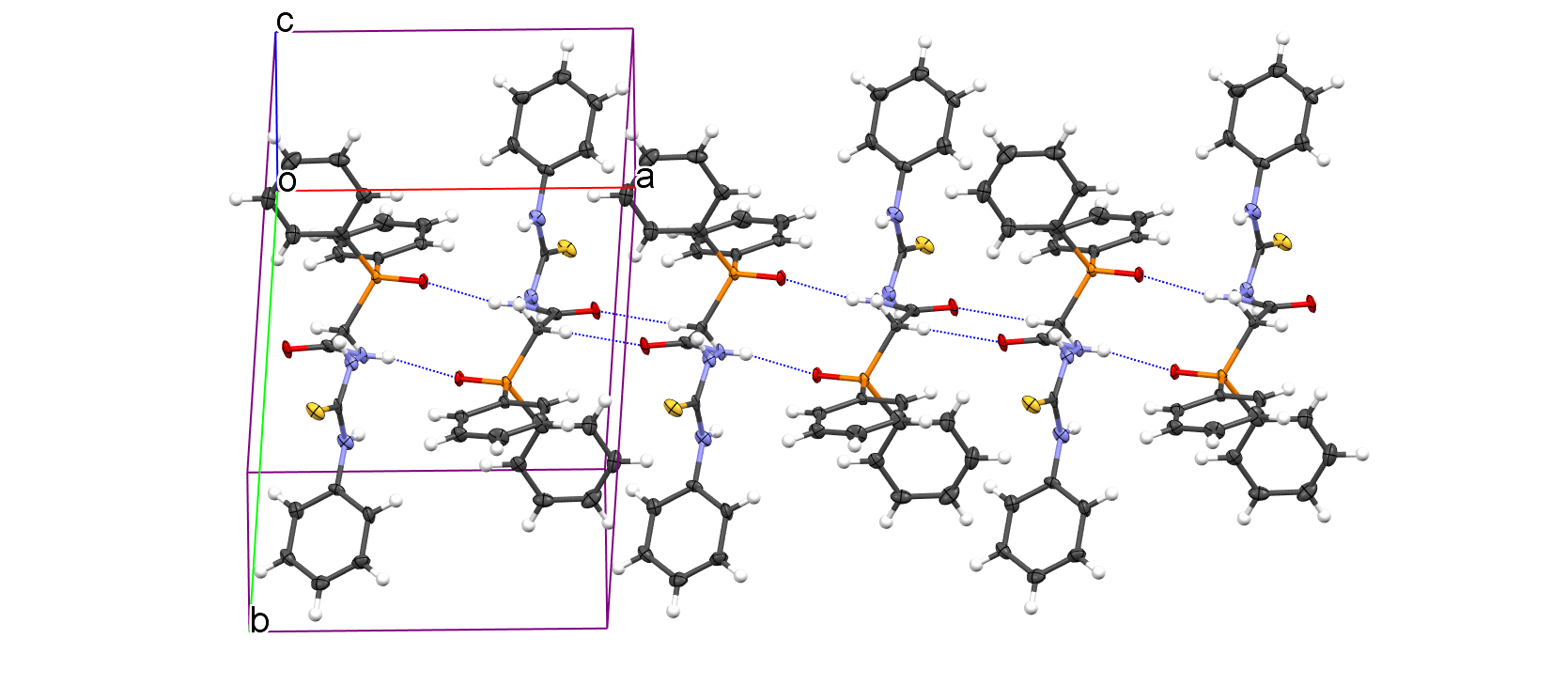
(a) (b)



**Figure S10.** Hirshfeld surfaces for (a) *A* and (b) *B* molecules of compound **3** with molecules participating in directed intermolecular interactions. The color scale corresponding to the value is taken from blue (1.2868) to red (–0.0500). Intermolecular interactions are shown with dashed dotted lines.

SUPRAMOLECULAR STRUCTURE IN THE CRYSTAL **3**





**Figure S11.** (a) Realization of paired centrosymmetric С12*B*–H12*D*⋅⋅⋅O11*В* interaction between two associates of compound **3** highlighted in blue; (b) one-dimensional motif along the *a* axis, formed by the participation of *B* molecules due to interactions of the N–H…O and C–H…O types.