SUPPLEMENTARY MATERIAL

Revealing Intra- and Intermolecular Interactions Determining Physico-chemical Features of Selected Quinolone Carboxylic Acid Derivatives

Kamil Wojtkowiak[1], Aneta Jezierska[1], Jarosław J. Panek[1]

[1] University of Wrocław, Faculty of Chemistry, ul. F. Joliot Curie 14, 50-383 Wrocław, Poland

Correspondence should be addressed to: aneta.jezierska@chem.uni.wroc.pl; jaroslaw.panek@chem.uni.wroc.pl

Table of contents:

VI. **Figure S2.** Dimers of the quinolone carboxylic acid derivatives obtained as a result of the geometry optimization at the PBE-D3/aug-cc-pVDZ level of theory studied based on the SAPT. Atom color coding: oxygen atoms -red, hydrogen atoms - white, carbon atoms - grey, chlorine atom - green, fluorine atoms - yellow and nitrogen atoms - blue.

VII. **Figure S3.** Topological maps of electron density based on AIM theory for the selected dimers of the quinolone carboxylic acid derivatives at the experimental X-ray geometry. Small green spheres denote Bond Critical Points (BCPs), small red spheres denote Ring Critical Points (RCPs). Atom color coding: oxygen atoms – red, hydrogen atoms – white, carbon atoms – grey, chlorine atom – green, fluorine atom – lime green and nitrogen atoms – blue.

VIII. **Table S5.** Bond Critical Points (BCPs) obtained for the intermolecular contacts in the selected dimers of the studied quinolone carboxylic acid derivatives at the experimental (X-ray) geometry. Electron density ρ_{BCP} is given in $e*a_0^{-3}$ atomic units, and its Laplacian $\nabla^2\rho_{BCP}$ in $e*a_0^{-5}$ units. The potential energy density V_{BCP} is given in $hartree*a_0^{-3}$ atomic units, while the corresponding dissociation energy $D_{e,BCP}$ is given in kcal/mol according to the Espinosa equation. The atoms marked with apostrophe are located in the monomer 2 of the dimeric system.

IX. **Figure S4.** Time evolution of atoms involved in the intramolecular hydrogen bond formation. Top panel: CPMD results of the gas phase. Bottom panel: CPMD results of the solid state.

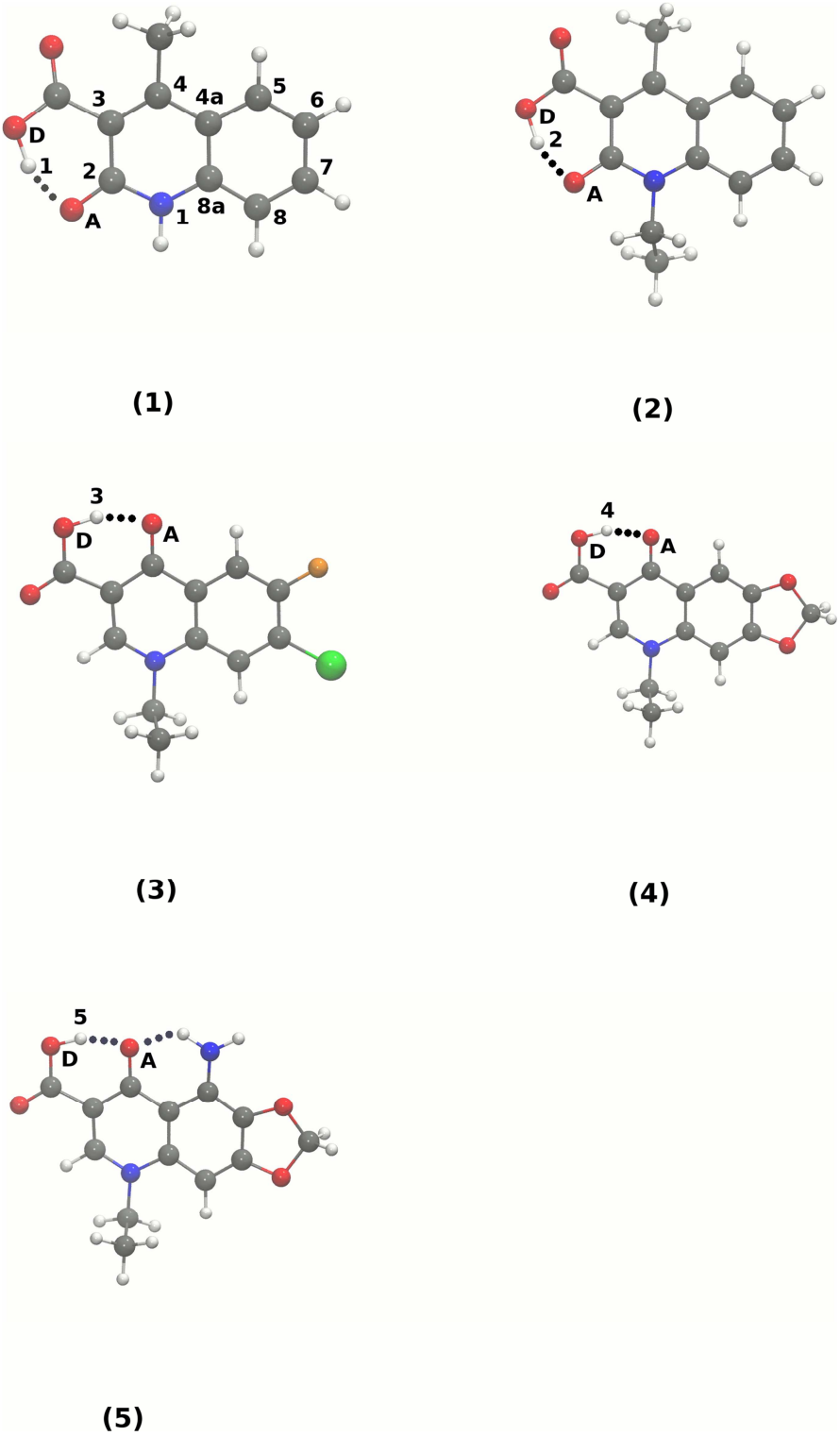


Figure S1. Molecular structures of the studied quinolone carboxylic acid derivatives. Dotted line indicates the presence of an intramolecular hydrogen bond. Atom color coding: oxygen atoms – red, hydrogen atoms – white, carbon atoms – grey, chlorine atom – green, fluorine atom – orange and nitrogen atoms – blue.

Table S1. Metric parameters of the intramolecular hydrogen bond. Comparison of experimental (X-ray) and computed data at the PBE-D3/aug-cc-pVTZ level of theory. Metric parameters are given in [Å] and [°]. For hydrogen bridge atoms notation see Figure S1.

Metric parameters	Experimental X-ray data	PBE-D3/aug-cc-pVTZ (*in vacuo*)	PBE-D3/aug-cc-pVTZ (PCM)*
Compound 1 Ref. [10]			
OD··OA	**2.465**	**2.5196**	**2.4767**
OD-H1	**0.895**	**1.0172**	**1.0355**
H1··OA	**1.638**	**1.5616**	**1.4910**
<ODH1OA	**152.14**	**154.83**	**156.81**
Compound 2 Ref. [17]			
OD··OA	**2.451**	**2.5079**	**2.4622**
OD-H2	**0.940**	**1.0177**	**1.0387**
H1··OA	**1.548**	**1.5506**	**1.4734**
<ODH2OA	**159.8**	**154.5**	**156.8**
Compound 3 Ref. [18]			
OD··OA	**2.549**	**2.5868**	**2.5253**
OD-H3	**0.820**	**1.0158**	**1.0346**
H1··OA	**1.785**	**1.6306**	**1.5405**
<ODH3OA	**154.5**	**154.9**	**157.0**
Compound 4 Ref. [11]			
OD··OA	**2.545**	**2.5703**	**2.5025**
OD-H4	**0.964**	**1.0205**	**1.0453**
H1··OA	**1.648**	**1.6056**	**1.5020**
<ODH4OA	**153.0**	**155.7**	**158.1**
Compound 5 Ref. [12]			
OD··OA	**2.518**	**2.5627**	**2.4991**
OD-H5	**0.941**	**1.0172**	**1.0402**
H1··OA	**1.626**	**1.6027**	**1.5056**
<ODH5OA	**156.6**	**155.4**	**157.6**

***water was used as a solvent**

Table S1 (Continuation). Metric parameters of the intramolecular hydrogen bond. Comparison of experimental (X-ray) and computed data at the PBE-D3/aug-cc-pVTZ level of theory. Metric parameters are given in [Å] and [°]. For hydrogen bridge atoms notation see Figure S1.

Metric parameters	Experimental X-ray data	PBE-D3/aug-cc-pVTZ (*in vacuo*)	PBE-D3/aug-cc-pVTZ (PCM)*
Compound 5 Ref. [12]			
N··OA	**2.664**	**2.6307**	**2.6608**
N-H	**0.865**	**1.0223**	**1.0193**
H··OA	**1.978**	**1.8343**	**1.8819**
<NHOA	**135.5**	**132.0**	**130.7**

***water was used as a solvent**

Table S2. AIM atomic charges of the O-H…O intramolecular hydrogen bond computed *in vacuo* and with solvent reaction field (PCM and water as a solvent) at the PBE-D3/aug-cc-pVTZ level of theory.

Atomic charge [e]	Gas phase	PCM
Compound 1		
qOD	**-1.1136**	**-1.1369**
qH1	**0.6254**	**0.6259**
qOA	**-1.1177**	**-1.1390**
Compound 2		
qOD	**-1.1159**	**-1.1391**
qH2	**0.6259**	**0.6261**
qOA	**-1.1179**	**-1.1331**
Compound 3		
qOD	**-1.1072**	**-1.1317**
qH3	**0.6191**	**0.6205**
qOA	**-1.0960**	**-1.1224**
Compound 4		
qOD	**-1.1110**	**-1.1366**
qH4	**0.6192**	**0.6186**
qOA	**-1.1045**	**-1.1335**

Table S2 (Continuation). AIM atomic charges computed *in vacuo* and with solvent reaction field (PCM and water as a solvent) at the PBE-D3/aug-cc-pVTZ level of theory.

Atomic charge [e]	Gas phase	PCM
Compound 5		
qOD	**-1.1126**	**-1.1381**
qH5	**0.6195**	**0.6207**
qOA	**-1.1173**	**-1.1318**
qN	**-1.1314**	**-1.1132**
qH	**0.4832**	**0.4658**
qOA	**-1.1173**	**-1.1318**

Table S3. Bond Critical Points (BCPs) obtained for the intramolecular hydrogen bridges in the studied quinolone carboxylic acid derivatives. Electron density ρ_{BCP} is given in $e^*a_0^{-3}$ atomic units, and its Laplacian $\nabla^2\rho_{BCP}$ in $e^*a_0^{-5}$ units.

BCP	Gas phase		PCM	
	ρ_{BCP}	$\nabla^2\rho_{BCP}$	ρ_{BCP}	$\nabla^2\rho_{BCP}$
Compound 1				
OD-H1	**0.3122**	**-2.1138**	**0.2949**	**-1.8894**
H1···OA	**0.0712**	**0.1045**	**0.0853**	**0.0909**
Compound 2				
OD-H2	**0.3117**	**-2.1050**	**0.2920**	**-1.8481**
H2···OA	**0.0731**	**0.1048**	**0.0891**	**0.0878**
Compound 3				
OD-H3	**0.3143**	**-2.1431**	**0.2965**	**-1.9174**
H3···OA	**0.0608**	**0.0975**	**0.0762**	**0.0879**
Compound 4				
OD-H4	**0.3098**	**-2.0868**	**0.2871**	**-1.7849**
H4···OA	**0.0648**	**0.0956**	**0.0841**	**0.0794**
Compound 5				
OD-H5	**0.3131**	**-2.1233**	**0.2915**	**-1.8441**
H5···OA	**0.0648**	**0.0988**	**0.0828**	**0.0846**
N-H	**0.3318**	**-1.9023**	**0.3361**	**-1.9002**
H···OA	**0.0372**	**0.1207**	**0.0333**	**0.1158**

Table S4. Wiberg bond indices calculated based on Natural Atomic Orbitals (NAO) at the PBE-D3/aug-cc-pVTZ level of theory.

Atom pair	Gas phase	PCM
H1···OA	**0.1283**	**0.1565**
H2···OA	**0.1296**	**0.1616**
H3···OA	**0.1143**	**0.1456**
H4···OA	**0.1237**	**0.1637**
H5···OA	**0.1172**	**0.1537**
H···OA	**0.0399**	**0.0328**

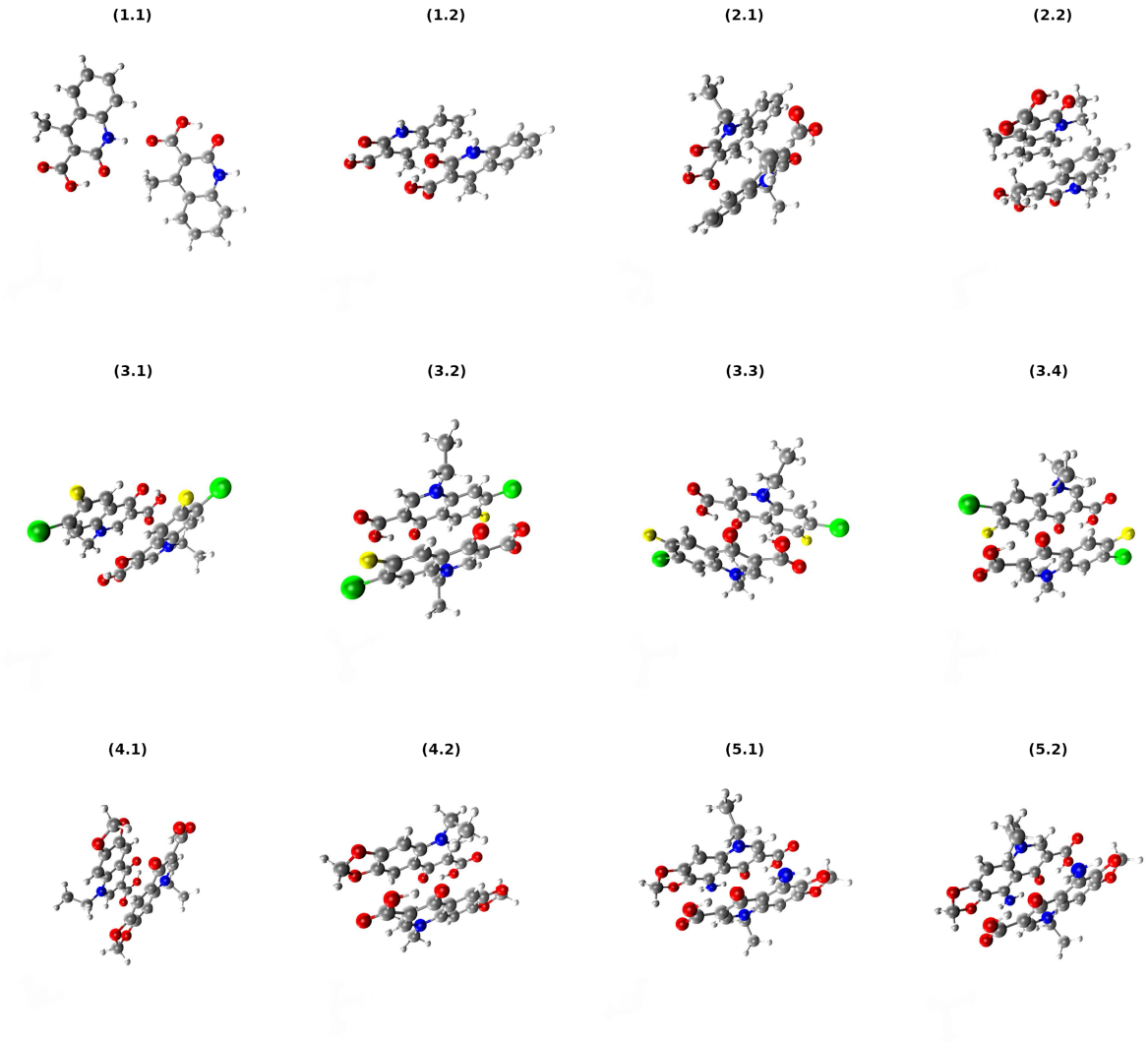


Figure S2. Dimers of the quinolone carboxylic acid derivatives obtained as a result of the geometry optimization at the PBE-D3/aug-cc-pVDZ level of theory studied based on the SAPT. Atom color coding: oxygen atoms -red, hydrogen atoms - white, carbon atoms - grey, chlorine atom - green, fluorine atoms - yellow and nitrogen atoms – blue.

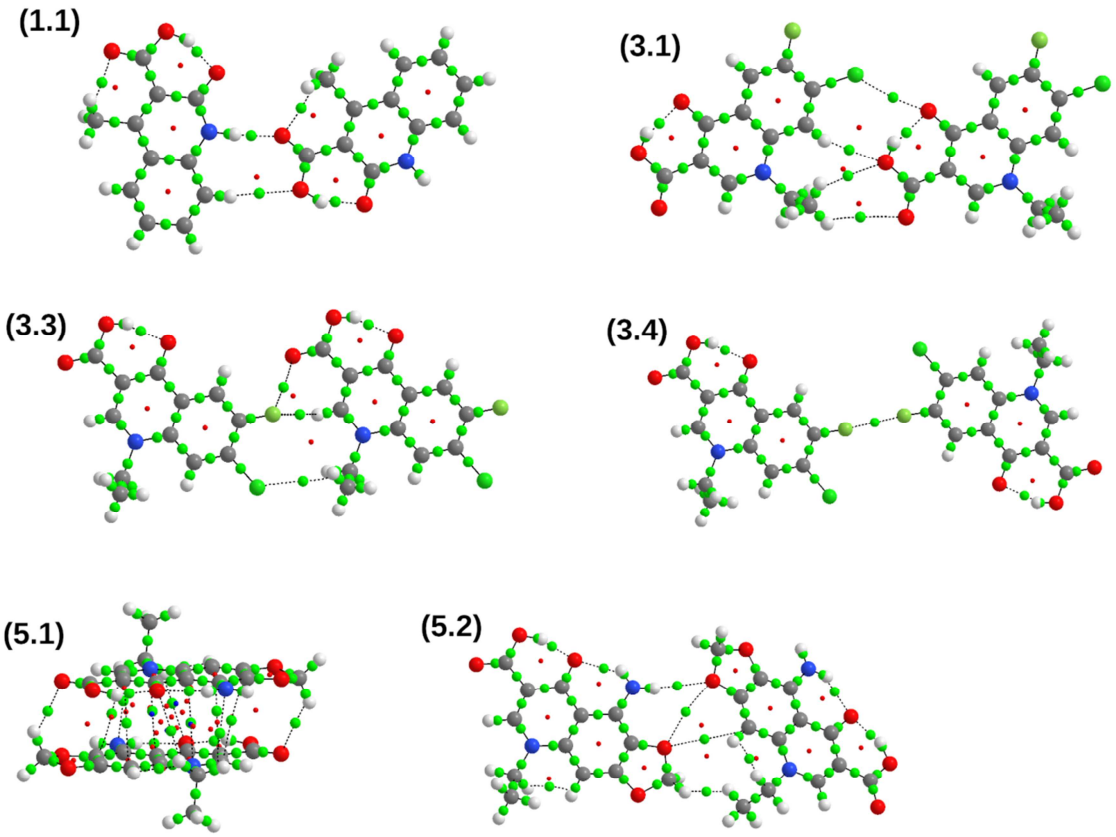
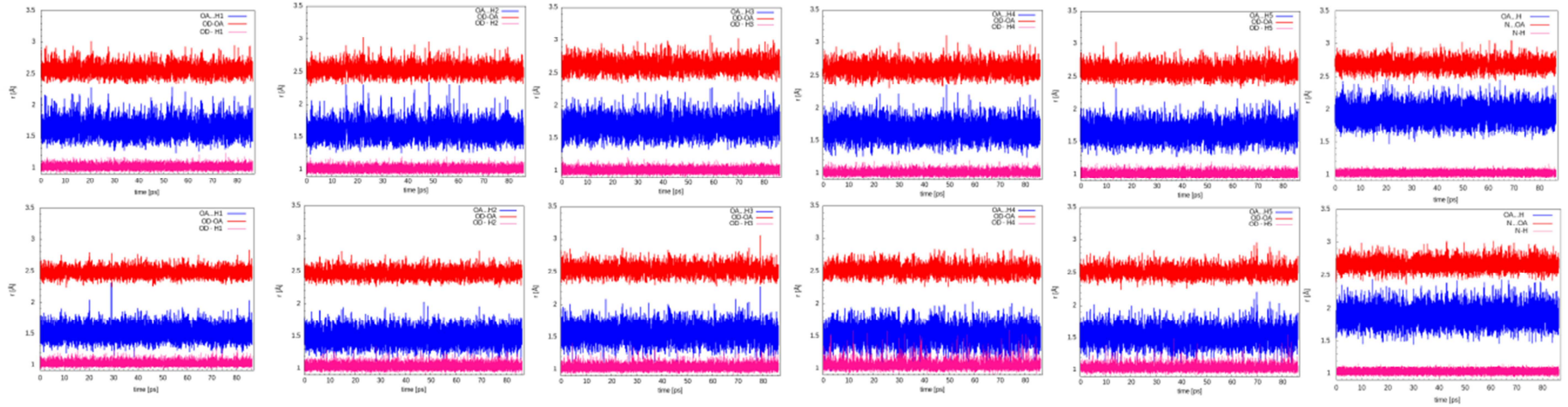


Figure S3. Topological maps of electron density based on AIM theory for the selected dimers of the quinolone carboxylic acid derivatives at the experimental X-ray geometry. Small green spheres denote Bond Critical Points (BCPs), small red spheres denote Ring Critical Points (RCPs). Atom color coding: oxygen atoms– red, hydrogen atoms – white, carbon atoms – grey, chlorine atom – green, fluorine atom – lime green and nitrogen atoms – blue.

Table S5. Bond Critical Points (BCPs) obtained for the intermolecular contacts in the selected dimers of the studied quinolone carboxylic acid derivatives at the experimental (X-ray) geometry. Electron density ρ_{BCP} is given in $e*a_0^{-3}$ atomic units, and its Laplacian $\nabla^2\rho_{BCP}$ in $e*a_0^{-5}$ units. The potential energy density V_{BCP} is given in $hartree*a_0^{-3}$ atomic units, while the corresponding dissociation energy $D_{e,BCP}$ is given in kcal/mol according to the Espinosa equation [85]. The atoms marked with apostrophe are located in the monomer 2 of the dimeric system.

Interaction:	ρ_{BCP}	$\nabla^2\rho_{BCP}$	V_{BCP}	$D_{e,BCP}$
Dimer 1.1				
N-H··O’	0.0330	0.1061	-0.02964	9.30
C8-H··OD’	0.0039	0.0139	-0.00190	0.60
			sum:	9.90
Dimer 3.1				
C7-Cl··OA’	0.0085	0.0352	-0.00485	1.52
C8-H··OD’	0.0079	0.0314	-0.00441	1.38
C-H(ethyl)··OD’	0.0032	0.0123	-0.00154	0.48
C-H(ethyl)··O’	0.0020	0.0067	-0.00083	0.26
			sum:	3.64
Dimer 3.3				
C6-F··O’	0.0040	0.0144	-0.00234	0.73
C6-F··H’-C2’	0.0057	0.0239	-0.00348	1.09
C7-Cl··H’-C’(ethyl)	0.0058	0.0210	-0.00278	0.87
			sum:	2.69
Dimer 3.4				
C6-F··F’-C6’	0.0063	0.0348	-0.00478	1.50
Dimer 5.1				
multiple (12) contacts between the stacked molecules	0.0039 ÷ 0.0060	0.0126 ÷ 0.0214	-0.00157 ÷ -0.00311	sum: 7.83
Dimer 5.2				
N-H··O(ring)’	0.0060	0.0246	-0.00342	1.07
O(ring3)··O(ring3)’	0.0020	0.0076	-0.00100	0.31
O(ring3)··C8’	0.0017	0.0061	-0.00069	0.22
C(ring3)-H··H’-C’(ethyl)	0.0129	0.0375	-0.00690	2.16
			sum:	3.76



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