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Supporting information for article:

VARIATIONS OF QUANTUM ELECTRONIC PRESSURE UNDER THE EXTERNAL COMPRESSION IN CRYSTALS WITH HALOGEN BONDS ASSEMBLED IN CL3, Br3, I3-SYNTHONS

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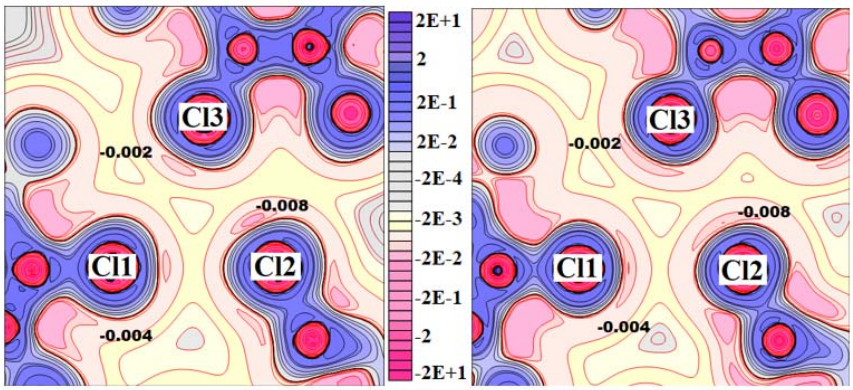

(*a*) (*b*)

Figure S1 Contour maps of quantum electronic pressure in the plane of Cl_3-synthons: reconstruction from (*a*) experimental electron density (Bui *et al.*, 2009) and (*b*) the electron density calculated in the present study

Table S1 Calculated cell parameters and volumes for the C_6Cl_6, C_6Br_6 и C_6I_6 crystals under external compression

External Compression (GPa)	a (Å)	b (Å)	c (Å)	β (˚)	Volume (Å^3)
		C_6Cl_6			
0	8.026	3.711	14.725	92.248	438.2
1	7.888	3.601	14.450	92.703	410.1
5	7.637	3.384	13.958	93.534	360.1
10	7.472	3.249	13.641	94.061	330.3
20	7.267	3.094	13.265	94.623	297.2
		C_6Br_6			
0	8.367	3.908	15.277	92.785	499.0
1	8.234	3.786	15.009	93.312	467.2
5	7.988	3.540	14.560	93.914	410.8
10	7.834	3.391	14.250	94.369	377.5
20	7.637	3.225	13.868	94.828	340.4
		C_6I_6			
0	8.820	4.131	16.132	93.521	586.7
1	8.730	4.016	15.965	93.686	558.6
5	8.537	3.778	15.515	94.302	498.9
10	8.382	3.631	15.196	94.664	461.0
20	8.182	3.450	14.741	95.212	414.4

Table S2 Experimental (HCLBNZ13 (Bui *et al.*, 2009), HBRBEN03 (Brezgunova *et al.*, 2012), HIBENZ11 (Ghosh *et al.*, 2007)) and calculated values of bond lengths in the C_6Hal_6 crystals; calculated and experimental electron density (Bui *et al.*, 2009) and quantum electronic pressure at bcp and rcp obtained from the calculated and experimental (Bui *et al.*, 2009) data.

Bond	$\rho(\mathbf{r}_{bcp})$ (a.u.)	QEP($\mathbf{r}_{bcp}$) (a.u.)	Bond lengths, l (Å)		
Halogen bond Cl…Cl			Cl…Cl	Br…Br	I…I
Calculated	0.006	–0.003	3.476	3.559	3.671
Experimental	0.008	–0.003	3.447	3.541	3.704
Covalent bond C–Cl			C–Cl	C–Br	C–I
Calculated	0.211	0.097	1.713	1.880	2.119
Experimental	0.208	0.127	1.712	1.869	2.104
Covalent bond C–C					
Calculated	0.307	0.221	1.401	1.402	1.406
Experimental	0.310	0.324	1.402	1.402	1.407
Stacking interactions Cl…Cl			Cl…Cl	Br…Br	I…I
Calculated	0.005	–0.002	3.711	3.908	4.131
Experimental	0.005	–0.002	3.763	3.933	4.225
(3, +1)		$\rho(r_{rcp})$		QEP(r_{rcp})	
			Cl_3-synthon		
Calculated		0.002		–0.001	
Experimental		0.003		–0.001	
			Benzene ring C_6		
Calculated		0.019		–0.020	
Experimental		0.022		–0.016	

Table S3 Calculated characteristic of the electron density and quantum electronic pressure at bcp (3, –1) for the C_6Cl_6 crystal

Bond	External Pressure (GPa)	$\rho(\mathbf{r}_{bcp})$ (a.u.)	$\nabla^2\rho(r_{bcp})$ (a.u.)	$g(\mathbf{r}_{bcp})$ (a.u.)	$QEP(\mathbf{r}_{bcp})$ (a.u.)	Bond lengths, l (Å)
$Cl_1\ldots Cl_2$	0	0.006	0.025	0.005	–0.003	3.476
	1	0.008	0.034	0.007	–0.004	3.337
	5	0.013	0.055	0.011	–0.007	3.108
	10	0.018	0.070	0.016	–0.008	2.977
	20	0.024	0.092	0.021	–0.010	2.834
$Cl_2\ldots Cl_3$	0	0.005	0.024	0.004	–0.003	3.498
	1	0.008	0.033	0.006	–0.004	3.345
	5	0.013	0.054	0.011	–0.007	3.103
	10	0.017	0.071	0.016	–0.008	2.970
	20	0.024	0.093	0.022	–0.010	2.828
$Cl_1\ldots Cl_3$	0	0.004	0.015	0.003	–0.002	3.705
	1	0.005	0.022	0.004	–0.003	3.537
	5	0.010	0.041	0.008	–0.005	3.249
	10	0.014	0.058	0.012	–0.007	3.081
	20	0.021	0.082	0.019	–0.009	2.897
C–Cl	0	0.211	–0.316	0.073	0.097	1.713
	1	0.212	–0.320	0.074	0.098	1.710
	5	0.216	–0.336	0.076	0.103	1.701
	10	0.220	–0.352	0.078	0.107	1.693
	20	0.227	–0.379	0.082	0.115	1.679
C–C	0	0.307	–0.823	0.100	0.221	1.401
	1	0.308	–0.827	0.100	0.222	1.400
	5	0.311	–0.841	0.102	0.226	1.396
	10	0.313	–0.856	0.103	0.230	1.391
	20	0.318	–0.883	0.106	0.238	1.383
$Cl\ldots Cl_{inter}$	0	0.005	0.018	0.003	–0.002	3.711
	1	0.006	0.023	0.004	–0.003	3.601
	5	0.010	0.036	0.007	–0.005	3.384
	10	0.013	0.048	0.010	–0.006	3.249
	20	0.017	0.065	0.014	–0.008	3.094

Table S4 Calculated characteristics of the electron density and quantum electronic pressure at rcp (3, +1) for the C_6Cl_6 crystal

Ring	External Compression (GPa)	$\rho(\mathbf{r}_{rcp})$ (a.u.)	$\nabla^2\rho(r_{rcp})$ (a.u.)	$g(\mathbf{r}_{bcp})$ (a.u.)	$QEP(\mathbf{r}_{rcp})$ (a.u.)
Cl_3	0	0.002	0.008	0.001	–0.001
	1	0.003	0.013	0.002	–0.002
	5	0.006	0.025	0.005	–0.003
	10	0.008	0.037	0.007	–0.005
	20	0.012	0.056	0.012	–0.007
C_6	0	0.019	0.150	0.029	–0.020
	1	0.020	0.152	0.029	–0.020
	5	0.020	0.156	0.030	–0.020
	10	0.021	0.160	0.031	–0.021
	20	0.022	0.168	0.033	–0.022

Table S5 Calculated characteristics of the electron density and quantum electronic pressure at bcp (3, –1) for the C_6Br_6 crystal

Bond	External Pressure (GPa)	$\rho(\mathbf{r}_{bcp})$ (a.u.)	$\nabla^2\rho(r_{bcp})$ (a.u.)	$g(\mathbf{r}_{bcp})$ (a.u.)	$QEP(\mathbf{r}_{bcp})$ (a.u.)	Bond lengths, l (Å)
$Br_1\ldots Br_2$	0	0.008	0.026	0.005	–0.003	3.559
	1	0.010	0.033	0.007	–0.004	3.431
	5	0.016	0.048	0.011	–0.006	3.216
	10	0.020	0.059	0.014	–0.007	3.091
	20	0.027	0.073	0.019	–0.008	2.959
$Br_2\ldots Br_3$	0	0.004	0.016	0.003	0.038	3.587
	1	0.006	0.022	0.004	–0.003	3.435
	5	0.012	0.037	0.008	–0.005	3.210
	10	0.016	0.050	0.011	–0.006	3.086
	20	0.024	0.067	0.016	–0.008	2.953
$Br_1\ldots Br_3$	0	0.007	0.024	0.005	–0.003	3.834
	1	0.010	0.032	0.007	–0.004	3.654
	5	0.016	0.048	0.011	–0.006	3.356
	10	0.020	0.060	0.014	–0.007	3.193
	20	0.027	0.075	0.019	–0.008	3.017
C–Br	0	0.164	–0.152	0.063	0.058	1.880
	1	0.165	–0.154	0.064	0.059	1.877
	5	0.168	–0.158	0.067	0.061	1.867
	10	0.171	–0.163	0.070	0.064	1.857
	20	0.178	–0.170	0.076	0.069	1.838
C–C	0	0.305	–0.809	0.101	0.219	1.402
	1	0.306	–0.813	0.101	0.220	1.401
	5	0.309	–0.827	0.103	0.224	1.397
	10	0.312	–0.843	0.105	0.229	1.391
	20	0.317	–0.874	0.108	0.238	1.382
$Br\ldots Br_{inter}$	0	0.005	0.018	0.003	–0.002	3.908
	1	0.007	0.022	0.004	–0.003	3.786
	5	0.011	0.033	0.007	–0.004	3.540
	10	0.014	0.042	0.010	–0.005	3.391
	20	0.020	0.055	0.014	–0.006	3.225

Table S6 Calculated characteristics of the electron density and quantum electronic pressure at rcp (3, +1) for the C_6Br_6 crystal

Ring	External Compression (GPa)	$\rho(\mathbf{r}_{rcp})$ (a.u.)	$\nabla^2\rho(r_{rcp})$ (a.u.)	$g(\mathbf{r}_{bcp})$ (a.u.)	$QEP(\mathbf{r}_{rcp})$ (a.u.)
Br_3	0	0.003	0.010	0.002	–0.001
	1	0.004	0.015	0.003	–0.002
	5	0.007	0.026	0.005	–0.003
	10	0.010	0.036	0.007	–0.004
	20	0.014	0.050	0.011	–0.006
C_6	0	0.020	0.151	0.029	–0.020
	1	0.020	0.153	0.029	–0.020
	5	0.021	0.157	0.030	–0.020
	10	0.021	0.162	0.031	–0.021
	20	0.022	0.171	0.033	–0.022

Table S7 Calculated characteristics of the electron density and quantum electronic pressure at bcp (3,–1) for the C_6I_6 crystal

Bond	External Pressure (GPa)	$\rho(\mathbf{r}_{bcp})$ (a.u.)	$\nabla^2\rho(r_{bcp})$ (a.u.)	$g(\mathbf{r}_{bcp})$ (a.u.)	$QEP(\mathbf{r}_{bcp})$ (a.u.)	Bond lengths, l (Å)
$I_1\ldots I_2$	0	0.012	0.028	0.006	–0.003	3.671
	1	0.014	0.031	0.007	–0.004	3.592
	5	0.020	0.040	0.010	–0.004	3.403
	10	0.025	0.046	0.013	–0.005	3.289
	20	0.032	0.052	0.016	–0.005	3.166
$I_2\ldots I_3$	0	0.012	0.027	0.006	–0.003	3.673
	1	0.014	0.031	0.007	–0.004	3.587
	5	0.020	0.040	0.010	–0.005	3.399
	10	0.025	0.047	0.013	–0.005	3.284
	20	0.032	0.055	0.017	–0.005	3.159
$I_1\ldots I_3$	0	0.008	0.020	0.004	–0.003	3.901
	1	0.010	0.024	0.005	–0.003	3.777
	5	0.015	0.034	0.008	–0.004	3.542
	10	0.021	0.041	0.011	–0.005	3.390
	20	0.028	0.051	0.015	–0.005	3.220
C–I	0	0.118	0.014	0.062	0.023	2.119
	1	0.119	0.014	0.063	0.024	2.114

	5	0.122	0.016	0.066	0.025	2.101
	10	0.125	0.018	0.070	0.027	2.086
	20	0.131	0.022	0.078	0.030	2.060
C–C	0	0.301	–0.784	0.101	0.213	1.406
	1	0.302	–0.788	0.101	0.215	1.405
	5	0.305	–0.805	0.103	0.220	1.399
	10	0.309	–0.825	0.106	0.225	1.392
	20	0.315	–0.861	0.110	0.236	1.381
I…I_{inter}	0	0.007	0.017	0.004	–0.002	4.131
	1	0.009	0.020	0.004	–0.002	4.016
	5	0.013	0.028	0.007	–0.003	3.778
	10	0.016	0.034	0.009	–0.004	3.631
	20	0.022	0.044	0.012	–0.004	3.450

Table S8 Calculated characteristics of the electron density and quantum electronic pressure at rcp (3, +1) for the C_6I_6 crystal

Ring	External Compression (GPa)	$\rho(\mathbf{r}_{rcp})$ (a.u.)	$\nabla^2\rho(r_{rcp})$ (a.u.)	$g(\mathbf{r}_{bcp})$ (a.u.)	$QEP(\mathbf{r}_{rcp})$ (a.u.)
I_3	0	0.005	0.014	0.003	–0.002
	1	0.006	0.017	0.003	–0.002
	5	0.010	0.026	0.006	–0.003
	10	0.013	0.034	0.008	–0.004
	20	0.017	0.045	0.011	–0.005
C_6	0	0.020	0.152	0.029	–0.020
	1	0.021	0.153	0.030	–0.020
	5	0.021	0.159	0.031	–0.021
	10	0.022	0.165	0.032	–0.021
	20	0.023	0.177	0.035	–0.023

Table S9 Bulk moduli, calculated form stiffness tensor in ELATE (https://github.com/fxcoudert/elate) (Gaillac *et al.*, 2016; Gaillac & Coudert, 2016) and by the 3rd order Birch-Murnaghan equation in PASCal (http://pascal.chem.ox.ac.uk/) (Cliffe& Goodwin, 2012) in comparison with experimentaly observed bulk moduli for C_6Hal_6 crystals

Crystal	Calculated bulk moduli		Experimentaly observed bulk moduli, B_0 (GPa)
	B^E, this work (GPa) ELATE	B^P, this work (GPa) PASCal	
C_6Cl_6	11.3	11.6	8.4 (Vaidya & Kennedy, 1971)
C_6Br_6	12.2	11.3	9.1 (Vaidya & Kennedy, 1971)
C_6I_6	17.3 17.2 (Tateyama & Ohno, 2002)	19.0	10.3 (Nakayama *et al.*, 2000) 14.4 (Tateyama & Ohno, 2002)

Table S10 Calculated values of the quantum electronic pressure differences between the halogen bonds and the centres of Hal_3-synthons (Δ_{Hal3}= QEP($\mathbf{r}_{rcp}$) – QEP($\mathbf{r}_{bcp}$)) and between the Hal…Hal stacking interaction and the centres of Hal_3-synthons (Δ_{Hal}= QEP($\mathbf{r}_{rcp}$) – QEP($\mathbf{r}_{bcp}$)) at cp for the C_6Cl_6, C_6Br_6, and C_6I_6 crystals

External compression (GPa)	Δ_{Hal3} (a.u.)	Δ_{Hal} (a.u.)
	C_6Cl_6	
0	0.00224	0.00126
1	0.00272	0.00130
5	0.00338	0.00126
10	0.00350	0.00107
20	0.00327	0.00065
	C_6Br_6	
0	0.00193	0.00091
1	0.00214	0.00081
5	0.00238	0.00062
10	0.00234	0.00038
20	0.00194	0.00003
	C_6I_6	
0	0.00153	0.00020
1	0.00146	0.00015
5	0.00113	0.00006
10	0.00057	0.00031
20	–0.00053	0.00069

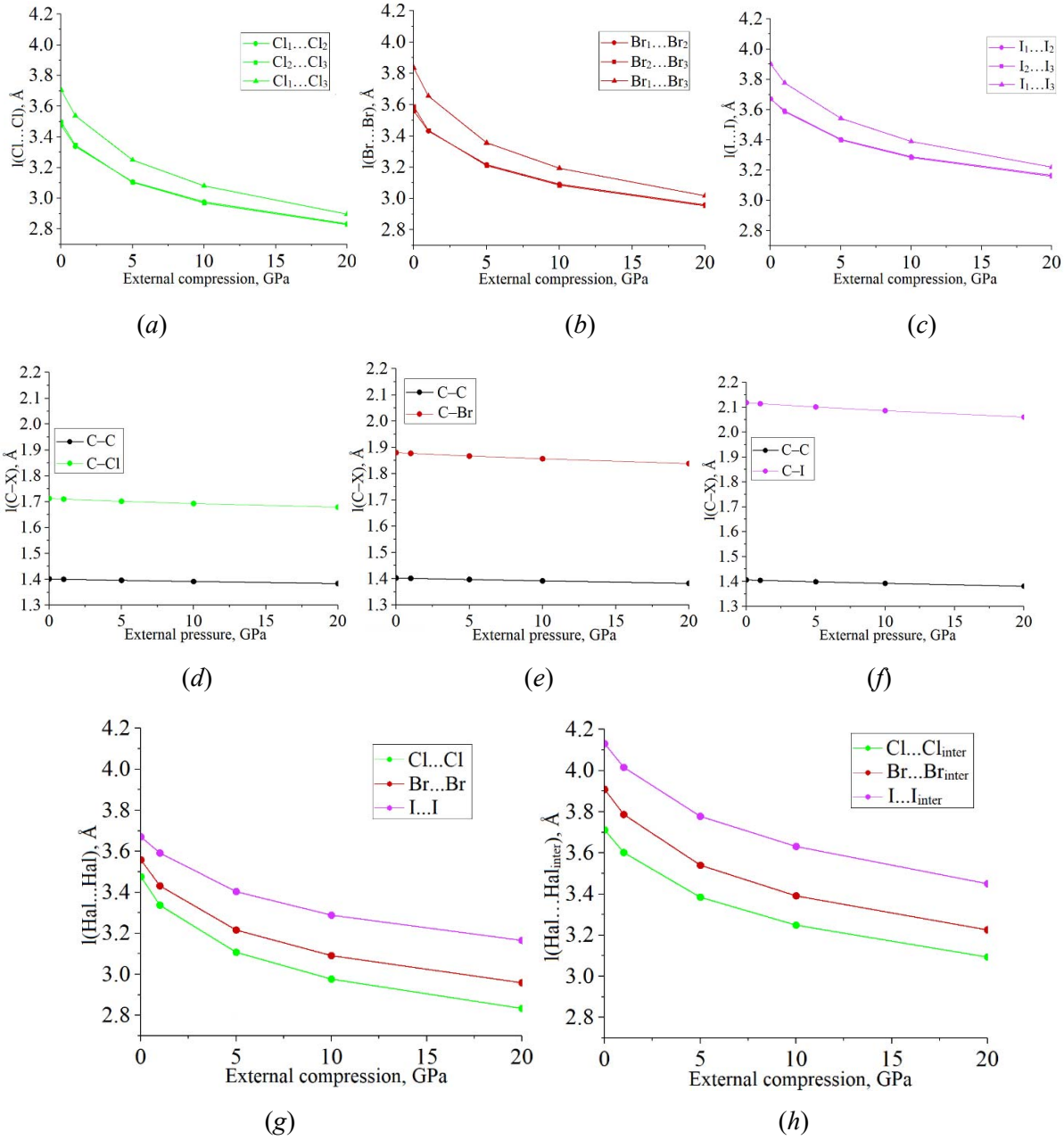

Figure S2 Changing of bond length under the external compression for (*a*) the Cl_3 halogen bonds, (*b*) the Br_3 halogen bonds, (*c*) the I_3 halogen bonds, and covalent bonds in (*d*) C_6Cl_6, (*e*) C_6Br_6 and (*f*) C_6I_6 crystals; comparison of the strongest halogen bond in Hal_3-synthon (*g*) with the strongest Hal…Hal stacking interactions (*h*)

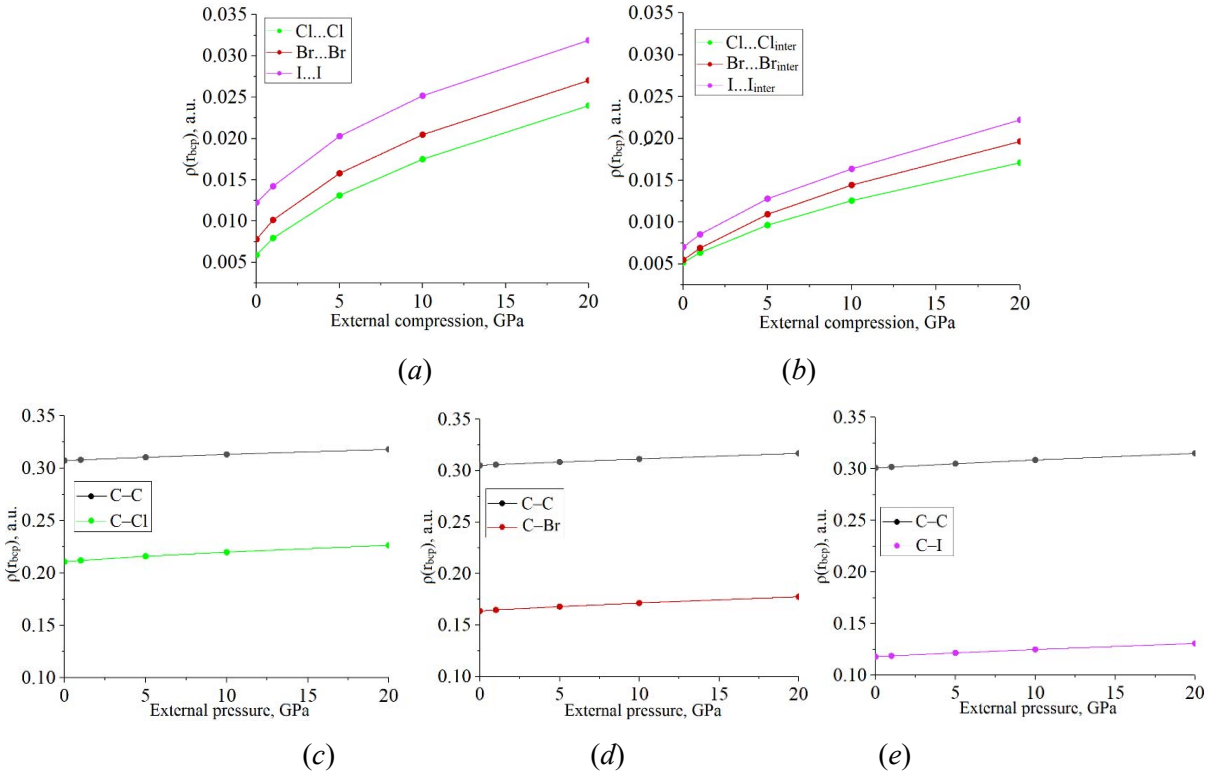

Figure S3 Changing of the electron density at bcp of (*a*) halogen bonds and (*b*) Hal…Hal stacking interactions, covalent bonds in (*c*) C_6Cl_6, (*d*) C_6Br_6 and (*e*) C_6I_6 crystals under the external compression

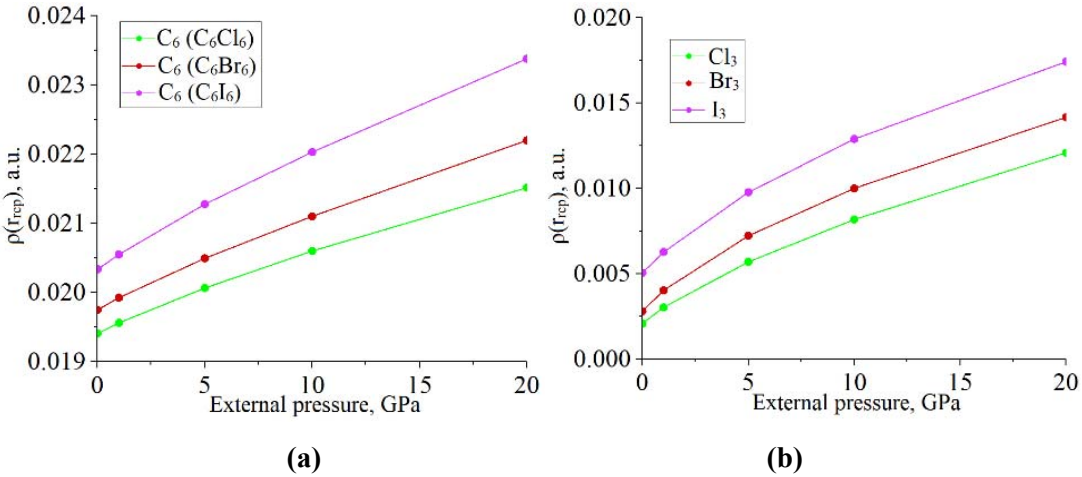

Figure S4 Changing of the electron density values $\rho(r_{rcp})$ of the (*a*) benzene ring C_6 and (*b*) Hal_3-synthon under the external compression

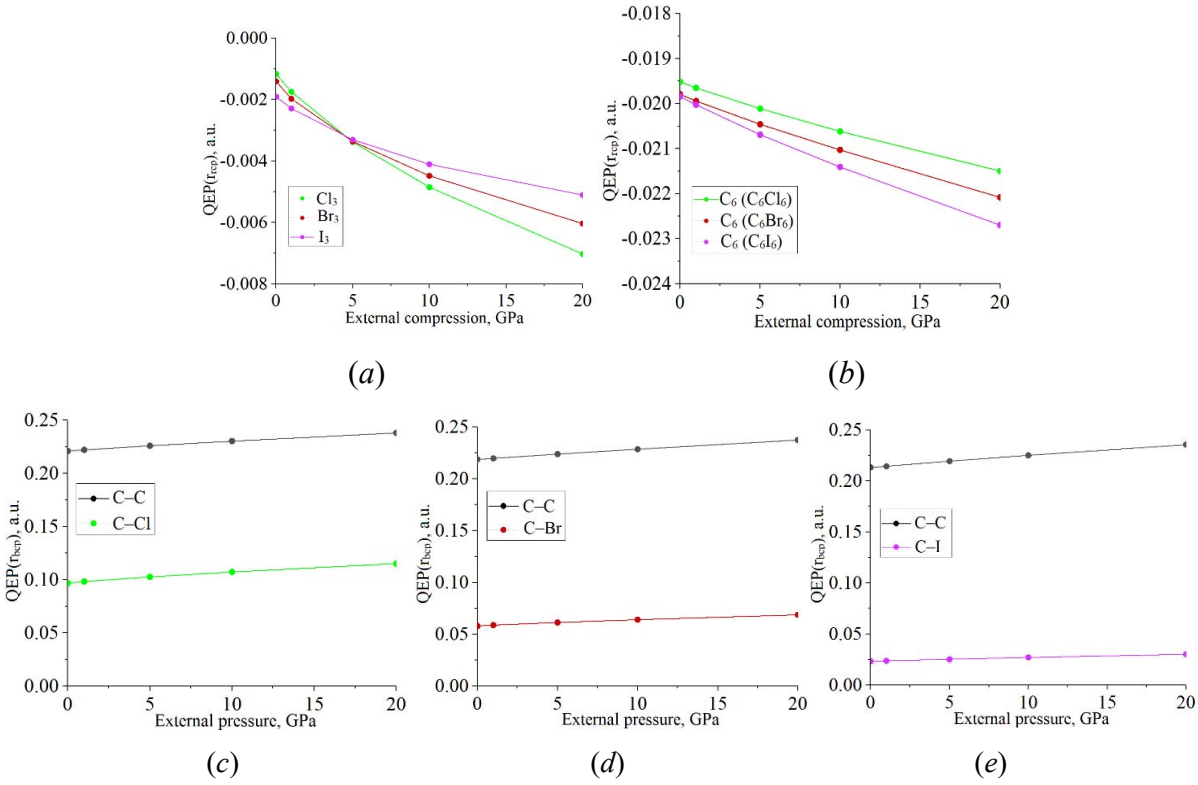

Figure S5 Changing of the quantum electronic pressure QEP($\mathbf{r}_{bcp}$) of the covalent bonds in (*a*) Hal_3-synthons, b) benzene rings C_6, covalent bonds in (*c*) C_6Cl_6, (*d*) C_6Br_6, and (*e*) C_6I_6 crystals under external compression

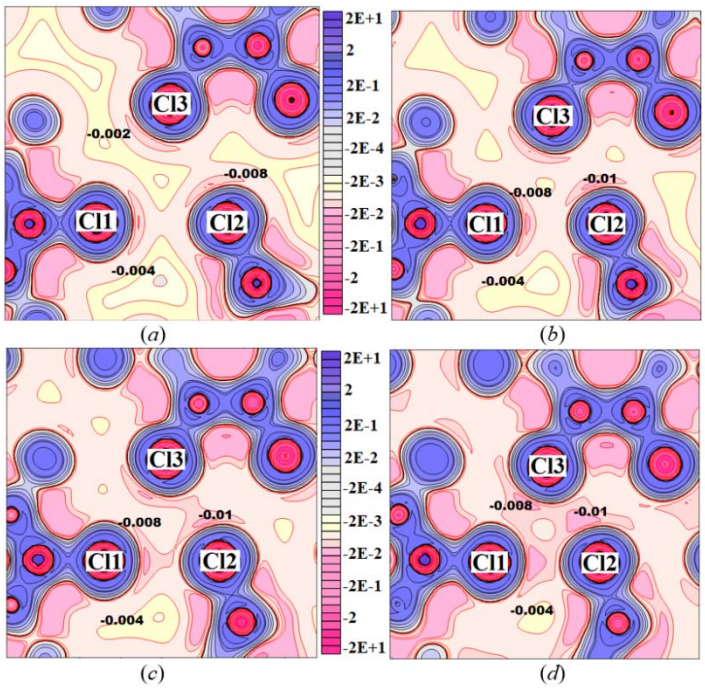

Figure S6 Contour maps of quantum electronic pressure QEP(**r**) in the plane of Cl_3-synthons under (*a*) 1 GPa, (*b*) 5 GPa, (*c*) 10 GPa, and (*d*) 20 GPa external compression in the C_6Cl_6 crystal

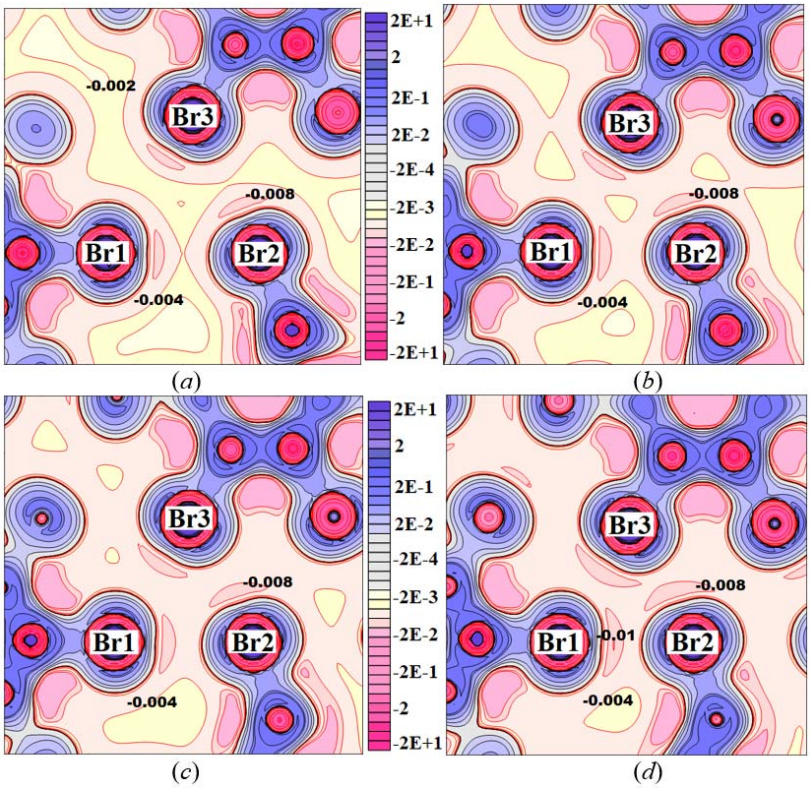

Figure S7 Contour maps of quantum electronic pressure QEP(**r**) in the plane of Br_3-synthons under (*a*) 1 GPa, (*b*) 5 GPa, (*c*) 10 GPa, and (*d*) 20 GPa external compression in the C_6Br_6 crystal

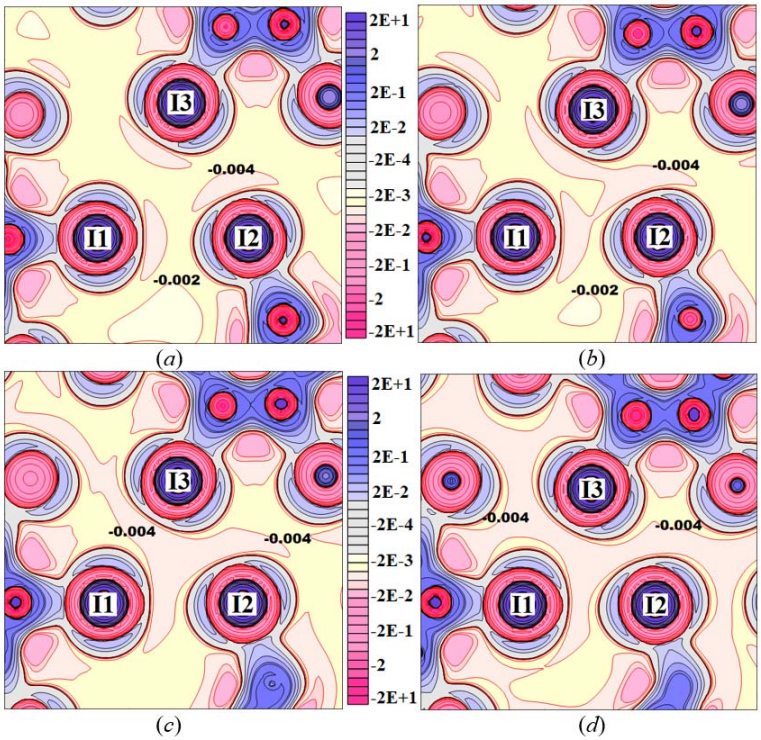

Figure S8 Contour maps of quantum electronic pressure QEP(**r**) in the plane of I_3-synthons under (*a*) 1 GPa, (*b*) 5 GPa, (*c*) 10 GPa, and (*d*) 20 GPa external compression in the C_6I_6 crystal