Supporting Information

Details of data collection, multipole refinement, and quantum chemical calculations:

Crystals of **1** ($C_5H_7I_2N_2$, M = 348.93) are triclinic, space group P-1, at 100K: a = 5.3648(5), b = 7.1380(7), c = 12.2613(12) Å, α = 96.671(5), β = 93.576(5), γ = 104.256(5)°, V = 449.97(8) Å^3, Z = 2 (Z' = 1), d_{calc} = 2.575 gcm^{-3}, μ(MoKα) = 69.16 cm^{-1}, F(000) = 314. Intensities of 71539 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71072Å, ω-scans, 2θ<95°] and 8329 independent reflections [R_{int} = 0.0274] were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. For **1** the refinement converged to wR2 = 0.0450 and GOF = 1.006 for all independent reflections (R1 = 0.0176 was calculated against F for 7705 observed reflections with I>2σ(I))**.** All calculations were performed using SHELXTL PLUS 5.0.

The multipole refinement was carried out within the Hansen-Coppens formalism [N. K. Hansen, P. Coppens, *Acta Crystallogr. A* **1978**, *34*, 909] using XD program package [T. S. Koritsansky, S. T. Howar, T. Richter, P. R. Mallinson, Z. Su, N. K. Hansen, **1995**] with the core and valence electron density derived from wave functions fitted to a relativistic Dirac-Fock solution [Z. W. Su, P. Coppens, *Acta Crystallogr. A* **1995**, *51*, 27]. Before the refinement C-H bond distances were normalized to the standard values of 1.08 Å. The level of multipole expansion was hexadecapole for iodine and octupole for nitrogen and carbon atoms. The dipole D_{10} was refined for all hydrogen atoms. The kappa and kappa' parameters were the same for the identical atoms of the independent molecules. The refinement was carried out against F and converged to R = 0.0124, wR = 0.0157 and GOF = 1.16 for 8238 merged reflections with I>3σ(I)). All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria. The total electron density function for **1** was positive everywhere. The residual electron density was not more than 0.46 eÅ^{-3} (the maximum is near the inversion centre far from the I(1)…I(2) line), which is rather low for compounds containing heavy elements like iodine. Analysis of topology of the ρ(**r**) function was carried out using the WinXPRO program package [A. Stash, V. Tsirelson, *J. Appl. Crystallogr.* **2002**, *35*, 371].

The potential energy density v(**r**) was evaluated through the Kirzhnits approximation [D. A. Kirzhnits, *Sov. Phys. JETP* **1957**, *5*, 54] for the kinetic energy density function g(**r**). Accordingly, the g(**r**) function is described as $(3/10)(3\pi^2)^{2/3}[\rho(\mathbf{r})]^{5/3}+(1/72)|\nabla\rho(\mathbf{r})|^2/\rho(\mathbf{r})+1/6\nabla^2\rho(\mathbf{r})$, in conjunction with the local virial theorem $(2g(\mathbf{r})+v(\mathbf{r})=1/4\nabla^2\rho(\mathbf{r}))$ leading to the expression for v(**r**) and, thus, for the electron energy density $h_e(\mathbf{r})$. The interaction energies were estimated by means of the Espinosa's correlation scheme – a semiquantitive relation between the energy of an interaction and the value of the potential energy density function v(**r**) in the CP (3, -1) (E. Espinosa, E. Molins, C. Lecomte, *Chem. Phys. Letts* **1998**, *285*, 170; E. Espinosa, I. Alkorta, I. Rozas, J. Elguero, E. Molins, *Chem.*

Phys. Letts **2001**, *336*, 457). This approach gives rather accurate estimates in many cases: for weak interactions such as H…H and C-H…O (see, e.g., K. A. Lyssenko, A. A. Korlyukov, M. Yu. Antipin. *Mendeleev Commun.* **2005**, 90), for interactions Mg...C and Ca…C (E. A. Pidko, R. A. van Santen. *ChemPhysChem*. **2006**, *7*, 1657; E. A. Pidko, J. Xu, B. L. Mojet, L. Lefferts, I. R. Subbotina, V. B. Kazansky, R. A. van Santen. *J. Phys. Chem. B* **2006**, *110*, 22618), for strong and intermediate hydrogen bonds (see, e.g., L. Sobczyk, S. J. Grabowski, T. M. Krygowski. *Chem. Rev*. **2005**, *105*, 3513), for Au-PPh_3 and Gd-OH_2 bonds (A. O. Borissova, A. A. Korlyukov, M. Y. Antipin, K. A. Lyssenko. *J. Phys. Chem. A* **2008**, *112*, 11519; L. N. Puntus, K. A. Lyssenko, M. Yu. Antipin, J.-C. G. Bunzli, *Inorg. Chem.* **2008**, *47*, 11095), which correspond to the intermediate type of interatomic interactions. In addition, we performed the quantum chemical calculations for the molecular complex I_2...I_2 (the I…I distance is 3.772 Å, the III angle is 175.5°) and compared the I…I interaction energies obtained by means of the Espinosa's correlation with those calculated as a difference between an energy of the complex and twice an energy of the molecule. The energies (BSSE and ZPE corrected) were 1.42 and 2.03 kcal/mole, respectively.

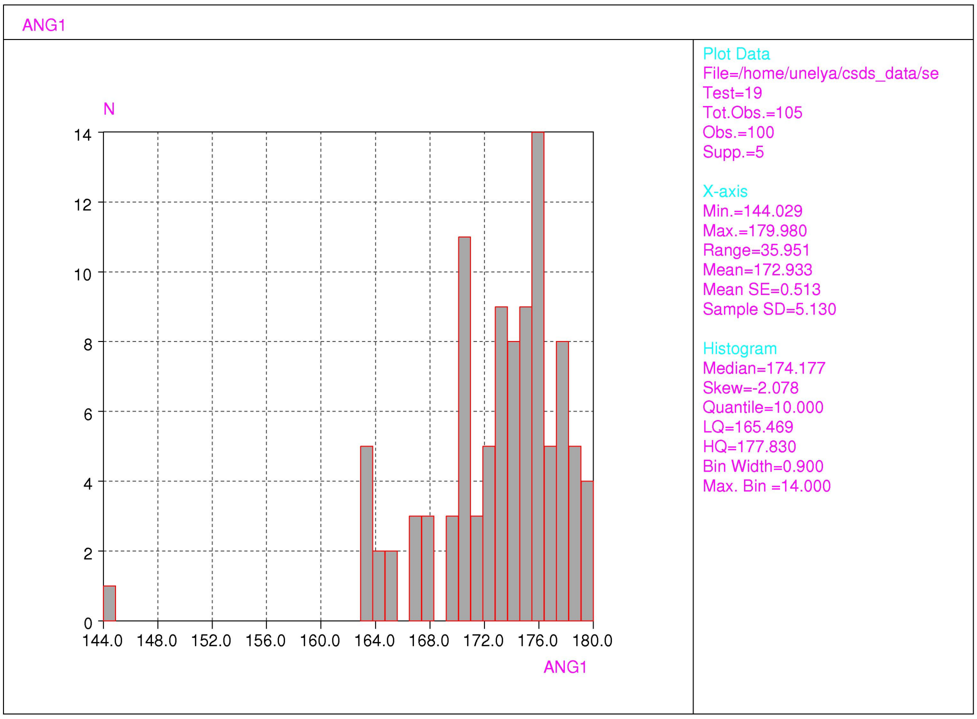
Ab intio calculations of the isolated dianion I_4^{2-} and the molecular complex I_2...I_2 were performed with the Gaussian09 program package at the MP2(FC) and the M05-2X levels for the dianion and at the M05-2X level for the model complex. Full optimization of both the dianion and the complex was carried out using Sadlej's standard polarised POL basis set [A.J. Sadlej. *Collec. Czech. Chem. Commun.* **53** (1988), p. 1995] starting from the X-ray diffraction data for **1** and crystalline diiodine (F. van Bolhuis, P. B. Koster, T. Migchelsen, Acta Cryst. **1967**, *23*, 90). The extremely tight threshold limits of $2 \cdot 10^{-6}$ and $6 \cdot 10^{-6}$ au were applied for the maximum force and displacement, respectively. The optimization was followed by the evaluation of the harmonic vibration frequencies. The topological analysis of the computed electron densities was performed using the AIMall program package [Keith, T. A. AIMAll (Version 08.01.25), 2008, http://aim.tkgristmill.com].

It is to be noted that the results of the topological analysis of the electron density distribution calculated for the isolated species are clearly basis- and method-dependent (see, e.g., J. Henn, D. Ilge, D. Leusser, D. Stalke, B. Engels, *J. Phys. Chem. A* **2004**, *108*, 9442). This, however, does not affect the conclusion that there is a sigma-hole near the covalently-bound iodine atom, which was already shown in numerous quantum chemical investigations of halogen-bonded species (see, e.g., references 5-11 in the text).

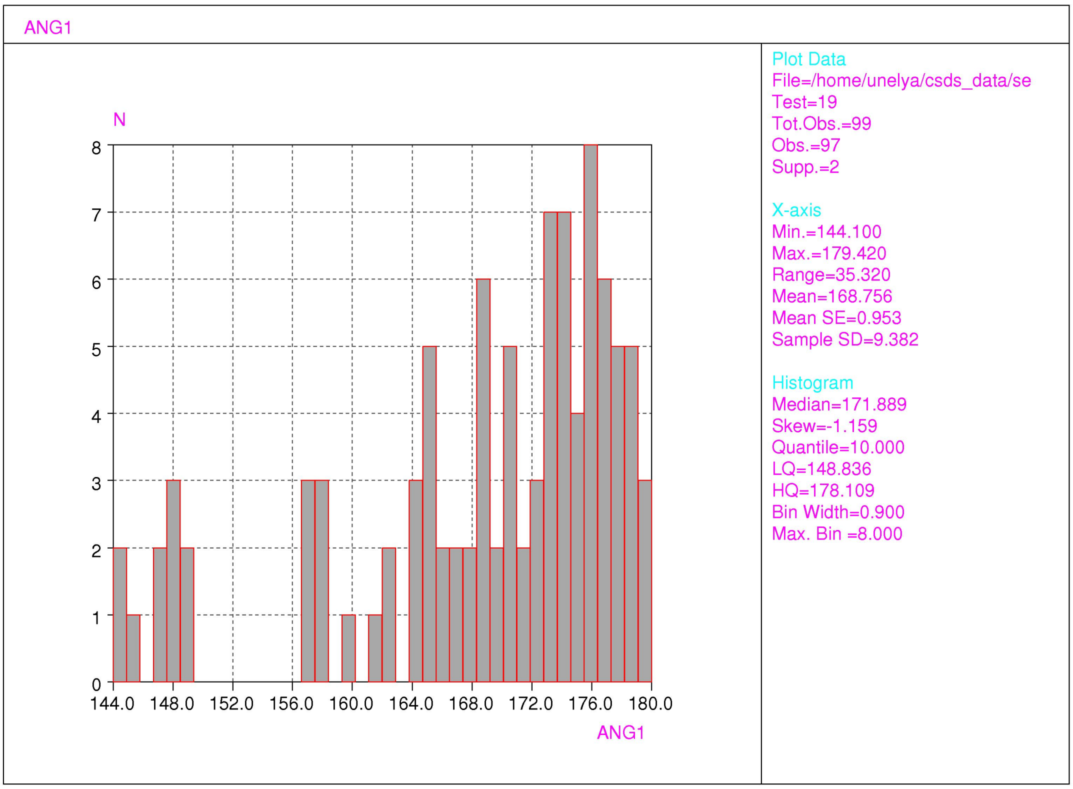
Figures:

Figure S1. Histograms of the CXX angle values in the ordered structures from CSD displaying C-X…X$^-$ halogen bonds:

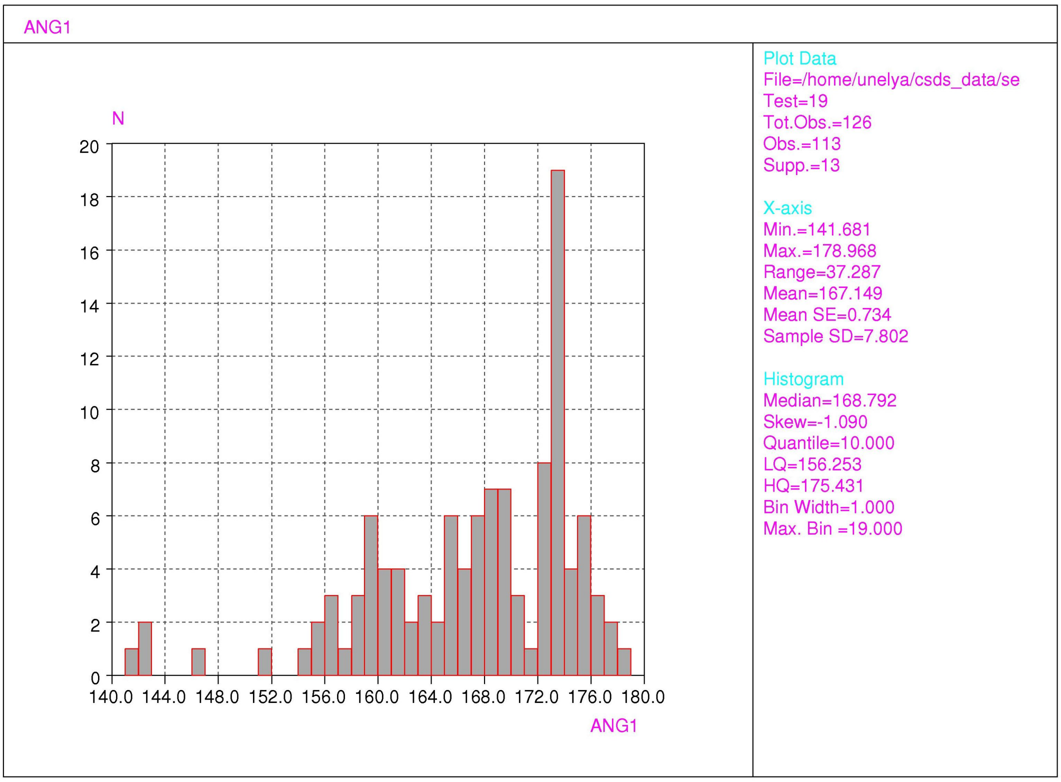
A) X = iodine, ANG1 = CII, °



B) X = bromine, ANG1 = CBrBr, °



C) X = chlorine, ANG1 = CClCl, °



Plot Data
File=/home/unelya/csds_data/se
Test=19
Tot.Obs.=126
Obs.=113
Supp.=13

X-axis
Min.=141.681
Max.=178.968
Range=37.287
Mean=167.149
Mean SE=0.734
Sample SD=7.802

Histogram
Median=168.792
Skew=-1.090
Quantile=10.000
LQ=156.253
HQ=175.431
Bin Width=1.000
Max. Bin =19.000

Figure S2. The 3D-distributions of the $\nabla^2\rho(\mathbf{r})$ (top) and ELF (bottom) functions in the section of the I(1)…I(2)-I(2A) contact in **1**. Isosurface of $\nabla^2\rho(\mathbf{r})$ equal to -2.6 eÅ^{-5} and that of ELF equal to 0.75 are shown by blue wireframe.

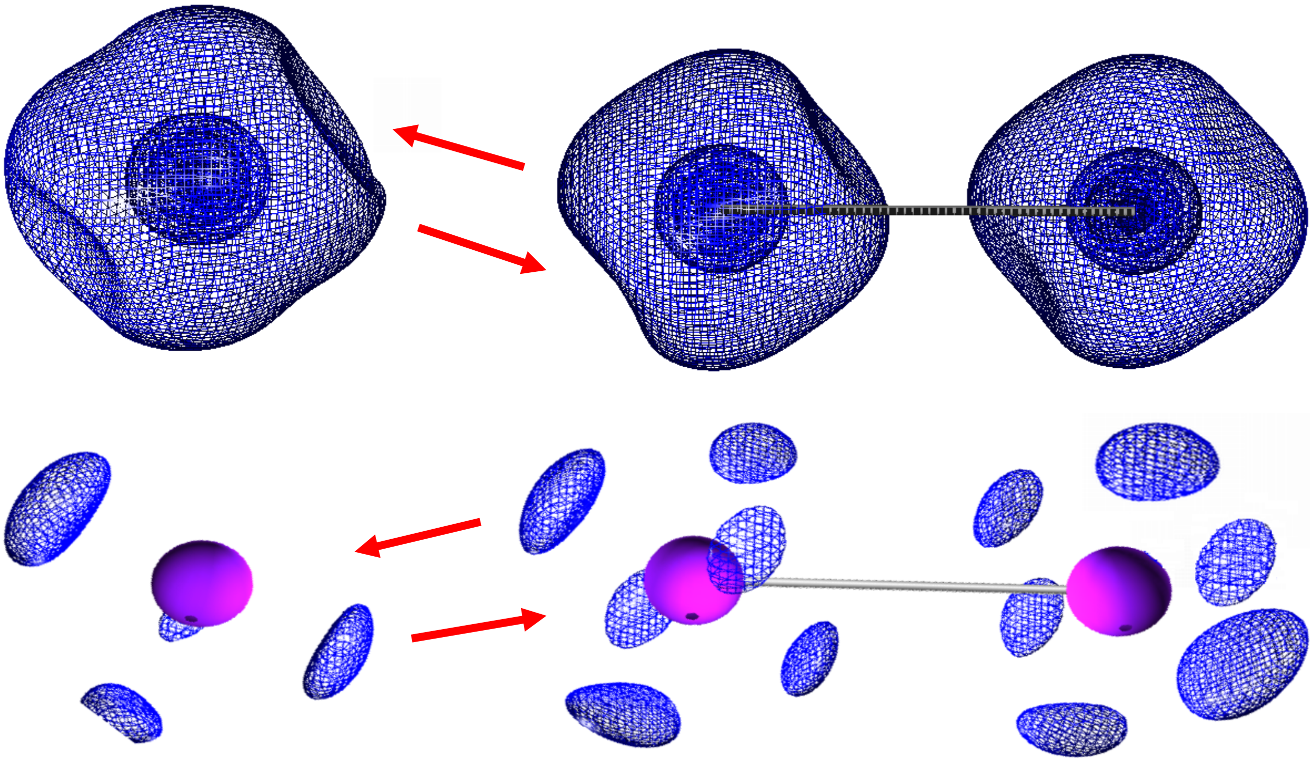
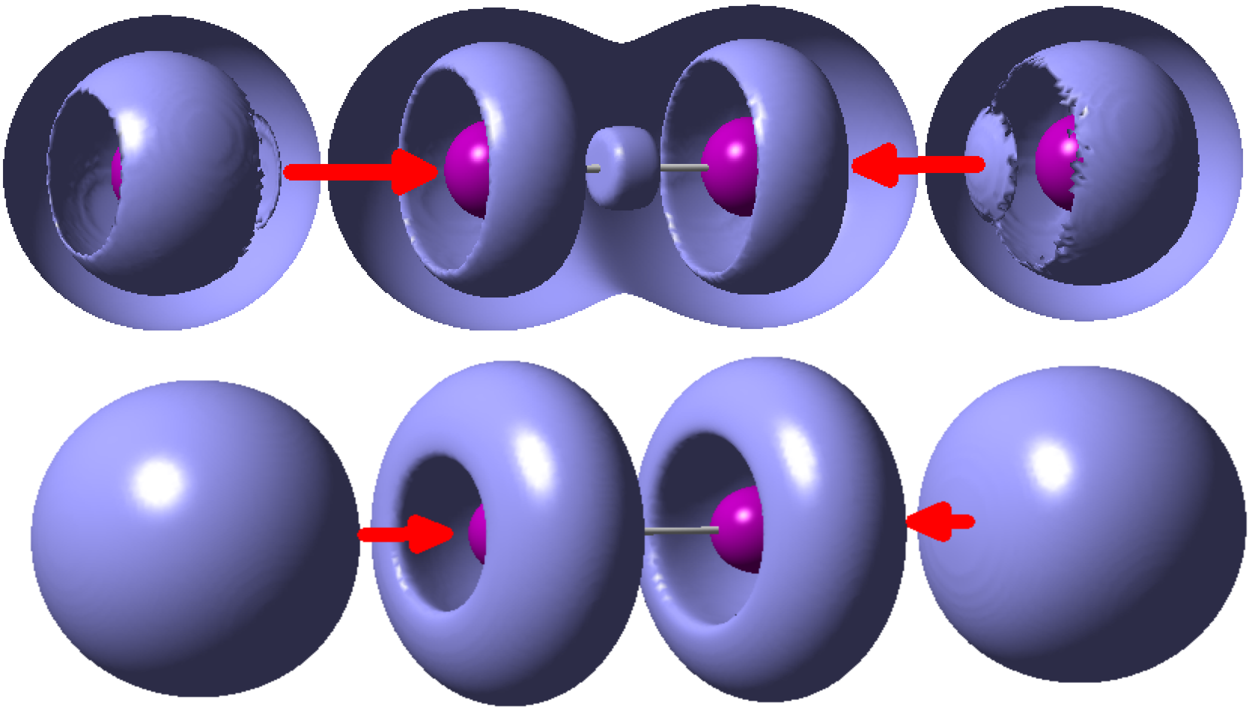


Figure S3. The 3D-distributions of the $\nabla^2\rho(\mathbf{r})$ (top) and ELF (bottom) functions in the isolated I_4^{2-} moiety (at the M05-2X level with Sadlej's standard polarised POL basis set). Isosurface of $\nabla^2\rho(\mathbf{r})$ equal to -0.72 eÅ^{-5} and that of ELF equal to 0.75 are shown by blue.



Tables:

Table S1. The topological parameters of $\rho(\mathbf{r})$ distribution in BCP of the I(2)-I(2A) bond and those of all the intermolecular interactions in **1**.[a)]

Interaction	R, Å[b)]	$\rho(\mathbf{r})$, eÅ^{-3}	$\nabla^2\rho(\mathbf{r})$, eÅ^{-5}	-v(r), a.u.	h_e (r), a.u.	E_{int}, kcal/mole[c)]
I(2)-I(2A)	2.789	0.403	2.02	0.059286	-0.01917	18.6
I(1)…I(2)	3.350	0.160	1.23	0.015425	-0.00135	4.8
I(1)…H(2)	3.434	0.033	0.32	0.001935	0.00693	0.6
I(1)…H(3)	3.240	0.046	0.44	0.002945	0.000799	0.9
I(1)…H(7A’)	3.152	0.050	0.47	0.003264	0.000819	1.0
I(1)…H(2”)	3.605	0.027	0.26	0.001461	0.00602	0.5
I(1)…H(7B”)	3.084	0.057	0.54	0.003875	0.000859	1.2
I(1)…H(7C”’)	3.018	0.062	0.55	0.004247	0.000735	1.3
I(1)…C(6*)	3.629	0.052	0.44	0.003302	0.000721	1.0
I(1)…C(7**)	3.685	0.037	0.39	0.002307	0.000851	0.7
I(2)…H(3)	3.091	0.060	0.54	0.004087	0.000756	1.3
I(2)…H(6’)	3.210	0.050	0.45	0.003187	0.000750	1.0
I(2)…C(3”’)	3.677	0.052	0.46	0.003301	0.000710	1.0
I(2)…H(5*)	3.540	0.039	0.36	0.002331	0.000703	0.7
N(4)…H(5***)	2.738	0.053	0.60	0.003863	0.001189	1.2
C(7)…H(7B””)	3.154	0.038	0.39	0.002380	0.000813	0.7

[a)] The symmetry-generated atoms are obtained from the basic ones by symmetry operations: I(2A) –x+2, –y+1, –z+1; H(7A’) and H(6’) x+1, y-1, z; H(2”) and H(7B”) –x+1, –y+1, –z; H(7C”’) and C(3””) x+1, y, z; C(6X*) and H(5X*) x, y-1, z; C(7**) -x, –y+1, -z; H(5***) -x+1, -y+2, -z+1; H(7B””) –x, –y+2, –z.

b) The distance is given between atoms that are directly bound.

c) The energy is calculated within the Espinosa’s correlation scheme.

Table S2. Atomic charges and volumes in **1**.

	q, e	V_{at}, Å^3
I(1)	–0,92	49,8
I(2)	+0,03	48,8
N(1)	–1,21	11,4
N(4)	–0,90	16,4
C(2)	+0,37	10,2
C(3)	+0,68	9,3
C(5)	+0,44	11,3
C(6)	+0,38	10,6
C(7)	+0,43	9,5
H(2)	+0,05	7,8
H(3)	+0,06	6,2
H(5)	+0,18	7,4
H(6)	+0,09	6,5
H(7A)	+0,10	6,1
H(7B)	+0,06	6,1
H(7C)	+0,14	6,3

Supporting Information for referees

Table S3. Monopole Populations, Radial Parameters and Net Atomic Charges.

Atom	Pval	Kappa	P00	Kappa'	Net charge
I(1)	7.948	1.038	0.000	1.294	-0.94840
I(2)	7.027	0.988	0.000	1.311	-0.02680
N(1)	5.177	0.989	0.000	0.923	-0.17670
N(4)	5.138	0.988	0.000	1.104	-0.13830
C(5)	4.085	1.004	0.000	0.993	-0.08530
C(7)	4.061	1.009	0.000	0.985	-0.06050
C(6)	4.091	1.004	0.000	0.993	-0.09150
C(2)	4.095	1.004	0.000	0.993	-0.09510
C(3)	3.931	1.004	0.000	0.993	+0.06880
H(2)	0.799	1.200	0.000	1.200	+0.20050
H(3)	0.790	1.200	0.000	1.200	+0.20990
H(5)	0.730	1.200	0.000	1.200	+0.27000
H(6)	0.756	1.200	0.000	1.200	+0.24410
H(7A)	0.770	1.200	0.000	1.200	+0.23010
H(7B)	0.829	1.200	0.000	1.200	+0.17060
H(7C)	0.771	1.200	0.000	1.200	+0.22880

Table S4. Dipole Population Parameters.

Atom	D11+	D11-	D10	Kappa'
I(1)	0.081(24)	0.044(24)	0.010(24)	1.294
I(2)	-0.006(22)	0.089(21)	-0.045(23)	1.311
N(1)	0.016(19)	0.037(22)	0.018(22)	0.923
N(4)	0.039(17)	-0.090(17)	-0.031(18)	1.104
C(5)	-0.097(26)	0.095(28)	0.097(28)	0.993
C(7)	0.058(25)	0.102(25)	-0.021(27)	0.985
C(6)	-0.035(24)	-0.170(26)	-0.053(27)	0.993
C(2)	0.028(24)	-0.143(26)	-0.043(27)	0.993
C(3)	-0.093(24)	0.060(27)	0.035(26)	0.993
H(2)	0.000	0.000	-0.001(28)	1.200
H(3)	0.000	0.000	-0.060(30)	1.200

H(5)	0.000	0.000	-0.025(33)	1.200
H(6)	0.000	0.000	-0.037(30)	1.200
H(7A)	0.000	0.000	0.066(31)	1.200
H(7B)	0.000	0.000	0.007(29)	1.200
H(7C)	0.000	0.000	-0.060(28)	1.200

Table S5. Quadrupole Population Parameters.

Atom	Q20	Q21+	Q21-	Q22+	Q22-	Kappa'
I(1)	-0.045(29)	0.066(28)	-0.211(28)	-0.194(28)	0.073(28)	1.294
I(2)	-0.210(30)	-0.089(29)	-0.136(30)	0.026(30)	-0.136(30)	1.311
N(1)	0.105(22)	0.011(19)	-0.006(21)	-0.108(19)	0.008(19)	0.923
N(4)	0.060(20)	0.011(19)	0.012(19)	-0.093(18)	-0.010(18)	1.104
C(5)	0.136(26)	-0.008(24)	-0.012(27)	-0.101(26)	0.056(26)	0.993
C(7)	0.029(24)	-0.075(23)	-0.016(23)	-0.113(23)	-0.113(23)	0.985
C(6)	0.155(25)	-0.098(23)	0.012(25)	-0.144(25)	-0.043(25)	0.993
C(2)	0.162(26)	0.022(23)	0.075(25)	-0.166(24)	0.071(25)	0.993
C(3)	0.128(24)	0.009(23)	-0.057(26)	-0.172(26)	0.032(26)	0.993
H(2)	0.000	0.000	0.000	0.000	0.000	1.200
H(3)	0.000	0.000	0.000	0.000	0.000	1.200
H(5)	0.000	0.000	0.000	0.000	0.000	1.200
H(6)	0.000	0.000	0.000	0.000	0.000	1.200
H(7A)	0.000	0.000	0.000	0.000	0.000	1.200
H(7B)	0.000	0.000	0.000	0.000	0.000	1.200
H(7C)	0.000	0.000	0.000	0.000	0.000	1.200

Table S6. Octupole Population Parameters.

Atom	O30	O31+	O31-	O32+	O32-	O33+	O33-	Kappa'
I(1)	-0.024(24)	-0.019(22)	-0.083(22)	-0.015(22)	-0.012(22)	0.051(22)	-0.051(21)	1.294
I(2)	-0.024(24)	0.025(23)	-0.009(22)	0.042(22)	0.029(22)	0.042(21)	0.015(21)	1.311
N(1)	0.215(28)	0.019(26)	-0.020(30)	0.169(26)	0.004(27)	0.034(25)	0.016(24)	0.923
N(4)	0.087(26)	-0.006(25)	0.019(26)	0.067(24)	0.023(25)	0.007(23)	-0.041(23)	1.104
C(5)	0.234(34)	0.047(31)	0.080(36)	0.147(32)	-0.036(35)	0.041(35)	0.011(33)	0.993

C(7)	0.208(32)	0.057(30)	0.050(29)	-0.011(31)	0.002(31)	0.005(30)	-0.177(30)	0.985
C(6)	0.228(33)	-0.025(29)	-0.032(35)	0.183(31)	-0.051(33)	-0.016(32)	0.003(31)	0.993
C(2)	0.272(32)	-0.005(30)	0.071(35)	0.167(31)	-0.047(33)	0.006(32)	-0.070(31)	0.993
C(3)	0.176(33)	-0.005(30)	0.045(35)	0.164(32)	-0.032(34)	-0.012(34)	0.014(33)	0.993
H(2)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(3)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(5)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(6)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(7A)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(7B)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(7C)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200

Table S7. Hexadecapole Population Parameters.

Atom	H40	H41+	H41-	H42+	H42-	H43+	H43-	H44+	H44-	Kappa'
I(1)	-0.003(29)	0.034(27)	0.198(27)	-0.087(28)	0.088(27)	0.234(28)	0.042(27)	-0.071(26)	-0.096(26)	1.294
I(2)	0.096(30)	0.068(28)	-0.095(28)	-0.116(28)	0.079(29)	-0.083(28)	-0.046(28)	0.201(26)	-0.132(26)	1.311
N(1)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.923
N(4)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.104
C(5)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.993
C(7)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.985
C(6)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.993
C(2)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.993
C(3)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.993
H(2)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(3)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(5)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(6)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(7A)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(7B)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(7C)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200

```
loop_
_atom_local_axes_atom_label
_atom_local_axes_atom0
```

```
_atom_local_axes_ax1
_atom_local_axes_atom1
_atom_local_axes_atom2
_atom_local_axes_ax2
I(1)    H(7A)   Z     I(1)    H(6)    Y
I(2)    N(4)    Z     I(2)    C(5)    Y
N(1)    C(6)    Z     N(1)    C(2)    Y
N(4)    C(3)    Z     N(4)    C(5)    Y
C(5)    H(5)    Z     C(5)    N(4)    Y
C(7)    H(7A)   Z     C(7)    H(7C)   Y
C(6)    H(6)    Z     C(6)    N(1)    Y
C(2)    H(2)    Z     C(2)    N(1)    Y
C(3)    H(3)    Z     C(3)    N(4)    Y
H(2)    C(2)    Z     H(2)    N(1)    Y
H(3)    C(3)    Z     H(3)    N(4)    Y
H(5)    C(5)    Z     H(5)    N(4)    Y
H(6)    C(6)    Z     H(6)    N(1)    Y
H(7A)   C(7)    Z     H(7A)   H(7B)   Y
H(7B)   C(7)    Z     H(7B)   H(7A)   Y
H(7C)   C(7)    Z     H(7C)   H(7B)   Y
-----------------------------------------------------------------


loop_
_atom_site_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_symmetry_multiplicity
_atom_site_U_iso_or_equiv
I(1)   0.598985    0.267664    0.137224    1   2   0.016
I(2)   1.124974   -0.425158    0.604881    1   2   0.017
N(1)   1.094342   -0.171552    0.189526    1   2   0.013
N(4)   1.444006   -0.128313    0.371532    1   2   0.020
C(5)   1.279647   -0.015438    0.366712    1   2   0.019
C(7)   0.912919   -0.193699    0.090168    1   2   0.017
C(6)   1.102673   -0.033749    0.275113    1   2   0.017
C(2)   1.254966   -0.289413    0.192229    1   2   0.016
```

```
C(3)   1.429411    -0.264227    0.284852    1   2   0.019
H(2)   1.251719    -0.38785     0.132815    1   2   0.021
H(3)   1.540031    -0.341004    0.284499    1   2   0.033
H(5)   1.288234     0.08558     0.425795    1   2   0.034
H(6)   1.005191     0.049506    0.264592    1   2   0.028
H(7A)   0.840034    -0.092178    0.097231    1   2   0.025
H(7B)   1.01328     -0.186306    0.025896    1   2   0.031
H(7C)   0.796525    -0.32313     0.083146    1   2   0.024
----------------------------------------------------------------------------------
```

```
loop_
_atom_site_aniso_label
_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_12
_atom_site_aniso_U_13
_atom_site_aniso_U_23
I(1) 0.018034 0.014601 0.013982 0.004281 -0.000668 0.001371
I(2) 0.018338 0.014463 0.019537 0.004849 -0.001223 0.002545
N(1) 0.013552 0.012084 0.013409 0.003598 0.001049 0.001919
N(4) 0.019169 0.021232 0.018414 0.004515 -0.003132 0.00182
C(5) 0.020509 0.019023 0.016348 0.004553 -0.001426 -0.002412
C(7) 0.018025 0.016916 0.015336 0.004938 -0.000541 0.003545
C(6) 0.017338 0.015084 0.017212 0.00573 0.00045 -0.001152
C(2) 0.017531 0.016078 0.015853 0.007668 -0.0001 0.000229
C(3) 0.018492 0.020525 0.020218 0.008741 -0.002052 0.001933
-----------------------------------------------------------------------------------
```

```
Differences of Mean-Squares Displacement Amplitudes (DMSDA)
           (1.E4 A**2) along interatomic vectors (*bonds)
ATOM--> ATOM    / DIST  DMSDA ATOM    / DIST  DMSDA ATOM    / DIST  DMSDA
 N(1)    N(4)      2.7617     12    C(5)     2.3606     1     C(7)     1.4792     8
         C(6)     *1.3429      1    C(2)    *1.3459    -1     C(3)     2.3533     4
 N(4)    C(5)     *1.3359      2    C(6)     2.3939     0     C(2)     2.3967   -13
         C(3)     *1.3377     -5
 C(5)    C(7)      3.7309      6    C(6)    *1.3970     3     C(2)     2.6989    -2
         C(3)      2.2794     -2
 C(7)    C(6)      2.4536     -4    C(2)     2.4351    -7     C(3)     3.7109    -3
```

```
 C(6)   C(2)       2.3319      -2    C(3)      2.6895     -4
 C(2)   C(3)      *1.3911       6
------------------------------------------------------------------------------------------------------------------------



data_FFT
_refine_diff_density_max    0.464
_refine_diff_density_min   -0.471
_refine_diff_density_rms    0.055
```

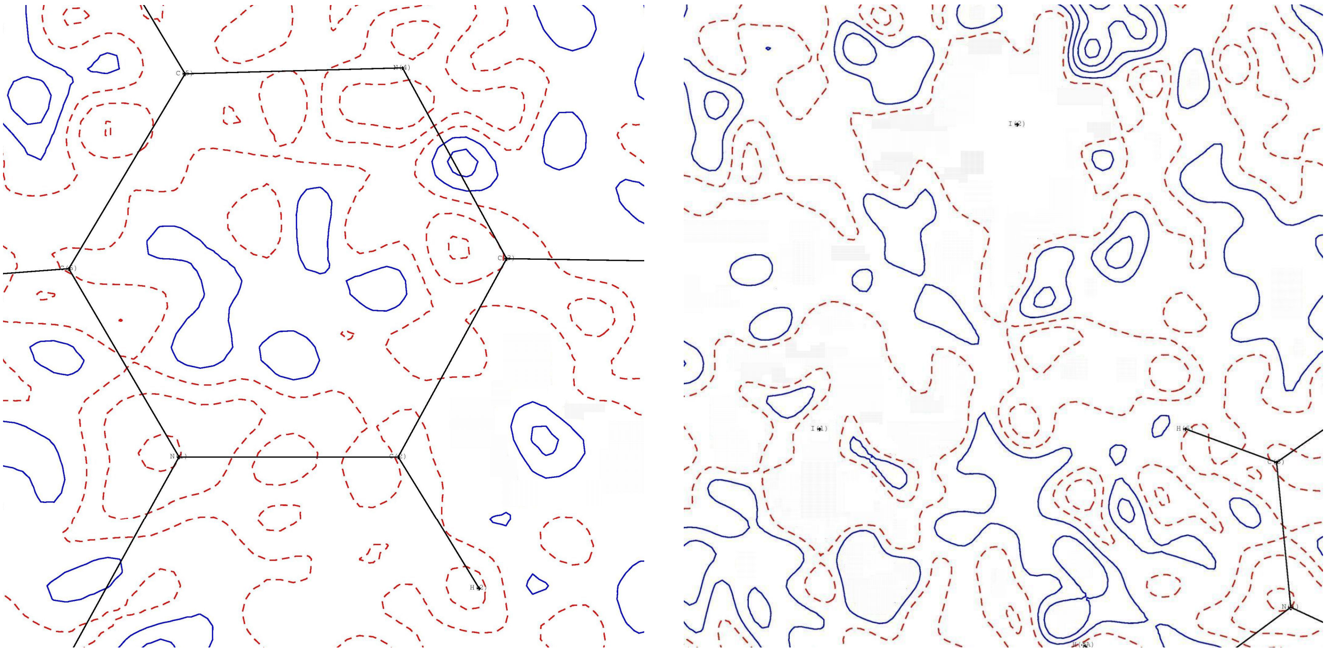


Figure S4. The residual electron density maps in the plane formed by N(1), C(2), and N(4) atoms (left) and by I(1), I(2), and H(6) atoms (right) in **1**. Contours are drawn with 0.1 eÅ^{-3} step, the non-positive ones are dashed.