The refinement strategy

The multipole refinement was carried out within the Hansen-Coppens formalism[1] using the XD program package[1,2]. Before each step of the refinement, C-H and N-H bond distances were normalized to the values obtained from the neutron data (1.08 and 1.05 Å, respectively).[3] The refinement was carried out against F (7551 merged reflections with $I > 3\sigma(I)$) and converged to R = 0.0299 Rw = 0.0300 and GOF = 1.2107. The refinement of atomic coordinates and anisotropic displacement parameters was preformed against high-angle data ($\sin\theta/\lambda > 0.7$), and the refinement of all other parameters was performed against all data. For all non-hydrogen atoms coordinates, anisotropic thermal displacement parameters, monopoles, dipoles, octupoles and kappas were refined. For hydrogen atoms only monopole and D10 dipole term were refined. For N-H hydrogen atoms the H40 hexadecapole term was included in the refinement for better description of strong hydrogen bonds according to XD2006 user manual.

The multipole refinement strategy can be described as follows:

Let's denote 4 steps of least-squares refinement of a *parameter set* as **LS**(*parameter set*)

Let's denote the following cycle

1. **LS**(multipole parameters)
2. **LS**(coordinates and anisotropic thermal displacement parameters)

repeated until R stops decreasing

as **C1**.

Then the refinement strategy employed for DCDA can be written as follows:

C1

LS(monopoles and first-order kappas)

C1

LS(second-order kappas)

C1

LS(overall scale factor)

C1

LS(monopoles and first-order kappas)

C1

After this refinement was performed, repeating of any of its steps did not lead to deviation from obtained parameters and/or decrease of R. The total electron density function

was positive everywhere and the values of residual electron density were in the range from -0.20 to 0.23 $e \cdot Å^{-3}$. The differences of mean-square displacement amplitudes of non-hydrogen atoms along covalent bonds did not exceed $1 \cdot 10^{-3}$ $Å^2$, satisfying the Hirshfield test.[4]

References:

1. N. K. Hansen and P. Coppens, *Acta Cryst. Sect. A*, 1978, **34**, 909-921.
2. Z. Su and P. Coppens, *Acta Cryst. Sect. A*, 1998, **54**, 646-652.
3. A. E. Cohen, B. M. Craven, and W. T. Klooster, *Acta Cryst. Sect. B*, 1997, **53**, 787-794.
4. F. L. Hirshfeld, *Theoretica Chimica Acta*, 1977, **44**, 129-138.
5. E. Espinosa, C. Lecomte, and E. Molins, *Chem. Phys. Lett.*, 1999, **300**, 745-748.
6. E. Espinosa, E. Molins, and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170-173.

Table S1. Summary of bonding contacts with azide anion in DCDA

Atom1	Atom2	Symmetry operation*	d, Å	$\rho(\mathbf{r})$, e·Å^{-3}	$\nabla^2\rho(\mathbf{r})$, e·Å^{-5}	$h_e(r)$, a.u.	v(r), a.u.	E (kcal/mol)**
N(2)	H(2A)	1_555	2.51	0.059	0.94	0.0022	-0.005	-1.7
N(2)	H(1A)	2_656	2.58	0.024	0.34	0.0007	-0.004	-1.2
N(2)	H(5B)	3_557	2.58	0.025	0.37	0.0007	-0.004	-1.3
N(2)	H(4B)	4_555	2.52	0.023	0.35	0.0007	-0.004	-1.2
N(2)	H(2N)	1_555	1.82	0.217	3.07	0.0013	-0.029	-9.2
N(4)	H(2B)	1_565	2.48	0.026	0.38	0.0007	-0.004	-1.4
N(4)	C(3)	3_557	3.2895(6)	0.021	0.28	0.0006	-0.003	-0.9
N(4)	H(4A)	3_557	2.87	0.016	0.24	0.0005	-0.002	-0.8
N(4)	H(1N)	3_657	1.86	0.109	1.43	0.0007	-0.025	-7.9
N(3)	H(6A)	4_565	2.53	0.027	0.40	0.0008	-0.004	-1.3

*Estimated within Espinosa-Lecomte-Molins correlation scheme (see above ref. [5,6])

**Summary of symmetry operations:

1_555: 'x, y, z'

2_555: '-x, y+1/2, -z+1/2'

3_555: '-x, -y, -z'

4_555: 'x, -y-1/2, z-1/2'

Table S2. The integrated values of electron population, volume and lagrangian of electron density for atomic basins of DCDA according to topological analysis of experimental ρ(**r**)

Atom	**ρ(Ω), a.u**	**V(Ω), Å^3**	**L(Ω)*10^4, a.u.**
O(1)	8.951	13.589	0.83
O(2)	8.923	13.845	1.71
N(1)	8.088	12.413	-3.78
N(2)	7.245	16.645	-0.10
N(3)	7.146	12.405	-0.13
N(4)	7.186	17.635	-0.66
C(1)	5.956	9.170	-4.99
C(2)	5.698	8.802	-0.75
C(3)	5.646	8.048	-5.17
C(4)	5.646	8.539	-1.84
C(5)	5.689	8.413	-1.74
C(6)	5.840	8.487	-4.51
H(2N)	0.600	2.759	-0.19
H(1N)	0.579	2.675	-0.88
H(1B)	0.870	5.992	-0.25
H(1A)	0.903	5.521	-0.54
H(2B)	0.881	7.095	-0.28
H(2A)	0.941	6.160	-0.58
H(3B)	0.912	6.056	-0.36
H(3A)	0.882	8.189	-0.35
H(4B)	0.872	6.460	-0.36
H(4A)	0.899	6.937	-0.41
H(5B)	0.889	6.989	0.32
H(5A)	0.926	5.888	-0.42
H(6B)	0.908	8.316	-0.43
H(6A)	0.905	6.162	-0.51
Total	93.983	223.188	-26.37
Calculated	94.000	224.6775	
Difference	-0.017	-1.489	

References:

1. N. K. Hansen and P. Coppens, *Acta Cryst. Sect. A*, 1978, **34**, 909-921.
2. Z. Su and P. Coppens, *Acta Cryst. Sect. A*, 1998, **54**, 646-652.
3. A. E. Cohen, B. M. Craven, and W. T. Klooster, *Acta Cryst. Sect. B*, 1997, **53**, 787-794.
4. F. L. Hirshfeld, *Theoretica Chimica Acta*, 1977, **44**, 129-138.
5. E. Espinosa, C. Lecomte, and E. Molins, *Chem. Phys. Lett.*, 1999, **300**, 745-748.
6. E. Espinosa, E. Molins, and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170-173.

Multipole refinement

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

Atom	Pval	Kappa	P00	Kappa'	Net charge
O(1)	6.312	0.985	0.000	0.976	-0.31210
O(2)	6.276	0.985	0.000	0.976	-0.27610
N(1)	5.194	0.988	0.000	1.005	-0.19400
N(2)	5.407	0.974	0.000	1.017	-0.40750
N(3)	4.979	1.014	0.000	0.964	+0.02070
N(4)	5.335	0.974	0.000	1.017	-0.33470
C(1)	4.122	1.006	0.000	1.003	-0.12220
C(2)	4.006	1.010	0.000	0.977	-0.00580
C(3)	4.000	1.010	0.000	0.977	-0.00050
C(4)	3.957	1.010	0.000	0.977	+0.04290
C(5)	4.038	1.010	0.000	0.977	-0.03810
C(6)	4.028	1.006	0.000	1.003	-0.02760
H(2N)	0.804	1.200	0.000	1.200	+0.19580
H(1N)	0.794	1.200	0.000	1.200	+0.20580
H(1B)	0.883	1.200	0.000	1.200	+0.11720
H(1A)	0.907	1.200	0.000	1.200	+0.09340
H(2B)	0.879	1.200	0.000	1.200	+0.12110
H(2A)	0.927	1.200	0.000	1.200	+0.07310
H(3B)	0.891	1.200	0.000	1.200	+0.10940
H(3A)	0.885	1.200	0.000	1.200	+0.11480
H(4B)	0.873	1.200	0.000	1.200	+0.12710
H(4A)	0.890	1.200	0.000	1.200	+0.10950
H(5B)	0.883	1.200	0.000	1.200	+0.11700

H(5A)	0.909	1.200	0.000	1.200	+0.09080
H(6B)	0.906	1.200	0.000	1.200	+0.09420
H(6A)	0.914	1.200	0.000	1.200	+0.08600

Table S4. Dipole Population Parameters.

Atom	D11+	D11-	D10	Kappa'
O(1)	-0.015(6)	-0.050(6)	-0.040(6)	0.976
O(2)	0.006(6)	-0.074(6)	-0.061(6)	0.976
N(1)	-0.009(7)	0.024(7)	0.025(7)	1.005
N(2)	0.035(7)	0.009(7)	-0.041(7)	1.017
N(3)	0.012(7)	-0.014(7)	-0.033(9)	0.964
N(4)	-0.006(7)	-0.021(7)	-0.070(8)	1.017
C(1)	-0.028(9)	0.056(9)	0.022(9)	1.003
C(2)	-0.059(9)	0.022(10)	0.028(10)	0.977
C(3)	0.026(10)	0.086(10)	-0.008(10)	0.977
C(4)	-0.035(10)	0.053(10)	0.035(10)	0.977
C(5)	0.037(10)	-0.019(10)	0.052(10)	0.977
C(6)	0.019(9)	0.049(10)	-0.012(10)	1.003
H(2N)	0.000	0.000	0.145(11)	1.200
H(1N)	0.000	0.000	0.160(11)	1.200
H(1B)	0.000	0.000	0.138(11)	1.200
H(1A)	0.000	0.000	0.128(11)	1.200
H(2B)	0.000	0.000	0.134(11)	1.200
H(2A)	0.000	0.000	0.131(11)	1.200
H(3B)	0.000	0.000	0.088(11)	1.200
H(3A)	0.000	0.000	0.134(11)	1.200
H(4B)	0.000	0.000	0.137(11)	1.200

H(4A)	0.000	0.000	0.118(11)	1.200
H(5B)	0.000	0.000	0.108(11)	1.200
H(5A)	0.000	0.000	0.107(11)	1.200
H(6B)	0.000	0.000	0.117(12)	1.200
H(6A)	0.000	0.000	0.149(11)	1.200

Table S5. Quadrupole Population Parameters.

Atom	Q20	Q21+	Q21-	Q22+	Q22-	Kappa'
O(1)	-0.053(7)	0.005(7)	0.061(6)	0.073(6)	-0.001(7)	0.976
O(2)	-0.048(7)	-0.021(7)	0.039(7)	0.025(6)	-0.013(6)	0.976
N(1)	0.039(8)	0.014(7)	-0.007(7)	0.013(7)	-0.008(7)	1.005
N(2)	0.040(8)	-0.007(8)	-0.017(8)	-0.026(7)	-0.023(7)	1.017
N(3)	0.274(8)	0.017(8)	-0.023(8)	-0.014(7)	0.026(7)	0.964
N(4)	0.008(8)	0.018(9)	-0.006(8)	0.003(8)	0.014(8)	1.017
C(1)	0.006(10)	0.036(9)	0.002(9)	-0.021(10)	0.076(9)	1.003
C(2)	0.032(10)	0.030(9)	-0.004(9)	-0.030(10)	0.068(10)	0.977
C(3)	0.000(10)	-0.033(9)	0.007(9)	-0.040(10)	-0.028(9)	0.977
C(4)	0.035(10)	0.026(9)	-0.020(9)	-0.029(10)	0.045(9)	0.977
C(5)	0.034(10)	-0.018(9)	0.043(9)	-0.020(10)	-0.030(10)	0.977
C(6)	0.046(10)	-0.025(9)	0.020(9)	-0.021(10)	-0.052(10)	1.003
H(2N)	0.000	0.000	0.000	0.000	0.000	1.200
H(1N)	0.000	0.000	0.000	0.000	0.000	1.200
H(1B)	0.000	0.000	0.000	0.000	0.000	1.200
H(1A)	0.000	0.000	0.000	0.000	0.000	1.200
H(2B)	0.000	0.000	0.000	0.000	0.000	1.200
H(2A)	0.000	0.000	0.000	0.000	0.000	1.200

H(3B)	0.000	0.000	0.000	0.000	0.000	1.200
H(3A)	0.000	0.000	0.000	0.000	0.000	1.200
H(4B)	0.000	0.000	0.000	0.000	0.000	1.200
H(4A)	0.000	0.000	0.000	0.000	0.000	1.200
H(5B)	0.000	0.000	0.000	0.000	0.000	1.200
H(5A)	0.000	0.000	0.000	0.000	0.000	1.200
H(6B)	0.000	0.000	0.000	0.000	0.000	1.200
H(6A)	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'
O(1)	0.077(9)	0.000(9)	-0.018(9)	0.053(9)	-0.008(9)	0.013(8)	-0.020(8)	0.976
O(2)	0.074(9)	-0.002(9)	-0.009(9)	0.051(9)	0.007(9)	-0.001(8)	-0.024(8)	0.976
N(1)	0.154(10)	-0.016(9)	0.001(9)	-0.007(9)	-0.008(9)	-0.014(9)	-0.149(9)	1.005
N(2)	0.068(11)	-0.011(11)	0.023(11)	0.018(10)	0.021(10)	0.003(9)	0.020(9)	1.017
N(3)	-0.038(11)	-0.008(12)	0.023(12)	-0.002(10)	-0.007(10)	-0.009(9)	0.001(9)	0.964
N(4)	0.033(11)	0.018(12)	0.012(11)	0.032(11)	-0.007(11)	-0.022(10)	-0.031(10)	1.017
C(1)	0.185(12)	-0.038(12)	-0.025(11)	-0.028(12)	-0.021(12)	0.010(12)	-0.179(12)	1.003
C(2)	0.216(13)	-0.021(12)	0.007(12)	-0.046(12)	0.027(12)	0.021(12)	-0.195(12)	0.977
C(3)	0.216(13)	-0.023(13)	0.038(12)	-0.058(12)	-0.027(13)	0.011(13)	-0.243(12)	0.977
C(4)	0.221(13)	0.001(13)	0.023(12)	-0.045(12)	0.009(12)	-0.007(13)	-0.219(12)	0.977
C(5)	0.186(13)	0.013(13)	0.012(12)	-0.073(13)	-0.007(13)	-0.043(13)	-0.233(13)	0.977
C(6)	0.185(13)	-0.020(12)	0.019(12)	-0.038(12)	0.030(12)	-0.014(13)	-0.174(12)	1.003
H(2N)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(1N)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(1B)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(1A)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(2B)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(2A)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200

H(3B)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(3A)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(4B)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(4A)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(5B)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(5A)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(6B)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200
H(6A)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.200

Table S7. Hexadecapole Population Parameters.

Atom	H40
H(2N)	0.082(26)
H(1N)	0.010(27)

(all other hexadecapole population parameters were set to zero)

Table S8. Differences of Mean-Squares Displacement Amplitudes (DMSDA)(1.E4 A2) along interatomic vectors (*bonds)**

ATOM-->	ATOM	/	DIST	DMSDA	ATOM	/	DIST	DMSDA	ATOM	/	DIST	DMSDA
O(1)	C(2)	*	1.4215	6	C(3)	*	1.4136	6				
O(2)	C(4)	*	1.4250	10	C(5)	*	1.4151	8				
N(1)	C(1)		1.4969	7								
N(2)	N(3)	*	1.1777	-5								
N(3)	N(4)	*	1.1788	8								
C(1)	C(2)	*	1.5111	6								
C(3)	C(4)	*	1.5134	0								
C(5)	C(6)	*	1.5156	1								

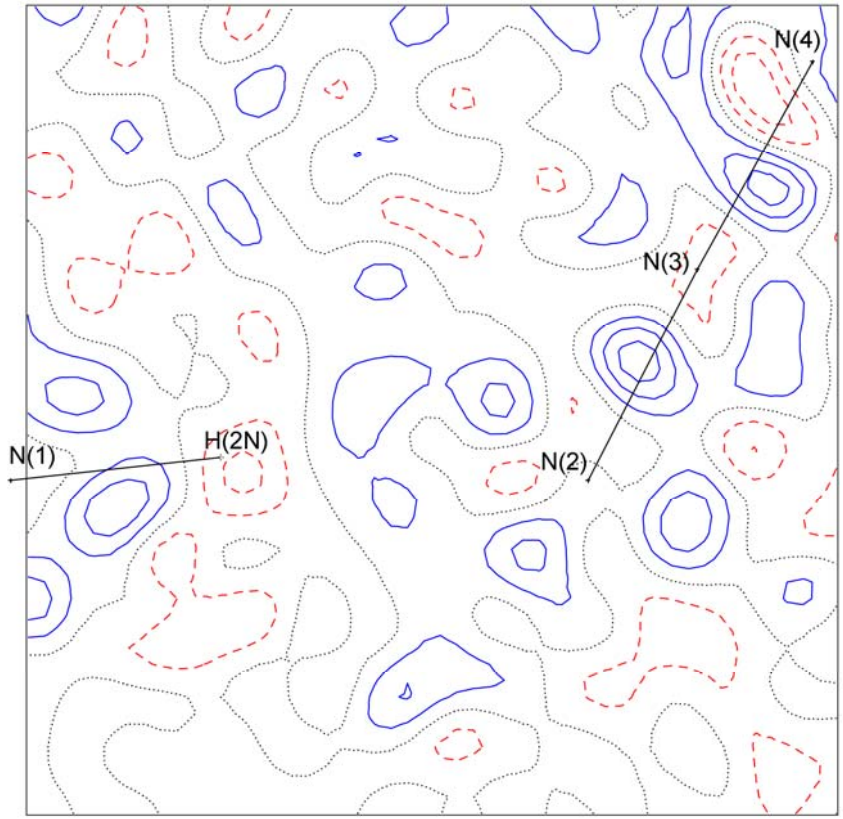

Figure S1. The map of residual electron density in N(1)-N(2)-N(3) plane, step size 0.05 e·Å^{-3}. Positive contours are solid blue, zero ones are dotted grey, negative ones are dashed red.