Supporting Information

The Unique Synthesis and Energetic Properties of Novel Fused Heterocycle: 7-Nitro-4-oxo-4,8-dihydro-[1,2,4]triazolo[5,1-d][1,2,3,5]tetrazine 2-oxide and Its Energetic Salts

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1 X-ray crystallography

Table S1 Crystallographic data and structure refinement parameters for 3·3H$_2$O and 7

Compound	3·3H$_2$O	7
Formula	C$_3$H$_6$N$_7$NaO$_7$	C$_4$H$_6$N$_{10}$O$_4$
Mw	275.14	258.19
Crystal system	orthorhombic	monoclinic
Space group	*Pnma*	*P2$_1$/c*
a Å	17.882(5)	10.426(4)
b Å	6.0919(18)	5.185(2)
c Å	9.281(3)	17.876(7)
*V*Å^3	1011.1(5)	960.7(7)
Z	4	4
*T*K	163(2)	163(2)
*λ*Å	0.71073	0.71073
ρ_{calcd} mg m^{-3}	1.807	1.785
*μ*mm^{-1}	0.21	0.16
F(000)	560	528
Crystal size mm^{-3}	0.54×0.35×0.22	0.64×0.16×0.08
θ range˚	2.8-31.5	2.0-31.5
index ranges	-26 ≤ h ≤ 25	-15 ≤ h ≤ 14
	-8 ≤ k ≤ 7	-7 ≤ k ≤ 7
	-13 ≤ l ≤ 13	-25 ≤ l ≤ 26
reflns collected	9667	10973
Independent reflns (R$_{int}$)	18160.028	3161(0.039)
data/retraints/parameters	1816/0/128	3161/0/187
GOF on F^2	1.001	1.003
RF^2 > 2σ(*F*^{2})	0.038	0.045
wR(F^2)	0.107[a]	0.120[b]

a. $w = 1/\sigma^2(F_o^2) + (0.0659P)^2 + 0.262P$, where $P = (F_o^2 + 2F_c^2)/3$;

b. $w = 1/\sigma^2(F_o^2) + (0.0596P)^2 + 0.219P$, where $P = (F_o^2 + 2F_c^2)/3$;

Crystals of **3**·3H$_2$O and **7** was removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was then selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream. Data for **3**·3H$_2$O and **7** were collected at 163(2) K using a Rigaku Saturn724 CCD (AFC10/Saturn724+ for 7) diffractometer equipped with a graphite-monochromatized MoKα radiation (λ = 0.71073 Å) using omega scans. Data collection and reduction were performed and the unit cell was initially refined by using CrystalClear -SM Expert 2.0 r2 software.[1] The reflection data were also corrected for Lp factors. The structure was solved by direct methods and refined by the least squares method on F^2 using the SHELXTL-

97 system of programs.[2] Structure were solved in the space group *Pnma* for **3**·3H$_2$O, *P*2$_1$/*c* for **7**, by analysis of systematic absences. In this all-light-atom structure the value of the Flack parameter did not allow the direction of polar axis to be determined and Friedel reflections were then merged for the final refinement. Band angles and dihedral angles of the data collection and refinement are given in Table S2, S3.

Table S2. Band angles and dihedral angles for the structure of **3**·3H$_2$O.

O5—Na1—O5^i	180.0	Na1—O5—H3	125.1 (11)
O5—Na1—O6^i	97.42 (4)	Na1^{iii}—O5—H4	109.7 (15)
O5^i—Na1—O6^i	82.58 (4)	Na1—O5—H4	109.7 (15)
O5—Na1—O6	82.58 (4)	H3—O5—H4	105 (3)
O5^i—Na1—O6	97.42 (4)	Na1—O6—Na1^{iii}	79.90 (4)
O6^i—Na1—O6	180.0	Na1—O6—H1	122.3 (11)
O5—Na1—O1^i	82.52 (3)	Na1^{iii}—O6—H1	122.3 (11)
O5^i—Na1—O1^i	97.48 (3)	Na1—O6—H5	113.8 (15)
O6^i—Na1—O1^i	94.91 (3)	Na1^{iii}—O6—H5	113.8 (15)
O6—Na1—O1^i	85.09 (3)	H1—O6—H5	104 (3)
O5—Na1—O1	97.48 (3)	H2—O7—H6	108 (2)
O5^i—Na1—O1	82.52 (3)	N2—N1—C1	119.07 (12)
O6^i—Na1—O1	85.09 (3)	O2—N2—N3	116.32 (12)
O6—Na1—O1	94.91 (3)	O2—N2—N1	115.88 (12)
O1^i—Na1—O1	180.0	N3—N2—N1	127.80 (12)
C1—O1—Na1^{ii}	131.26 (5)	N2—N3—C2	113.26 (11)
C1—O1—Na1	131.26 (5)	C2—N4—C3	100.46 (11)
O4—N7—C3	117.02 (13)	C3—N5—N6	99.36 (11)
O1—C1—N1	123.89 (12)	N5—N6—C2	110.98 (11)
O1—C1—N6	121.20 (12)	N5—N6—C1	126.58 (11)

N1—C1—N6	114.91 (11)	C2—N6—C1	122.44 (11)
N4—C2—N3	127.78 (12)	O3—N7—O4	125.59 (14)
N4—C2—N6	109.71 (12)	O3—N7—C3	117.40 (14)
N3—C2—N6	122.51 (13)	N5—C3—N4	119.49 (13)
Na1^{ii}—O1—Na1	78.47 (4)	N5—C3—N7	119.10 (13)
Na1^{iii}—O5—Na1	80.48 (4)	N4—C3—N7	121.42 (13)
Na1^{iii}—O5—H3	125.1 (11)	C3—N5—N6—C2	0.0
O5—Na1—O1—C1	87.02 (10)	C3—N5—N6—C1	180.0
O5^{i}—Na1—O1—C1	−92.98 (10)	Na1^{ii}—O1—C1—N1	122.71 (7)
O6^{i}—Na1—O1—C1	−176.12 (10)	Na1—O1—C1—N1	−122.71 (7)
O6—Na1—O1—C1	3.88 (10)	Na1^{ii}—O1—C1—N6	−57.29 (7)
O1^{i}—Na1—O1—C1	84.3 (3)	Na1—O1—C1—N6	57.29 (7)
O5—Na1—O1—Na1^{ii}	−137.22 (3)	N2—N1—C1—O1	180.0
O5^{i}—Na1—O1—Na1^{ii}	42.78 (3)	N2—N1—C1—N6	0.0
O6^{i}—Na1—O1—Na1^{ii}	−40.36 (3)	N5—N6—C1—O1	0.0
O6—Na1—O1—Na1^{ii}	139.64 (3)	C2—N6—C1—O1	180.0
O1^{i}—Na1—O1—Na1^{ii}	−139.98 (3)	N5—N6—C1—N1	180.0
O5^{i}—Na1—O5—Na1^{iii}	23 (7)	C2—N6—C1—N1	0.0
O6^{i}—Na1—O5—Na1^{iii}	137.58 (4)	C3—N4—C2—N3	180.0
O6—Na1—O5—Na1^{iii}	−42.43 (4)	C3—N4—C2—N6	0.0
O1^{i}—Na1—O5—Na1^{iii}	43.57 (3)	N2—N3—C2—N4	180.0
O1—Na1—O5—Na1^{iii}	−136.43 (3)	N2—N3—C2—N6	0.0
O5—Na1—O6—Na1^{iii}	42.20 (4)	N5—N6—C2—N4	0.0
O5^{i}—Na1—O6—Na1^{iii}	−137.80 (4)	C1—N6—C2—N4	180.0

O6^i—Na1—O6—Na1^{iii}	108.10 (8)	N5—N6—C2—N3	180.0
O1^i—Na1—O6—Na1^{iii}	−40.87 (3)	C1—N6—C2—N3	0.0
O1—Na1—O6—Na1^{iii}	139.13 (3)	N6—N5—C3—N4	0.0
C1—N1—N2—O2	180.0	N6—N5—C3—N7	180.0
C1—N1—N2—N3	0.0	C2—N4—C3—N5	0.0
O2—N2—N3—C2	180.0	C2—N4—C3—N7	180.0
N1—N2—N3—C2	0.0	O3—N7—C3—N5	180.0
O3—N7—C3—N4	0.0	O4—N7—C3—N5	0.0
O4—N7—C3—N4	180.0		

Table S2. Band angles and dihedral angles for the structure of **7**.

N2—N1—C1	119.22 (11)	C4—N9—H9B	118.6 (13)
O2—N2—N3	116.32 (11)	H9A—N9—H9B	126.0 (18)
O2—N2—N1	115.23 (11)	C4—N10—H10A	120.7 (14)
N3—N2—N1	128.45 (11)	C4—N10—H10B	119.8 (16)
N2—N3—C2	112.93 (11)	H10A—N10—H10B	119 (2)
C2—N4—C3	100.17 (11)	O1—C1—N1	123.58 (12)
C3—N5—N6	99.10 (10)	O1—C1—N6	121.88 (12)
C2—N6—N5	110.59 (10)	N1—C1—N6	114.54 (11)
C2—N6—C1	122.32 (11)	N4—C2—N3	127.15 (12)
N5—N6—C1	127.05 (11)	N4—C2—N6	110.32 (11)
O3—N7—O4	124.86 (12)	N3—C2—N6	122.53 (12)
O3—N7—C3	117.55 (11)	N5—C3—N4	119.81 (12)
O4—N7—C3	117.59 (11)	N5—C3—N7	119.04 (11)
C4—N8—H8A	121.5 (13)	N4—C3—N7	121.15 (12)
C4—N8—H8B	116.6 (13)	N8—C4—N10	120.19 (13)
H8A—N8—H8B	121.2 (18)	N8—C4—N9	120.12 (13)

C4—N9—H9A	114.7 (12)	N10—C4—N9	119.67 (13)
C1—N1—N2—O2	179.46 (12)	N2—N3—C2—N4	−178.60 (12)
C1—N1—N2—N3	−0.4 (2)	N2—N3—C2—N6	0.68 (18)
O2—N2—N3—C2	−179.81 (12)	N5—N6—C2—N4	0.47 (15)
N1—N2—N3—C2	0.08 (19)	C1—N6—C2—N4	178.27 (11)
C3—N5—N6—C2	−0.16 (13)	N5—N6—C2—N3	−178.92 (12)
C3—N5—N6—C1	−177.84 (12)	C1—N6—C2—N3	−1.12 (19)
N2—N1—C1—O1	−179.75 (12)	N6—N5—C3—N4	−0.20 (15)
N2—N1—C1—N6	0.02 (18)	N6—N5—C3—N7	−179.51 (11)
C2—N6—C1—O1	−179.53 (13)	C2—N4—C3—N5	0.47 (16)
N5—N6—C1—O1	−2.1 (2)	C2—N4—C3—N7	179.76 (12)
C2—N6—C1—N1	0.70 (18)	O3—N7—C3—N5	178.83 (12)
N5—N6—C1—N1	178.13 (12)	O4—N7—C3—N5	−0.97 (18)
C3—N4—C2—N3	178.83 (13)	O3—N7—C3—N4	−0.47 (19)
C3—N4—C2—N6	−0.52 (14)	O4—N7—C3—N4	179.73 (13)

2 Theoretical study

The standard enthalpies of formation for neutral compound HBCM and its anion were calculated by the Gaussian-3 (G3)[3] methods using the Gaussian 03 package.[4] All of the optimized structures were predicted to be genuine minima with all real vibrational frequencies.

Two low-lying structures were found for the neutral compounds HBCM, namely N6-H and N8-H (Fig. 1). The global minimum is the N8-H tautomer, which lies below N6 by 7.9 kcal/mol.

In the present study, theoretical enthalpies of formation at 0 K are calculated according to Equation 1,

$$\Delta_f H^o(M,0K) = \sum_{atoms} x\Delta_f H^o(X,0K) - \sum D_0(M) = \sum_{atoms} x\Delta_f H^o(X,0K) - \left(\sum_{atoms} x\varepsilon_0(X) - \varepsilon_0(M) \right)$$

(Equation 1)

In the Equation 1, **M** will be used to stand for the molecule, and **X** to represent each element which makes up **M**, and x will be the number of atoms of **X** in **M**. $\varepsilon_0(X)$ and $\varepsilon_0(M)$ are the total energies of the atom and molecule, respectively. $D_0(M)$ is the

atomization energy of the molecule, which are readily calculated from the total energies of the molecule $\varepsilon_0(X)$ and $\varepsilon_0(M)$. $\Delta_f H^0(X,0K)$ is the heats of formation of the atoms at 0K, which can be taken directly from experimental data[5]. $\Delta_f H^0(M,0K)$ is the heat of formation of the molecule at 0 K.

Theoretical enthalpies of formation at 298 K, $\Delta_f H^0(M,298K)$, are calculated by correction to $\Delta_f H^0(M, 0 K)$ as follows:

$$\Delta_f H^o(M,298K) = \Delta_f H^o(M,0K) + \left(H_M^o(298K) - H_M^o(0K)\right) - \sum_{atoms} x\left(H_X^o(298K) - H_X^o(0K)\right)($$

Equation 2)

In the Equation 2, $(H_X^0(298K) - H_X^0(0K))$ is the enthalpy corrections of the atomic elements, they are taken directly from experimental data.[3] $(H_M^0(298K) - H_M^0(0K))$ is the enthalpy corrections of the molecule.

Table S4 The enthalpies of formation（$\Delta_f H$）and total energies after zero-point energy correction (E_{ZPE}, in hartree) calculated by the Gaussian-3 (G3) method.

	$\Delta_f H(298K)(kJ\ mol^{-1})$	E_{ZPE}(in hartree)
Anion	62.046	-797.969181
N6 (neutral)	426.917	-798.412706
N8 (neutral)	392.512	-798.425346

N8-H Tautomer   N6-H Tautomer
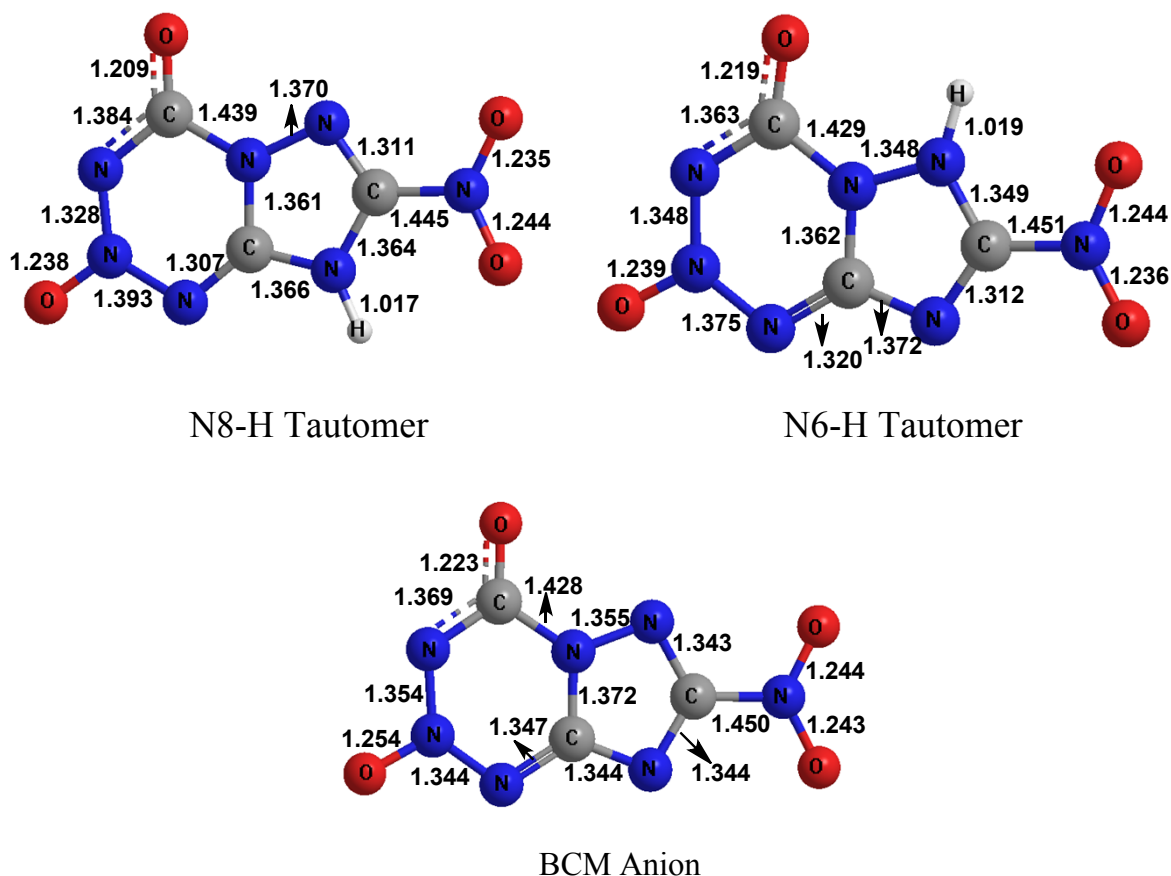
BCM Anion

Figure S1 The optimized geometries for the neutral compound HBCM and its anion by the Gaussian-3 (G3) method. The distances are given in angstrom.

3 References

1 CrystalClear: SM Expert 2.0 r2, An Integrated Program for the Collection and Processing of Area Detector Data, Rigaku Corporation, **2009**.

2 Sheldrick, G. M. SHELXTL-97, Structure Determination Software Suite. Bruker AXS, Madison WI, **2008**.

3 a) Curtiss, L. A.; Raghavachari, K.; Redfern P. C.; Rassolov, V.; Pople J. A. *J. Chem. Phys.* **1998**, 109, 7764–7776; b) Curtiss, L. A.; Redfern, P. C.; Rassolov, V.; Kedziora, G.; Pople, J. A. *J. Chem. Phys.* **2001**, 114, 9287–9295.

4 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr. T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J.

J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision D.02*, Gaussian, Inc., Wallingford CT, **2004**.

5 Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* 14, **1985**, Suppl. No. 1.