3,4-Bis(3-tetrazolylfuroxan-4-yl)furoxan: A Linear C−C Bonded Pentaheterocyclic Energetic Material with High Heat of Formation and Superior Performance

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1 X-ray Crystallography

Table S1. Crystallographic data for BTTFO·H_2O

Empirical formula	$(C_8H_2N_{14}O_6)_2(H_2O)_2$
FW /g mol^{-1}	816.50
Temperature /K	296
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Crystal size(mm)	0.23 ×0.16 × 0.14
a(Å)	5.383(3)
b(Å)	12.923(7)
c(Å)	43.54(2)
V (nm^3)	3.029(3)
Z	4
D_c (g cm^{-3})	1.791
μ (mm^{-1})	0.158
F(000)	1648
θ range for data collection	1.87 to 25.24
Dataset h	-6; 7
Dataset k	-16; 17
Dataset l	-58; 42
Reflections collected	7195
Independent reflections	5073
Data/restraints/parameters	7195 / 0 / 556
Goodness-of-fit on F^2	0.990
R_1, wR_2 [$I>2\sigma(I)$]	0.0432, 0.0899
R_1, wR_2	0.0707, 0.993
Resd. Dens./e $Å^{-3}$	0.244 and -0.185
Absorption correction	multi-scan
CCDC	1987360

3 ^{1}H and ^{13}C NMR spectra

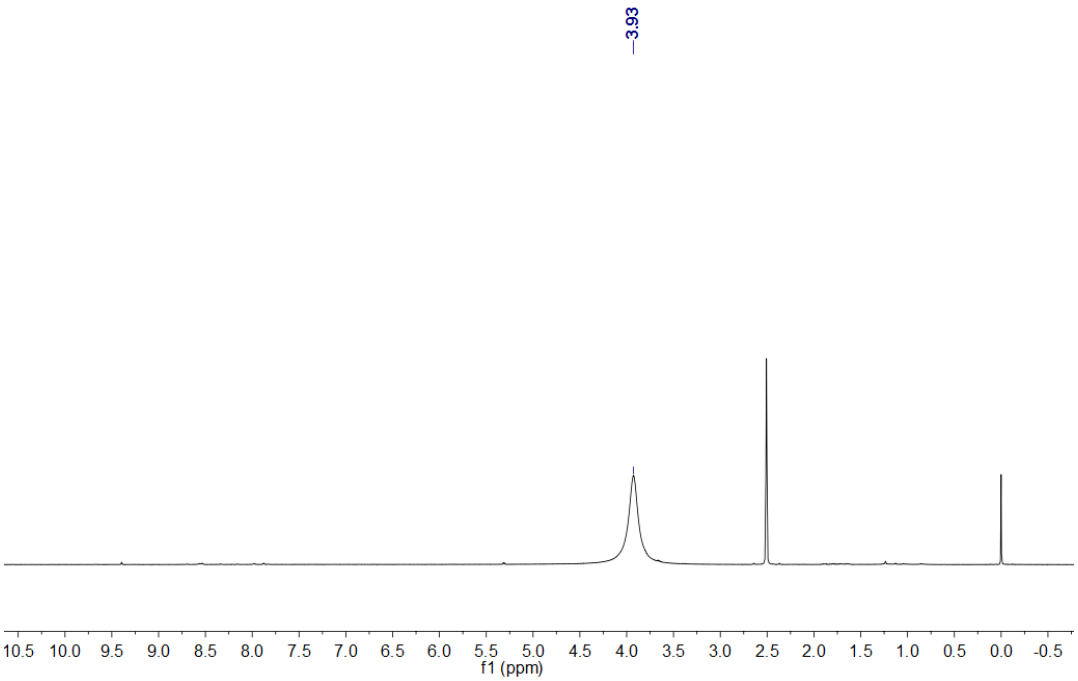


Figure S1. ^{1}H NMR spectrum of BTTFO in [D_6]DMSO

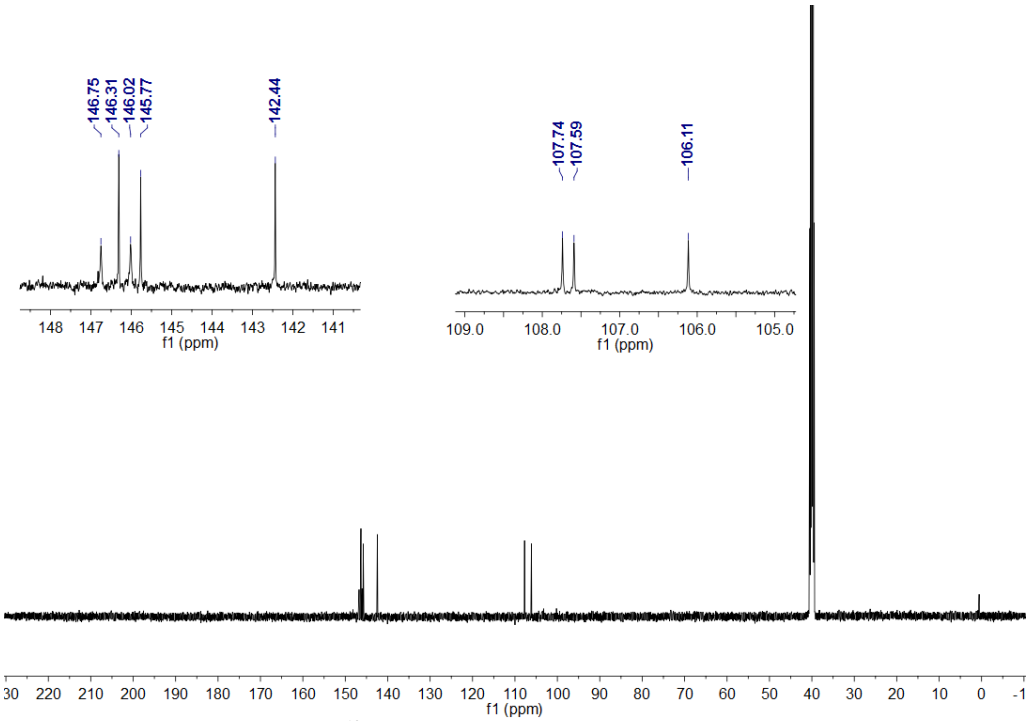


Figure S2. ^{13}C NMR spectrum of BTTFO in [D_6]DMSO

4. DFT Calculations

All quantum chemical calculations were carried out using the Gaussian 09 (Revision A.02) program package[1] and visualized by GaussView 5.08.[2] The geometric optimization and frequency analyses of the structures were carried out using the B3LYP functional with 6–31+G** basis set,[3] and single energy points were calculated at the MP2/6–311++G** level.[4] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

The heat of formation was determined using an isodesmic reaction (Figure S3). The heats of formation for furoxan, and tetrazole were obtained by an atomization approach using CBS-4M method [5, 6]. The heats of formation of CH_4 and CH_3CH_3 were obtained from the NIST WebBook.[7] Some parameters (E, *ZPE*, H, HOF) were listed in Table S2.

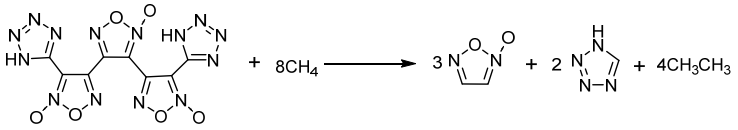


Figure S3. Isodesmic reaction for calculating heat of formation for BTTFO.

Table S2. Calculated total energy, zero-point energy, values of the correction and gas phase heats of formation (HOF).

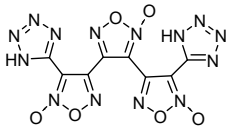
Comp.	ZPE [a] (au)	H_{cor} [b] (au)	E_{B3LYP} [c] (au)	E_{MP2} [d] (au)	H [e] (au)	HOF (kJ·mol^{-1})
CH_4	0.044793	0.048605	-40.5261442	-40.3796224	-40.33280912	-74.9 [f]
CH_3CH_3	0.074599	0.079027	-79.8416413	-79.5716299	-79.49558686	-84.0 [f]
Furoxan	0.049510	0.054821	-337.2249822	-336.4521556	-336.399315	225.3 [g]
Tetrazole	0.046860	0.051289	-258.2680432	-257.6538576	-257.6044436	331.3 [g]
BTTFO	0.163919	0.185740	-1523.4059122	-1519.9902246	-1519.8110416	1380.1

[a] Zero-point correction; [b] Thermal correction to Enthalpy; [c] Total energy (B3LYP); [d] Total energy (MP2); [e] $H=E_{MP2}+H_{cor}-(1-0.96)ZPE$; [f] Data from NIST; [g] Calculated by atomization at the CBS-4M level.

The solid-state enthalpy of formation for a neutral compound can be estimated by subtracting the heat of sublimation from gas phase heat of formation. On basis of the literatures [8, 9], the heat of sublimation can be estimated with Trouton's rule according to eq 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

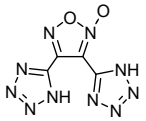
ΔH_{sub}=188/J mol^{-1} K$^{-1}\times T$ (1)

Cartesian Coordinates of Optimized geometries

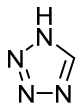


O	2.22392	2.079254	-1.98442
O	-0.254102	-2.78503	-0.387843
O	-1.680164	2.518857	0.984774
O	1.905138	-2.649916	-1.134268
N	1.211268	1.200102	-1.853491
N	3.319445	1.67701	-1.071836
N	0.91353	-2.033336	-0.75669
N	-1.215113	-1.902868	-0.000155
N	-0.801987	1.56531	0.64312
N	-3.054367	1.967532	0.829984
C	2.880754	0.572161	-0.448743

C	1.571082	0.314036	-0.955777
C	0.627721	-0.74089	-0.582488
C	-0.719338	-0.691522	-0.103779
C	-1.477357	0.49392	0.296526
C	-2.892276	0.702124	0.401193
O	4.325531	2.344357	-1.054591
O	-3.986041	2.684458	1.092655
C	3.677713	-0.097611	0.563933
N	3.816034	-1.43848	0.689976
N	4.374415	0.482058	1.529138
N	4.611078	-1.684217	1.748051
H	3.452228	-2.189665	0.10748
N	4.936485	-0.528916	2.236568



N	1.092288	1.988782	0.662795
C	0.397811	0.909137	0.317198
C	1.322028	-0.123783	0.132581
N	2.578055	0.301958	0.294709
O	2.482927	1.650312	0.647995
C	-1.109283	0.912986	0.167983
C	1.021538	-1.584741	-0.202883
N	-1.737432	0.113409	-0.660626
N	-3.068467	0.440154	-0.547515
N	-3.245108	1.433156	0.315761
N	-2.018659	1.735936	0.763385
N	1.065934	-2.552960	0.682216
N	0.730109	-3.696164	-0.007436
N	0.475522	-3.427648	-1.282733
N	0.645763	-2.103197	-1.401697
O	0.777815	3.155229	0.990468
H	-1.891037	2.498993	1.419698
H	0.480196	-1.651561	-2.291900



C	-0.964212	-0.521049	0.000404
N	-0.69151	0.798943	-0.00058
N	0.176358	-1.179068	-0.000212
N	0.652198	0.961633	0.000358
H	-1.303607	1.60306	0.000452
N	1.154914	-0.228387	-0.000042
H	-1.95484	-0.948617	0.000465

N	-0.76129000	0.09509300	-0.00013400

N	1.38213500	-0.71964000	-0.00004400
O	-1.97612900	-0.03902100	0.00007300
O	0.07236400	-1.10666000	0.00003300
C	0.08240800	1.12243100	0.00004000
C	1.39182200	0.59012600	0.00002100
H	2.32894700	1.12875000	0.00025600
H	-0.29012300	2.13318000	-0.00021200

CH_3CH_3

C	0.00000000	0.00000000	0.76604800
H	0.50997400	0.88394300	1.16513600
H	0.51053000	-0.88362200	1.16513600
H	-1.02050400	-0.00032100	1.16513600
C	0.00000000	0.00000000	-0.76604800
H	1.02050400	-0.00032100	-1.16513600
H	-0.51053000	-0.88362200	-1.16513600
H	-0.50997400	0.88394300	-1.16513600

CH_4

C	0.00000000	0.00000000	0.00000000
H	0.63088200	0.63088200	0.63088200
H	-0.63088200	-0.63088200	0.63088200
H	-0.63088200	0.63088200	-0.63088200
H	0.63088200	-0.63088200	-0.63088200

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