Supporting Information

Electron-Induced Decomposition of Solid 1,1-Diamino-2,2-Dinitroethylene (FOX-7) at Cryogenic Temperatures

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Table S1. Experimental infrared band positions of FOX-7 compared to previous values.

Mode	This work (cm^{-1})	Thin Layer[a] (cm^{-1})	Powder[a] (cm^{-1})	Assignment[a]
1	3442	3425		$\nu_{as}(NH_2)$
2	3411	3406	3402	$\nu_{as}(NH_2)$
3	3337	3333	3329	$\nu_{s}(NH_2)$
4	3313	3298	3295	$\nu_{s}(NH_2)$
5	1649	1633	1632	$\nu_{s}(C–NH_2)$
6	1606	1608	1605	$\delta_{s}(NH_2)$
7	1525	1523	1520	$\delta_{s}(NH_2)$
8	1498	1503		$\nu(C–C)$
	1470	1470	1470	$\nu_{17} + \nu_{24}$
	1450			
9	1383	1392	1390	$\nu(C–C)$
10	1352	1352	1350	$\nu_{as}(NO_2)$
11	1311	1312		$\rho(NH_2)$, $\nu_{s}(C–NO_2)$
	1261			$\rho(NH_2)$, $\nu_{as}(C–NO_2)$
12	1228	1221	1212	
13	1178	1169	1166	$\rho(NH_2)$, $\nu_{s}(NO_2)$
14	1145	1141	1140	$\rho(NH_2)$, $\nu_{s}(NO_2)$
15	1068	1063		$\rho(NH_2)$
16	1038	1025	1022	$\rho(NH_2)$
17	862	858	857	$\delta_{s}(NO_2)$
18	771	790	789	$\tau(NH_2)$
19	748	751	749	$\delta_{s}(NO_2)$
20	737	739	738	$\delta(C{-}NO_2)$, $\tau(NH_2)$
21	679	674	673	$\delta(C{-}NO_2)$, $\tau(NH_2)$
22		644		$\omega(NH_2)$
23		635	636	$\tau(NH_2)$
24	623	620	617	$\tau(NH_2)$

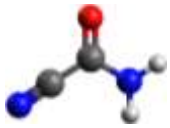
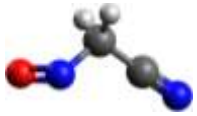
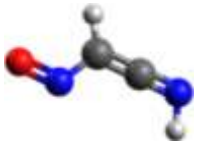
Notes:

[a] Data and assignments from Turner et al. 2022. Thin layer solid sample recorded under UHV conditions and powdered sample spectrum obtained at ambient conditions

Computational Methods

The adiabatic ionization energies (IE) were calculated as the energy difference between the vibrational ground state of the neutral molecules and their corresponding cations. The geometries and unscaled zero-point energies (ZPEs) of the neutral molecules and cations were calculated with dispersion-corrected density functional theory (DFT-D3) M06-2X-D3[1-2] with the triple-zeta basis set def2-TZVPP[3] in NWChem (Version 6.8.1).[4] The energies of optimal geometries were refined at open-shell unrestricted explicitly correlated couple-cluster single and double excitations and a perturbative treatment of triple excitations (UCCSD(T)-F12A/cc-pVTZ-F12) level with molecular orbitals from restricted Hartree–Fock (RHF) calculations[5-9] in Molpro (Version 2021.2),[10-11] which followed the same scheme as the previous FOX-7 studies.[12-13] In addition, to deal with the convergence issue of open-shell cations (i.e., $[NH_2CHO]^+$, $[(NH_2)_2CO]^+$, $[(NH_2C(O)CN)]^+$) in RHF calculations, DFT calculations were performed and used as initial orbitals guess for RHF calculations.

Table S2: Calculated ionization energies with ZPE for $H_2C_2N_2O$ isomers.

Name	Ionization Energy (eV)	Relative Energy (kJ mol^{-1})	Structure[a]
furazan	11.32	225	
cyanoformamide	11.15	0	
hydroxyimino-acetonitrile	10.87–11.10	203–228	
1,3,4-oxadiazole	10.77	89	
nitroso-acetonitrile	10.01–10.03	267–272	
nitroso-ethenimine	8.16	342–349	

Notes:
[a]Calculated coordinates for molecules and any conformers are presented below.

Table S3. Geometries (in Angstroms) underlying the calculated energies for $H_2C_2N_2O$ isomers in Table S2.

Atom	X	Y	Z	Atom	X	Y	Z
		Furazan				Cyanoformamide	
C	-0.69622658	-0.89376894	0.00000171	C	0.12875695	0.47517591	-0.00000001
C	0.72387103	-0.8714897	-0.00000387	N	-1.09438882	1.04415481	-0.00000002
N	-1.11906798	0.32978834	0.00000043	H	-1.15380297	2.04865068	0.00000000
H	-1.38321181	-1.72143206	0.00000007	H	-1.9333551	0.49214343	0.00000001
N	1.10825593	0.36465177	0.00000363	C	0.06607435	-1.00970495	0.00000005
H	1.43613991	-1.67754729	0.00000037	O	1.18009369	1.05405946	0.00000000
O	-0.01723681	1.10347289	-0.00000232	N	0.01972324	-2.15357	-0.00000003
		Hydroxyimino-acetonitrile (1)				Hydroxyimino-acetonitrile (2)	
C	-0.08670633	0.45708339	0.00000224	C	-0.05129826	0.42472094	0.0012764
C	1.34203698	0.33772847	-0.00000072	C	1.373929	0.27200148	-0.00418468
N	-0.77912785	-0.60538839	0.00000158	N	-0.77889216	-0.61528609	-0.00007374
H	-0.53328223	1.44652947	0.00000002	H	-0.45058528	1.43883364	0.0079634
N	2.48763713	0.29925905	-0.00000064	N	2.51850667	0.21308136	-0.00555756
O	-2.11259096	-0.32774001	-0.00000155	O	-2.1117975	-0.42380336	0.01005416
H	-2.5331872	-1.19244626	-0.00000093	H	-2.3165793	0.52499136	0.02496172
		Hydroxyimino-acetonitrile (3)				Hydroxyimino-acetonitrile (4)	
C	0.9094352	-0.1912535	-0.1039424	C	0.96995924	-0.22302126	-0.10817763
C	0.31614256	1.10252993	0.10082638	C	0.39529555	1.08121834	0.08748916
N	0.25220425	-1.27447511	-0.18060013	N	0.2594171	-1.27653079	-0.19642957
H	1.98285213	-0.26066147	-0.20006355	H	2.04070202	-0.33290935	-0.18526261
N	-0.11547142	2.15207023	0.26213862	N	-0.14637057	2.08098706	0.24361353
O	-1.08812419	-1.09150745	-0.04967795	O	-1.07357518	-1.16487713	-0.10321641
H	-1.45574136	-1.9774825	-0.11558226	H	-1.33833808	-0.23701342	0.0282677
		nitroso-acetonitrile (1)				nitroso-acetonitrile (2)	
C	-0.5286916	0.83282234	0.01817874	C	-0.1575047	0.60878321	0.00971365
C	0.91228557	0.62925543	0.00634299	C	1.27514399	0.35263873	0.00025403
N	-1.34534426	-0.43908705	0.00805929	N	-0.93804419	-0.69761161	0.01261249
N	2.04311508	0.45199914	-0.00060069	N	2.40097823	0.14666921	-0.00748305
O	-0.7090711	-1.43112161	-0.03284445	O	-2.10041139	-0.49344438	-0.01858379
H	-0.8572843	1.3974648	-0.85515352	H	-0.46091031	1.17407495	-0.87100038
H	-0.84575148	1.38067632	0.90582856	H	-0.44788065	1.16117477	0.90326183
		nitroso-ethenimine (1)				nitroso-ethenimine (2)	
H	-0.46741836	2.86206263	-0.74627589	H	-0.40108236	2.60911621	-0.42777616
N	-0.24302739	2.31191135	0.07793212	O	-1.14351572	-1.18953419	-0.02926919
C	0.13149513	1.17700048	-0.02448991	C	0.42359521	0.91786795	0.03426328
O	-0.03914522	-2.19687395	0.03118573	N	-0.05527755	1.98364611	0.29343332
H	1.58852343	-0.35478597	-0.04632498	H	1.95589854	-0.50767012	-0.22888189
N	-0.46495798	-1.0713853	0.028209	N	0.03109976	-1.43129285	-0.11491412
C	0.54224499	-0.0836862	-0.01398477	C	0.90434878	-0.309901	-0.11470937
		1,3,4-oxadiazole					
N	-0.66446809	-0.98155704	0.0000032				
N	0.72590868	-0.9370897	-0.00000451				
C	-1.05484938	0.23705743	-0.00000109				
C	1.03751011	0.30402126	0.00000458				
O	-0.03583943	1.11956711	-0.00000165				
H	-2.06045777	0.61833974	-0.00000013				
H	2.01670498	0.74877384	-0.0000004				

Table S4. Calculated infrared band positions (in cm^{-1}) for $H_2C_2N_2O$ isomers presented in Table S2.

Normal Modes	Furazan	Cyano-formamide	Hydroxyimino-acetonitrile (1)	(2)	(3)	(4)	Nitroso-acetonitrile (1)	(2)	Nitroso-ethenimine (1)	(2)	1,3,4-oxadiazole
ν_1	673	204	215	209	193	177	191	145	167	177	660
ν_2	675	294	222	216	327	336	227	207	212	311	694
ν_3	894	312	482	497	438	490	390	389	521	472	884
ν_4	940	501	487	504	484	542	436	519	546	528	915
ν_5	964	576	540	541	647	658	768	541	609	629	967
ν_6	982	633	588	585	756	767	778	894	730	812	972
ν_7	1019	776	962	930	904	881	895	904	875	839	1038
ν_8	1063	784	1059	1078	993	999	1008	1019	897	861	1144
ν_9	1097	1123	1117	1125	1076	1086	1221	1210	1092	974	1173
ν_{10}	1222	1354	1302	1331	1345	1348	1312	1312	1121	1152	1250
ν_{11}	1384	1620	1452	1473	1403	1480	1439	1430	1391	1357	1346
ν_{12}	1503	1857	1743	1710	1749	1681	1787	1773	1652	1657	1592
ν_{13}	1635	2421	2425	2426	2419	2402	2434	2438	2170	2160	1610
ν_{14}	3294	3614	3179	3124	3243	3252	3108	3105	3227	3285	3314
ν_{15}	3315	3738	3872	3709	3874	3664	3146	3154	3547	3560	3324

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