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Bis(furazano)pyridinone *N*,*N'*-dioxide: a new high-density insensitive explosive

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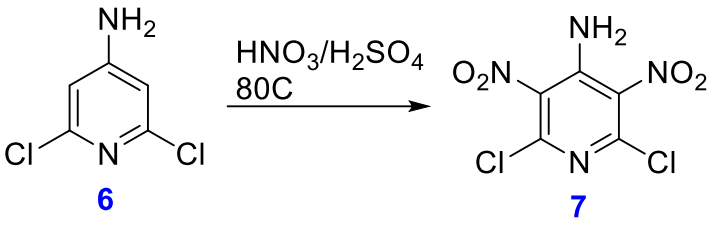
Experimental Section

General: All the reagents were of analytical grade, purchased from commercial sources, and used as received. Infrared spectra were determined in KBr pellets on a Perkin–Elmer Model 577 spectrometer. Mass-spectra were recorded on a Varian MAT-311 A instrument. The ^{1}H, ^{13}C, ^{15}N, and ^{14}N NMR spectra were recorded on a Bruker AM-300 instrument at 300.13, 75.47, 50.7, and 21.68 MHz, respectively. The chemical shift values (δ) are expressed relative to the chemical shift of the [D]solvent or to external standard without correction nitromethane (^{14}N and ^{15}N). Analytical TLC was performed using commercially pre-coated silica gel plates (Kieselgel 60 F_{254}), and visualization was effected with short-wavelength UV-light. Melting points were determined on Gallenkamp melting point apparatus and they are uncorrected. Elemental analyses were obtained by using a CHNS/O Analyzer 2400 (Perkin–Elmer instruments Series II). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out on a Netzsch STA 449 F3 instrument, using dry oxygen-free nitrogen as the dynamic atmosphere (flow rate 100 mL min^{-1}) under 50 bar pressure. About 1.5 mg of a sample was hermetically sealed in aluminum pans. The measurements were conducted from room temperature to 600 °C at a heating rate of 5 °C min^{-1}.

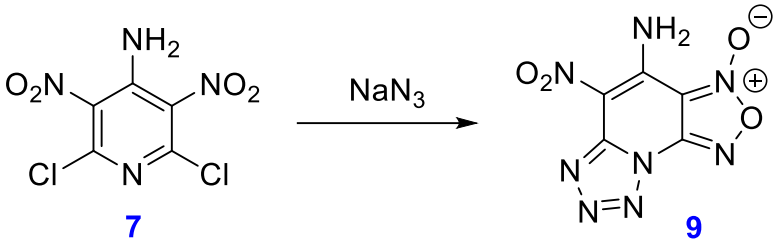
CAUTION! All reported here nitro compounds are potentially explosive and should be handled with appropriate precautions.

4-Amino-2,6-dichloro-3,5-dinitropyridine (**7**)



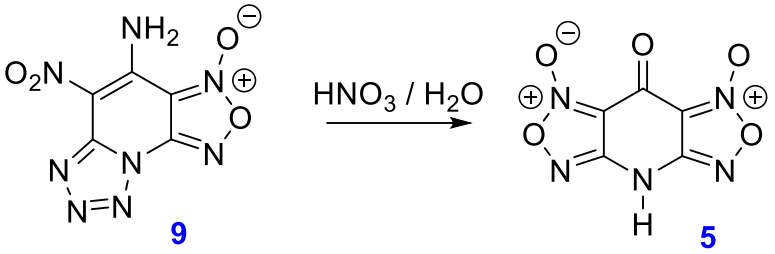
Compound **6** (4.89 g, 0.03 mol) was dissolved in H_2SO_4 (d 1.84 g cm^{-3}, 25 mL), and the mixture was cooled to 10°C in an ice-bath. A mixture of nitric acid (d 1.5 g cm^{-3}, 2.5 mL) and sulfuric acid (d 1.84 g cm^{-3}, 25 mL) was then added dropwise, keeping the flask temperature below 15°C. After the addition was complete, the mixture was heated at 70-75°C, and then the second similar portion of the nitration mixture was added dropwise for 40 min. The mixture was cooled to 20°C and poured onto crushed ice with stirring. The precipitate was collected by filtration, washed with ethanol and diethyl ether, dried at 60-65°C, and recrystallized from $CHCl_3/CCl_4$ to give **7** as a beige crystalline solid, 6.4 g (84%), mp 167-167.5°C (lit.[S1] mp 167°C). R_f = 0.75 (CH_2Cl_2); IR (KBr) ν (cm^{-1}): 3424, 3320, 3227, 1633, 1589, 1526, 1463, 1351, 1226, 1130, 999, 942, 828, 775; ^{1}H NMR (DMSO-d_6) δ 8.27 (s, 2H, NH_2); ^{13}C NMR (DMSO-d_6) δ 143.4, 142.0, 133.0. HRMS (ESI): *m/z* calcd. for $C_5H_3Cl_2N_4O_4$. $[M+H]^+$ 252.9531, 254.9502; found, 252.9526, 254.9497, 256.9467. Anal. Calcd for $C_5H_2Cl_2N_4O_4$ (252.99): C, 23.74; H, 0.80; N, 22.15. Found: C, 23.83; H, 0.82; N, 22.09.

4-Amino-5-nitro-furazano[3,4-*e*]tetrazolo[1,5-*a*]pyridine 3-oxide (**9**)



To a solution of compound **7** (2.53 g, 0.01 mol) in a mixture of acetone (50 mL) and methanol (20 mL), a solution of NaN_3 (1.36 g, 0.021 mol) in water (5 mL) was added dropwise. The resulting mixture was stirred at 40°C for 3 h and half the volume of solvents was removed under reduced pressure. The residue was cooled to 10 °C, and the precipitate was filtered, washed with water, methanol, and dried. The material was then recrystallized from acetic acid to give tricycle **9** (2.14 g, 90%) as yellow-green solid, mp 190°C dec (lit.[S2] mp 150°C dec). IR (KBr) ν (cm^{-1}): 3399, 3294, 1640, 1598, 1496, 1447, 1311, 1253, 1173, 1116, 1075, 1023, 994, 956. ^{1}H NMR (DMSO-d_6) δ 10.18 (s, 1H, NH), 9.48 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 149.4, 144.7, 142.3, 111.7, 105.5. HRMS (ESI): *m/z* calcd. for $C_5H_2N_8NaO_4$ $[M+Na]^+$ 261.0097; found 261.0097. Anal. Calcd for $C_5H_2N_8O_4$ (238.12): C, 25.22; H, 0.85; N, 47.06. Found: C, 25.29; H, 0.87; N, 47.00.

4*H*,8*H*-Bis(furazano)[3,4-*b*:3',4'-*e*]pyridin-8-one 1,7-dioxide (5)



Compound **9** (2.38 g, 0.01 mol) was mixed with 65% HNO_3 (10 mL) and heated to reflux for 15 min. The reaction mixture was poured onto crushed ice with stirring. After 0.5 h, the solid was collected by filtration, washed with water, and dried. The product was recrystallized from toluene to give compound **5** (1.41 g, 67%) as a yellow powder; mp 196–196.5 °C. IR (KBr) ν 3330, 1733, 1708, 1618, 1593, 1324, 1187, 1067, 1007, 913, 826, 804 cm^{-1}. ^1H NMR (DMSO-d_6) δ 13.0 (br.s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 160.6, 153.6, 107.9. HRMS (ESI) *m*/*z* calcd for $C_5H_4N_5NaO_5$ $[M + 3H + Na]^+$ 236.0032, found 236.0026. Anal. Calcd for $C_5HN_5O_5$ (211.09): C, 28.45; H, 0.48; N, 33.18. Found: C, 28.51; H, 0.50; N, 33.12.

Crystal packing analysis of compound 5

Geometry optimization of isolated molecule was carried out at the M052X/6-311G(df,pd) level of theory. The GAUSSIAN program was used for calculation.[S3]

Crystal packing analysis was carried out using two methods. The first one is based on combination of geometrical and energetic approaches. It is based on analysis of close and shortened intermolecular contacts between central molecule and its closest environment in the crystal, and estimation of interaction energy between central molecule and each molecule from its closest environment (pair interaction energies or dimerization energies). Molecule is included in the closest environment if at least one atom…atom contact is shorter than sum of van-der-Waals radii plus 0.5Å.

Interaction energy of a molecular pair (dimer) was estimated according to well-known general formula $E_{int} = E_{AB} - E_A - E_B$, where E_{AB} – energy of a dimer, and E_A, E_B – energies of isolated molecules from which this dimer consists of. In the case of one symmetrically independent molecule in the unit cell, $E_A = E_B$. For E_{int} estimation, the structures of a dimer and isolated molecules were taken from the X-ray data without further optimization. The BSSE correction was taken into account.

The second method for crystal packing analysis is related to recently proposed approach based on Δ_{OED} (overlap of electron density) criterion and densification analysis, and described below.

Table S1. Pair intermolecular interaction energies (kcal mol^{-1}), shortened contacts (Å), and Δ_{OED} criterion (g cm^{-3}) of molecule of compound **5** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry code	Atomic pair		Distance	Energy	Δ_{OED}	Type of interaction
1	1.5-x,-y,-1/2+z	O4	O3	2.990	-0.1	0.008	O…O
2	1.5-x,-y,1/2+z	O3	O4	2.990	-0.1	0.008	O…O
3	1-x,-1/2+y,1/2-z	N4 C4 C5	N1 N1 N1	3.159 3.171 3.105	-2.1	0.026	N…π
4	1-x,1/2+y,1/2-z	N1 N1 N1	N4 C4 C5	3.159 3.171 3.105	-2.1	0.026	N…π
5	-1/2+x,1/2-y,1-z	O1 O2 O2	O5 N5 C4	2.983 2.888 3.116	-3.1	0.026	O…π
6	1/2+x,1/2-y,1-z	O5 N5 C4	O1 O2 O2	2.983 2.888 3.116	-3.1	0.026	O…π
8	-1/2+x,y,1/2-z	O1 N1	N4 N4	3.012 3.146	-3.5	0.022	N…π
9	1/2+x,y,1/2-z	N4 N4	O1 N1	3.012 3.146	-3.5	0.022	N…π
12	1.5-x,-1/2+y,z	O5 O5 O5	C1 C2 C3	3.004 3.059 3.300	-4.0	0.031	O…π
13	1.5-x,1/2+y,z	C1 C2 C3	O5 O5 O5	3.004 3.059 3.300	-4.0	0.031	O…π
10	x,1/2-y,-1/2+z	N3 H3	O3 O3	2.891 2.038	-7.1	0.027	H-bond
11	x,1/2-y,1/2+z	O3 O3	N3 H3	2.891 2.038	-7.1	0.027	H-bond
7	1-x,-y,1-z	O2 O3 O5 C3	O5 C3 O2 O3	2.967 3.064 2.967 3.064	-9.0	0.043	O…O and π…π interactions between antiparallel C=O groups

Acording to Table S1, the most strongest interactions in the crystal are those formed by π…π interactions between carbonyl groups and hydrogen bonds. All the other interactions are of O(N)…π type which are mostly observed in dense crystals and are thought to be responsible for their high density.[S4,S5] At the same time, relatively strong hydrogen bonds are usually not favourable for the formation of the dense crystal packing.[S6-S8] In order to find correlation (or its abcense) between energy of pair interaction and densification of molecules upon such dimer

formation, we analysed crystal packing of compound **5** in terms of Δ_{OED}-based densification approach.

Upon dimer formation, two molecules interact to each other which leads to a decrease of their volume relative to the volume of free molecule. Similarly, density of an isolated molecule (d_{mol}) is lower than that in a dimer (d_{dim}). The values of d_{mol} and d_{dim} can be estimated by analysis of the electron density of optimized isolated molecule in terms of the AIM theory. It is defined as a ratio of molecular mass per molecular volume (the latter is presented as the sum of atomic volumes)

$$d_{mol} = m_{mol}/V_{mol}\ ; \qquad m_{mol} = M_{mol}/N_A\ ; \qquad V_{mol} = \sum_i V_{at}^{(i)} \tag{1}$$

Here, M_{mol} and m_{mol} are molar and molecular masses, respectively, N_A is Avogadro number, V_{mol} and V_{at} are molecular and atomic volumes, respectively. It is convenient to present d_{mol} in g/cm^3 units. Evidently, the volume and density of any molecular fragment can be calculated in a similar way. For estimation of V_{mol}, isodensity surface of 0.0004 e/a_o^3 (a_o – Bohr radius) was utilized for integration procedure. So estimated molecular volume comprises about 99.8% of all electrons (nearly whole molecule), and charge leakage does not exceed 0.002 e/Å^3 that approximately corresponds to numerical error of integration of calculated electron density.

It is evident, that the difference between density of a dimer and molecular density can be served as a measure of how pronounced is the overlap of molecular electron densities upon dimer formation. Therefore, the Δ_{OED} criterion defined as

$$\Delta_{OED} = d_{dim} - d_{mol} \tag{2}$$

would characterize a degree of molecular densification and, therefore, tightness of molecular packing.

From Table S1, one can see that the most and less energetically favourable interactions are characterized by the smallest and the highest value of Δ_{OED}, respectively. However, no correlation is observed for the other molecular pairs (dimers). At the same time, the strongest O…π interaction (entries 9,10) has the highest value of Δ_{OED} among dimers formed by interaction of O(N)…π type. The other dimers formed by O(N)…π contacts (entries 3-8) do not differ significantly in energy (1.4 kcal mol^{-1}) and variation in Δ_{OED} value is also quite small (0.004 g cm^{-3}). The H-bonded dimer (entries 11,12) breaks interrelation between energy and Δ_{OED} to the most extent. For instance, being nearly twice higher in energy in comparison to O…π bonded dimer (entries 9,10), it has lower Δ_{OED} value. This result confirms our recent observation that relatively strong hydrogen bonds connect molecules tightly which decreases flexibility and therefore an ability of molecules to come closer to each other in the crystal structure.

One more interesting observation can be made by a comparison of densities of **5** obtained at room temperature (298 K) and at 100 K. In our recent studies on highly dense polynitro compounds, we discovered that a decrease of crystal density from 100 K to room temperature vary in relatively narrow range of 3-4%. In contrary, decrease of density for compound **5** appears to be smaller (2.4%) which can be related, in our opinion, to higher flexibility of the nitrogroups (in comparison to rigid hetrocycles) which are more susceptible to an increase of temperature.

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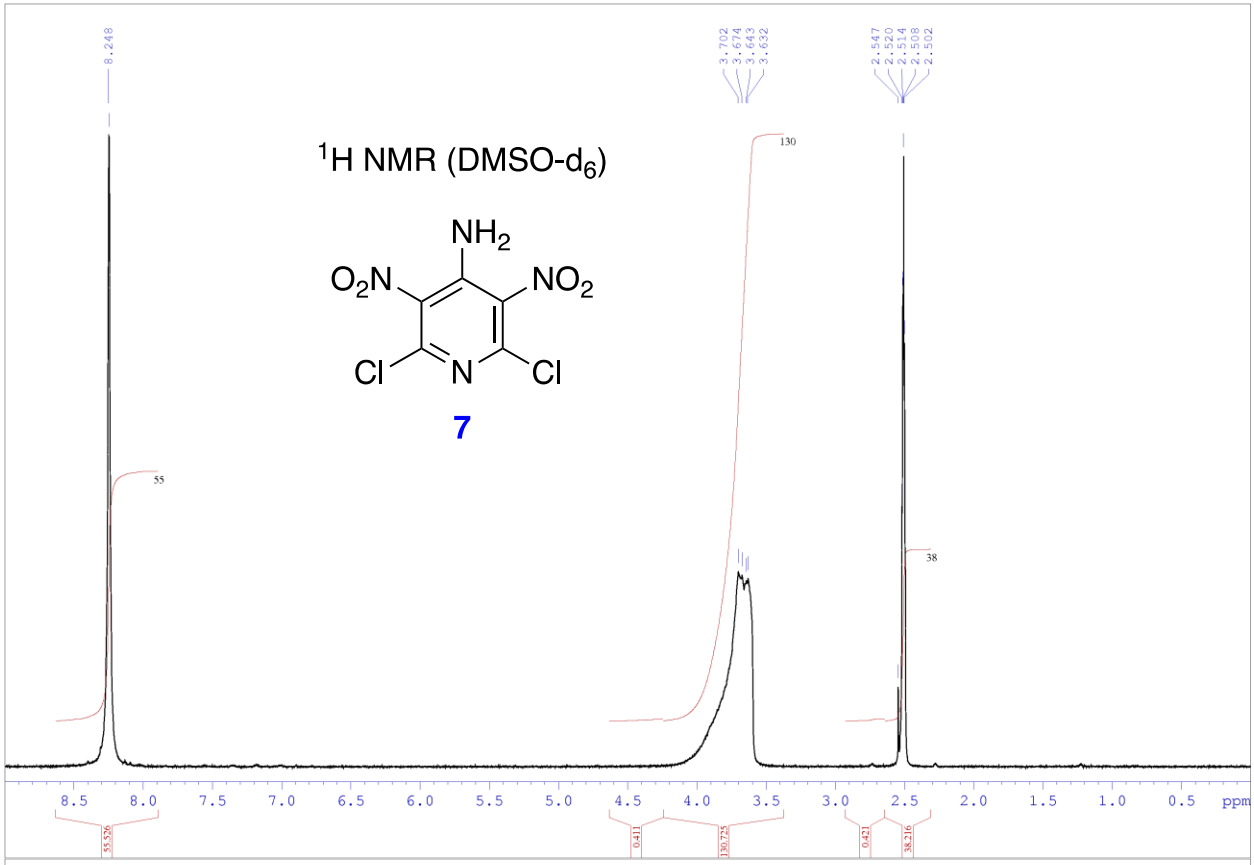
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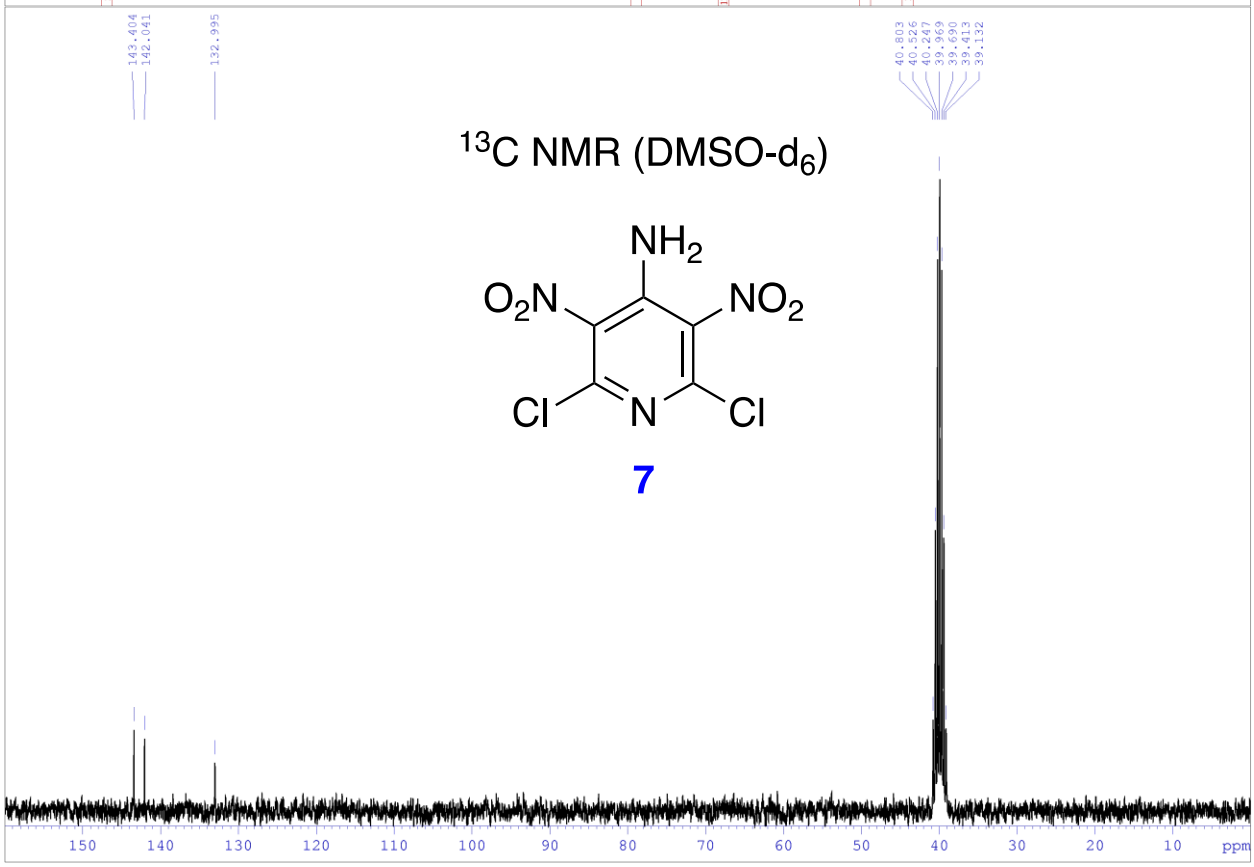
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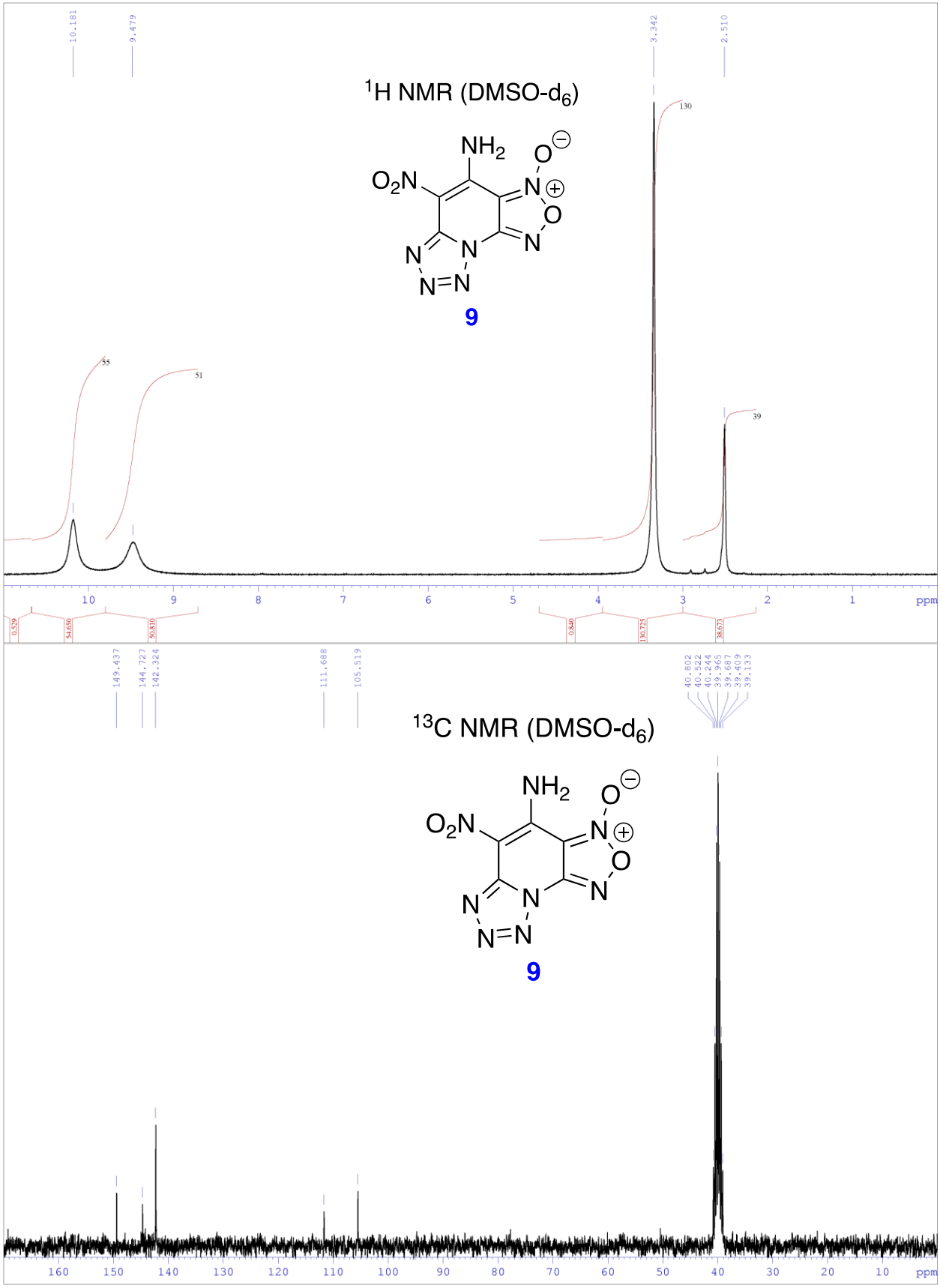
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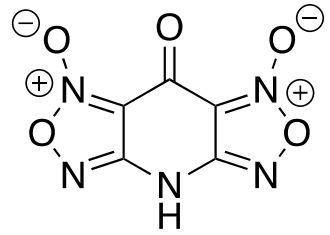

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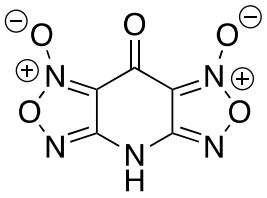

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