Supplementary Material (ESI) for Chemical Communications

Energetic salts of azotetrazolate, iminobis(5-tetrazolate) and 5, 5'-bis(tetrazolate)

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Experimental Section

Caution! *Although we have not experienced any problems in handling these compounds, on the basis of the high positive heats of formation, all materials should be handled with extreme care.*

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively, using DMSO-d_6 as solvent unless otherwise indicated. Chemical shifts were reported relative to TMS. Densities of solid salts were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry. In some cases, compounds with very high nitrogen content do not analyze very well.

Calorimetry Apparatus and Procedure. The heat of combustion was determined using a Parr (series 1425) semimicro oxygen bomb calorimeter. The substances were burned in an oxygen atmosphere at a pressure of 3.04 MPa. The energy equivalent of the calorimeter was determined with a standard reference sample of benzoic acid (SRM 39i, NIST). Since Parr 45C10 alloy fuse wire was used, a correction of 2.3 (IT) calories/cm of wire burned has been applied in all standardization and calorific value determinations.

General procedure: To a mixture of 1-methyl-4-nitro-imidazole (2 mmol) in CH_3CN (25 mL) in Schlenk tube, methyl iodide (3 mmol) was added. The tube was sealed after evacuation at -195 ºC and the mixture was stirred at a 90 ^{o}C. The reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated at reduced pressure. The residue was dissolved in water and an aqueous solution of Ag_2SO_4 (1 mmol) was added. After 30 min, the precipitate (AgI) was filtered off, the solid was washed with water, and barium azotetrazolate (I) (1 mmol) was added. After 1 hour stirring, the precipitate was removed by filtration, the water was removed at reduced pressure, and the residue was recrystallized from an appropriate solvent to afford the desired pure salt.

1-butyl-3-methyl-imidazolium azotetrazolate (1): ^{1}H NMRδ 0.81 (t, 3H, *J* = 7.3 Hz), 1.18 (hex, 2H, *J* = 7.3 Hz), 1.72 (quant, 2H, *J* = 7.3 Hz), 3.92 (s, 3H), 4.21 (t, 2H, *J* = 7.3 Hz), 7.78(s, 1H), 7.84 (s, 1H), 9.60(s, 1H), ^{13}C NMR δ 14.5, 20.0, 32.7, 36.9, 49.8, 123.5, 124.9, 138.6, 174.8. Anal. Calcd for C18H30N14 C, 48.85; H, 6.83; N, 44.31; found C, 47.64, H, 7.10, N, 43.93.

1,3-dimethyl-4-nitro-imidazolium azotetrazolate (2): ^{1}H NMR (CD_3CN)δ 3.95 (s, 3H), 4.11 (s, 3H), 9.02 (s, 1H), 9.49 (s, 1H). ^{13}C NMR δ 38.4, 38.5, 127.0, 141.4, 174.8. Anal. Calcd for $C_{12}H_{16}N_{16}O_4$ C, 32.15; H, 3.60; N, 49.98; found C, 31.81, H, 3.73, N, 49.33.

1,4-dimethyl-triazolium azotetrazolate (3): 1-methyltriazole was quaternized with methyliodide at 50 ^{o}C and followed by metathesis reaction. ^{1}H NMR δ 3.94 (s, 3H), 4.09 (s, 3H), 9.14 (s, 1H), 10.15 (s, 1H). ^{13}C NMR δ 35.3, 39.9, 144.8, 146.7, 174.8. Anal. Calcd for $C_{10}H_{16}N_{16}$ C, 33.33; H, 4.48; N, 62.19; found C, 32.80, H, 4.41, N, 61.53.

1,4-dimethyl-3-azido-triazolium azotetrazolate (4): 1-methyl-3-azide-triazole [1] was quaternized with methyliodide at 50 ^{o}C in CH_3CN and followed by metathesis reaction. ^{1}H NMR δ 3.64 (s, 3H), 4.04 (s, 3H), 9.94 (s, 1H). ^{1}H NMR (D_2O) δ 3.53 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (D_2O) δ 32.8, 39.8, 172.7. Anal. Calcd for $C_{10}H_{14}N_{22}$ C, 27.15; H, 3.19; N, 69.66; found C, 26.82, H, 3.05, N, 68.61.

4-amino-1-methyl- triazolium azotetrazolate (5): 4-amino-1,2,4-triazole was quaternized with methyliodide in CH_3CN at 25 ^{o}C for one week and followed by metathesis reaction. ^{1}H NMR δ 4.07 (s, 6H), 7.30 (s, 2H), 9.25 (s, 2H), 10.32 (s, 2H). ^{13}C NMR δ 40.2, 144.6, 146.4, 174.5. Anal. Calcd for $C_8H_{14}N_{18}$ C, 26.52; H, 3.89; N, 69.59; found C, 26.55, H, 3.81, N, 69.00.

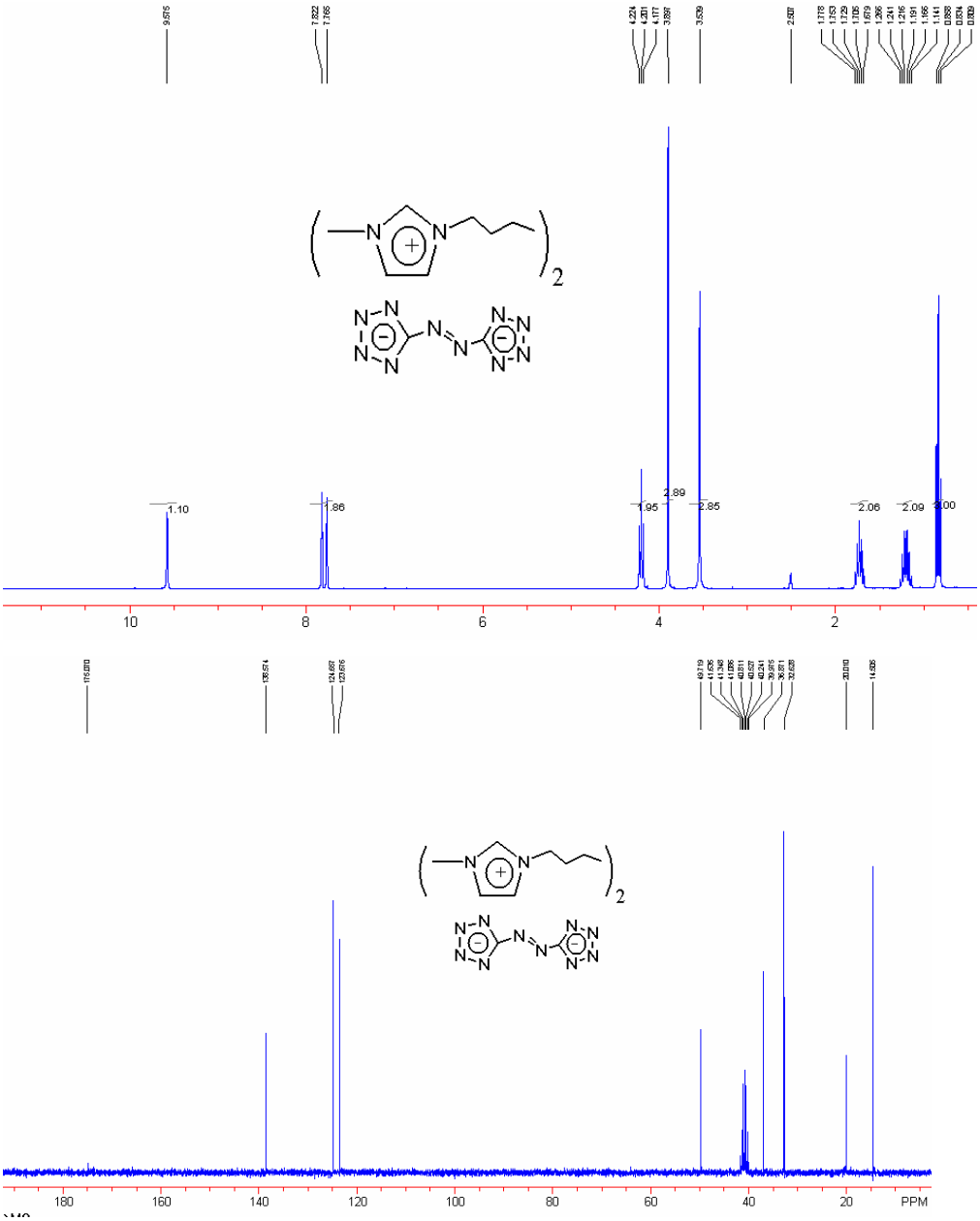
1,4-diaminotriazolium azotetrazolate (6): 4-amino-1,2,4-triazole was quaternized with O-(2,4-dinitrophenyl)-Hydroxylamine in H_2O [2] and followed by metathesis reaction. ^{1}H

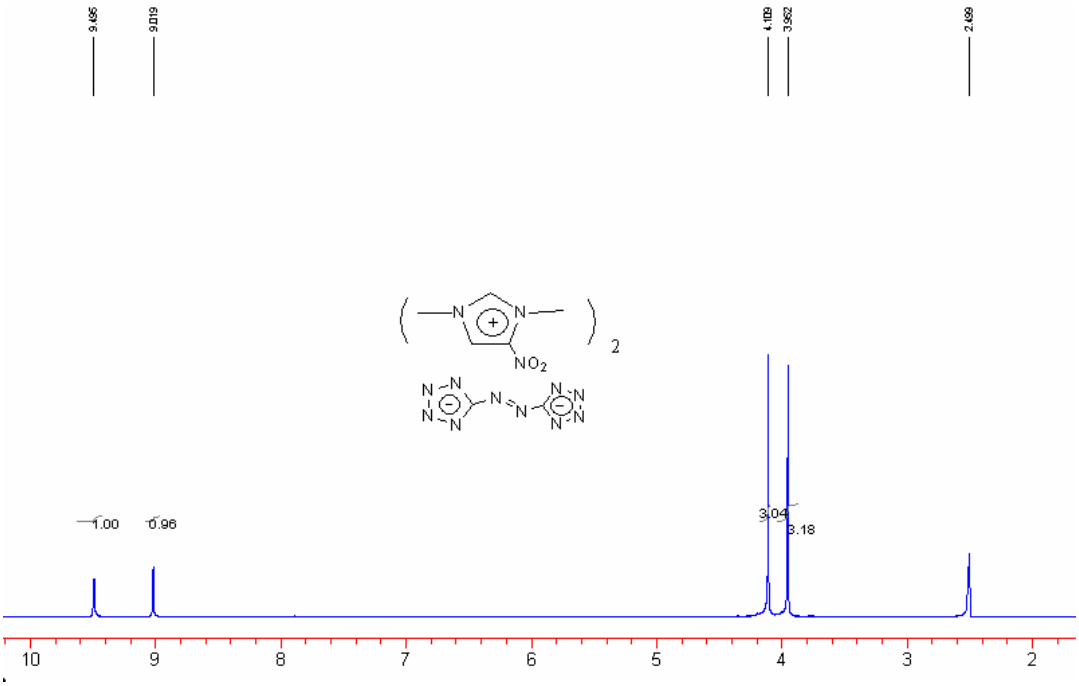
NMR δ 7.09 (s, 2H), 7.48 (s, 2H), 9.09 (s, 1H), 10.29 (s, 1H). ^{13}C NMR δ 142.1, 144.7, 174.5. Anal. Calcd for $C_6H_{12}N_{20}$ C, 19.78; H, 3.32; N, 76.90; found C, 18.93, H, 3.56, N, 75.86.

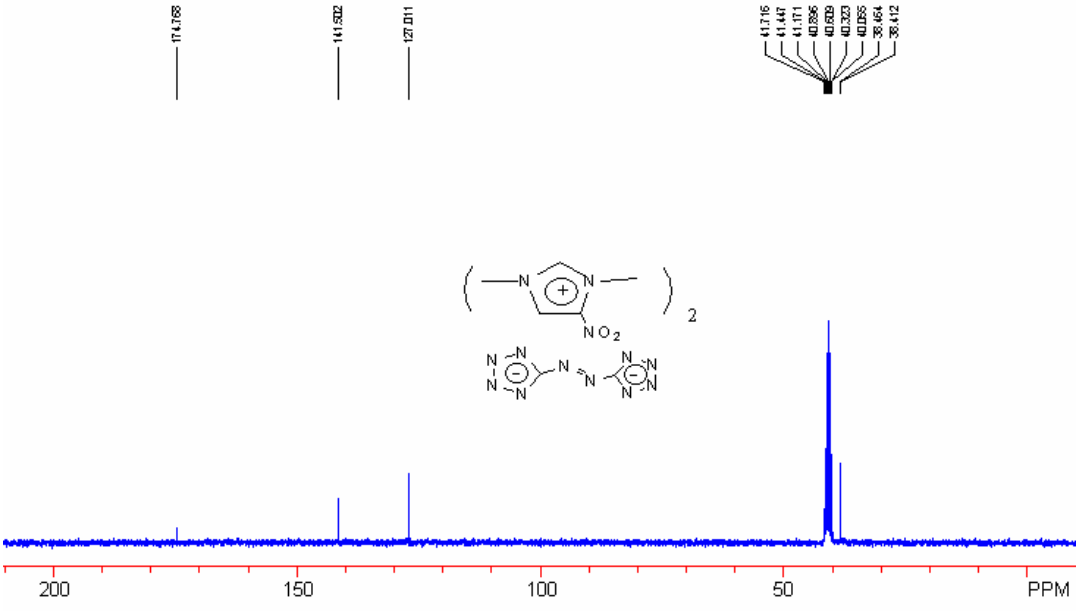
1,2,5-trimethyltetrazolium azotetrazolate (7): 1, 5-dimethyltetrazole [3] was quaternized with methyliodide at 90 ^{o}C in CH_3CN and followed by metathesis reaction. ^{1}H NMR δ 2.89 (s, 3H), 4.29 (s, 6H) ^{13}C NMR δ9.7, 37.6, 154.1, 174.6. Anal. Calcd for $C_{10}H_{18}N_{18}$. H_2O C, 29.41; H, 4.94; N, 61.74; found C, 27.07, H, 4.49, N, 61.95.

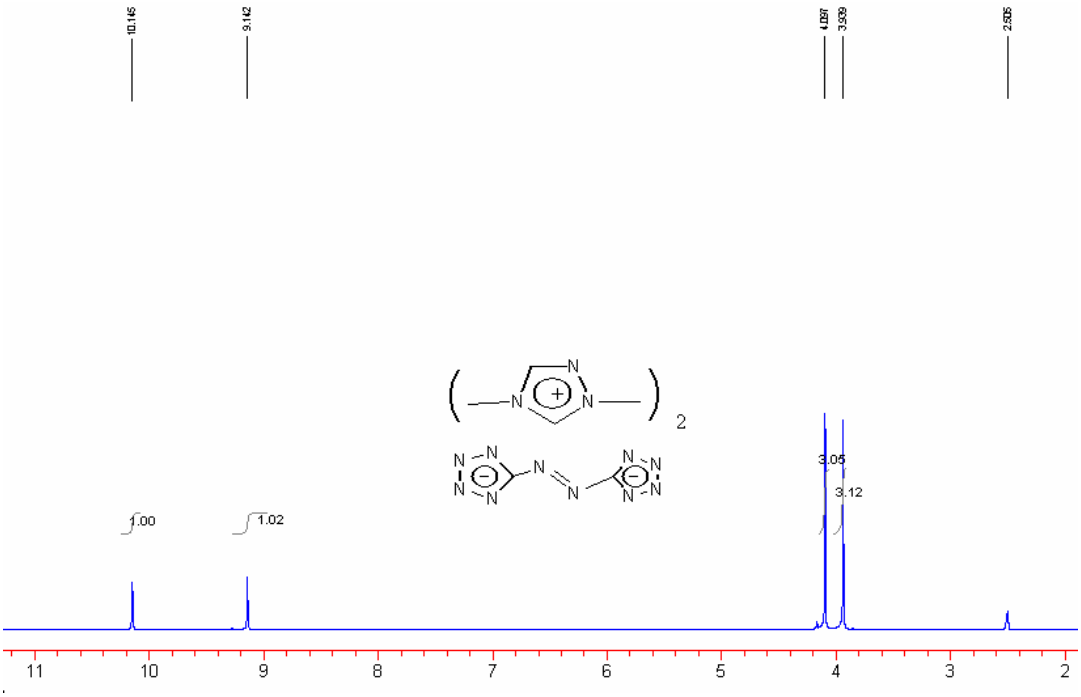
4-amino-1-hydro- triazolium imino-bis(5-tetrazolate) (8) : 4-amino-1,2,4-triazole was quaternized with N-1H-tetrazol-5-yl-1H-tetrazol-5-amine [4] in methanol. ^{1}H NMR δ 8.47 (s, 2H) ^{13}C NMR δppm, 145.5, 154.8. Anal. Calcd for $C_6H_{11}N_{17}$ C, 22.43; H, 3.45; N, 74.12 found C, 21.52, H, 3.22, N, 74.76.

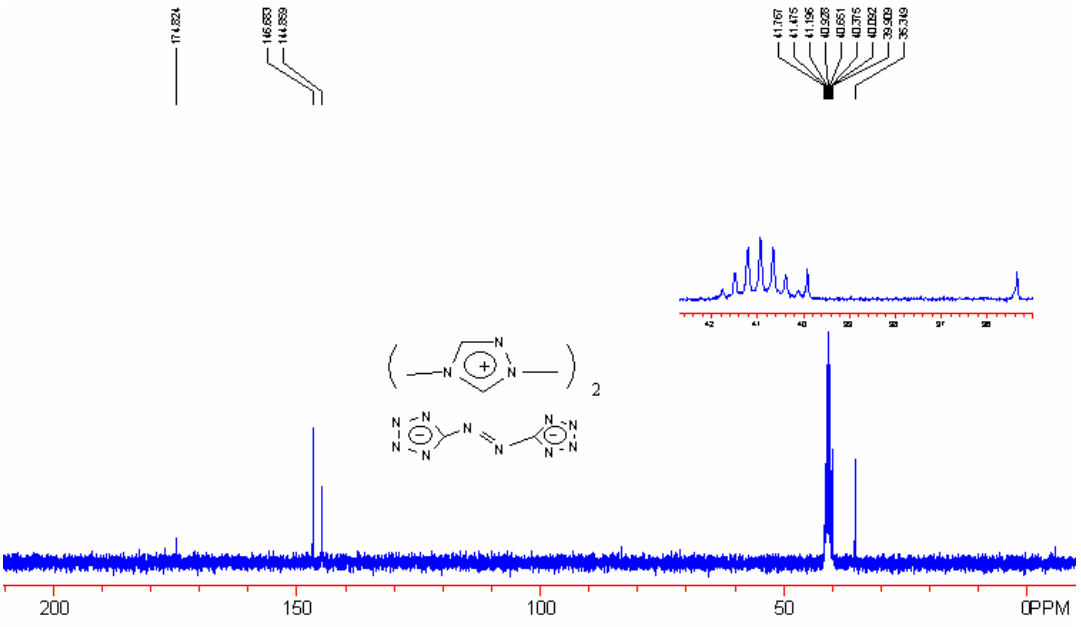
4-amino-1-hydro- triazolium 5,5'-bistetrazolate (9): 4-amino-1,2,4-triazole was quaternized with 5,5'-Bi-1H-tetrazole [5] in methanol. ^{1}H NMR δ 8.77 (s, 2H), 10.10 (broad s, 2H). ^{13}C NMR δ 145.5, 149.9. Anal. Calcd for $C_6H_{10}N_{16}$ C, 23.53; H, 3.29; N, 73.18 found C, 23.71, H, 3.30, N, 72.74.

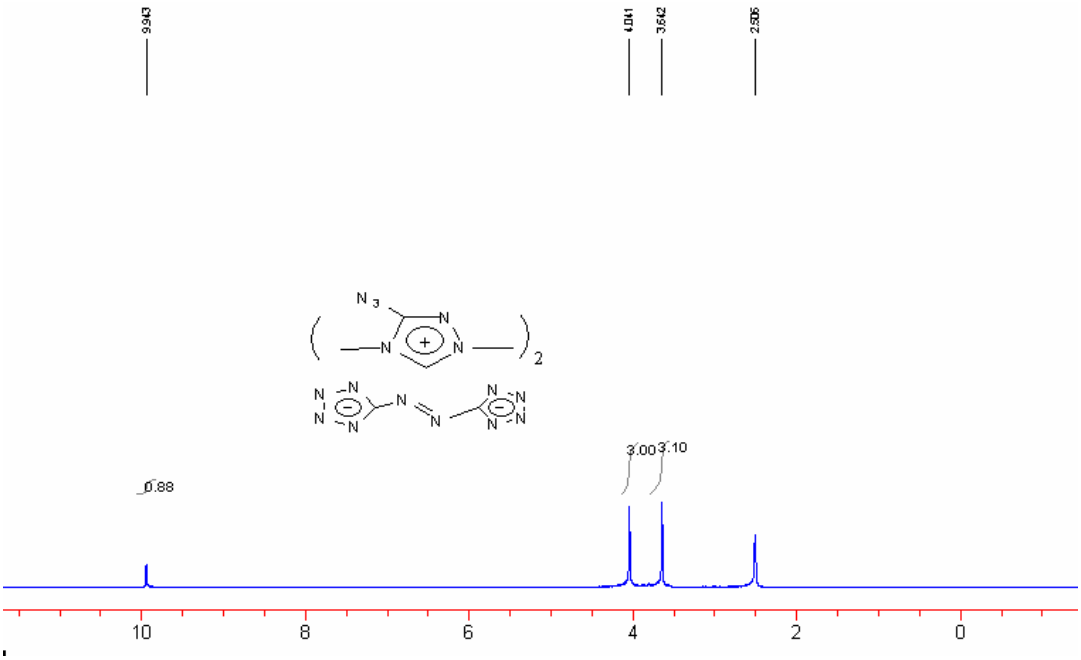


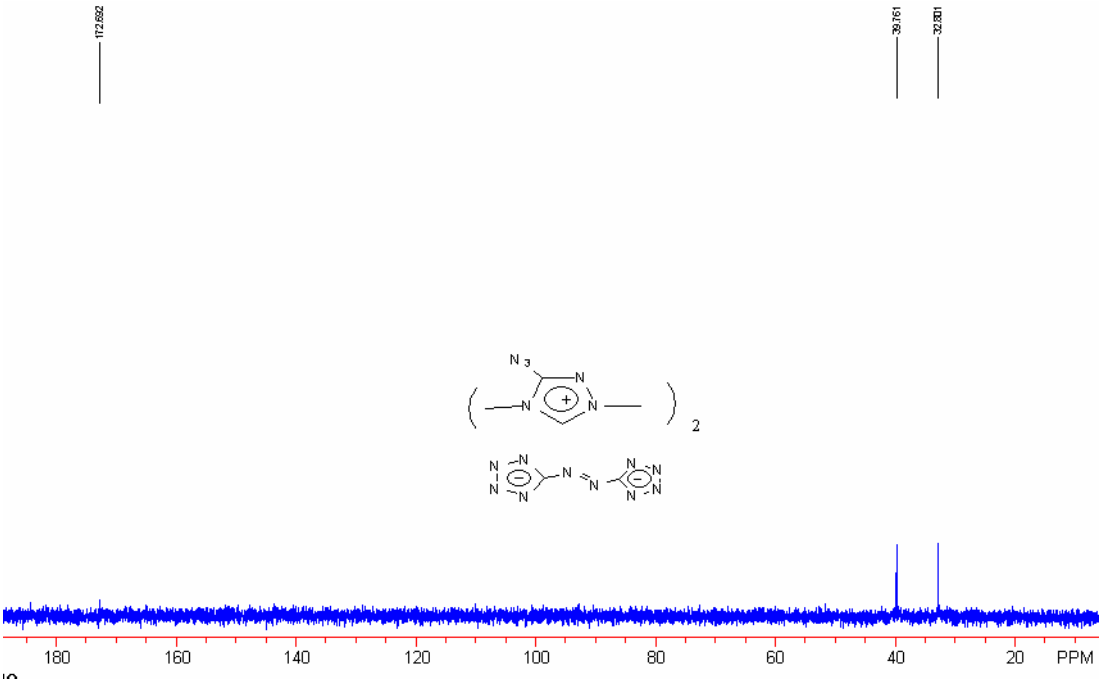


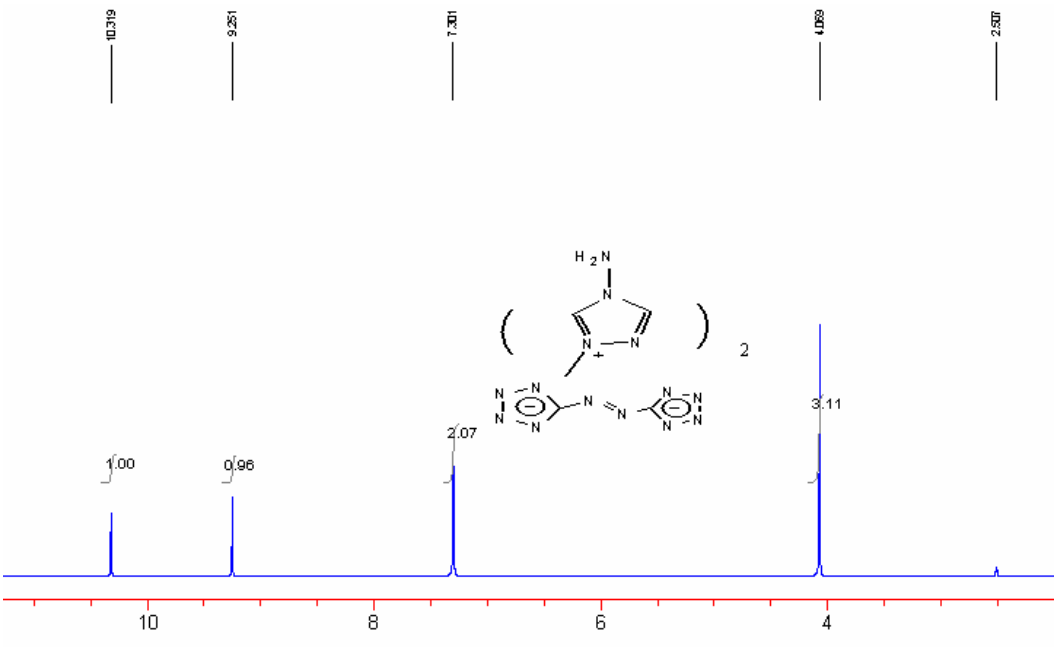


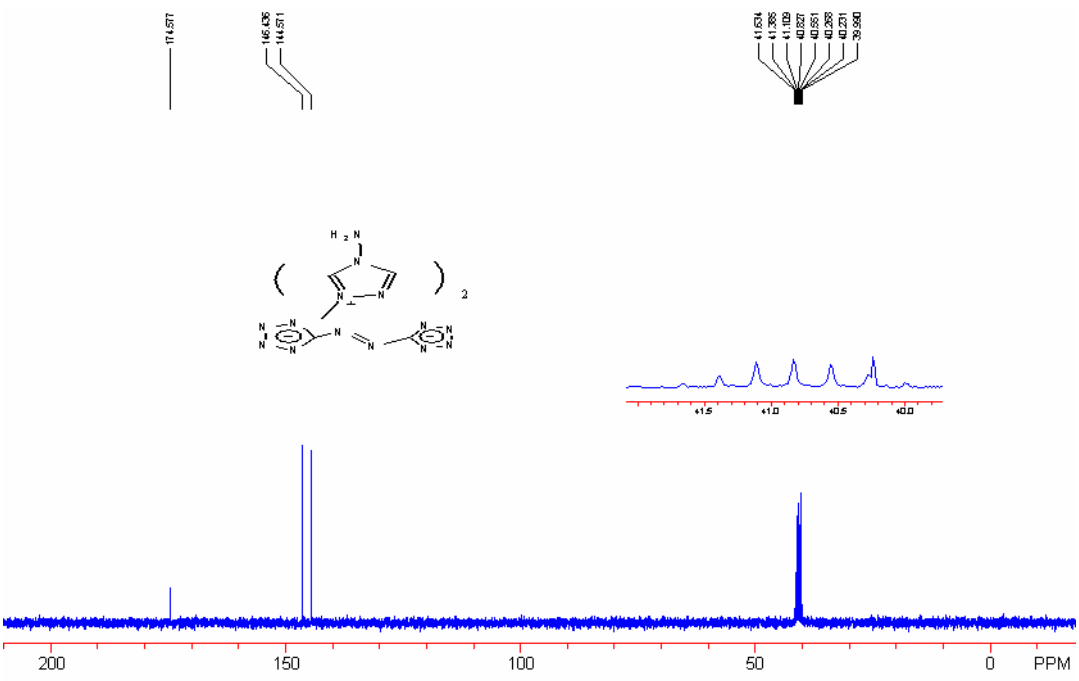


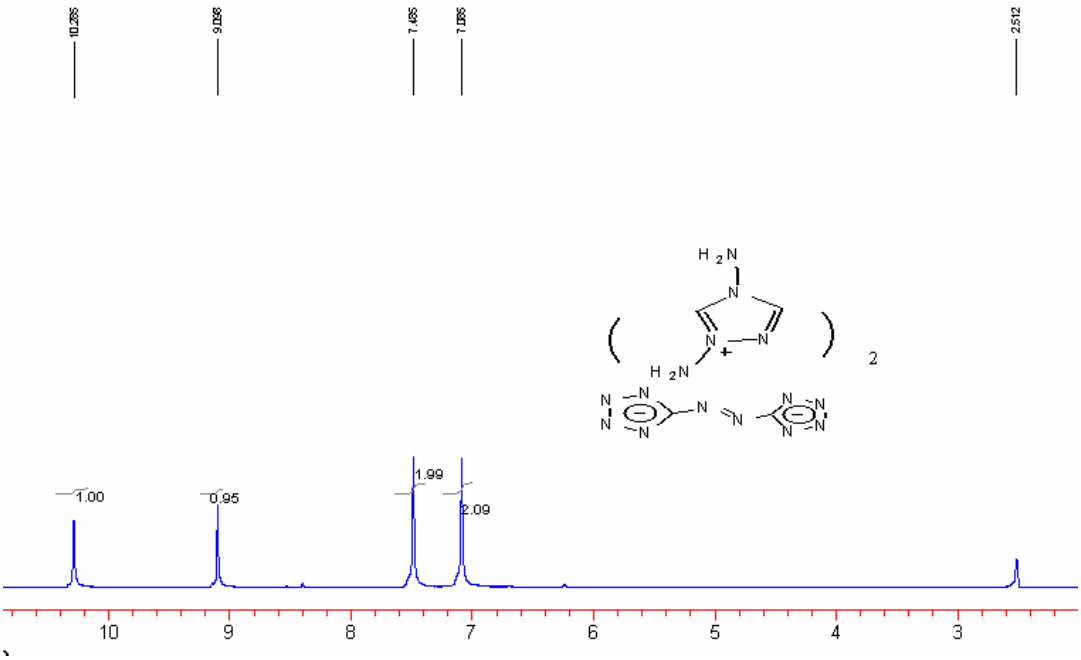


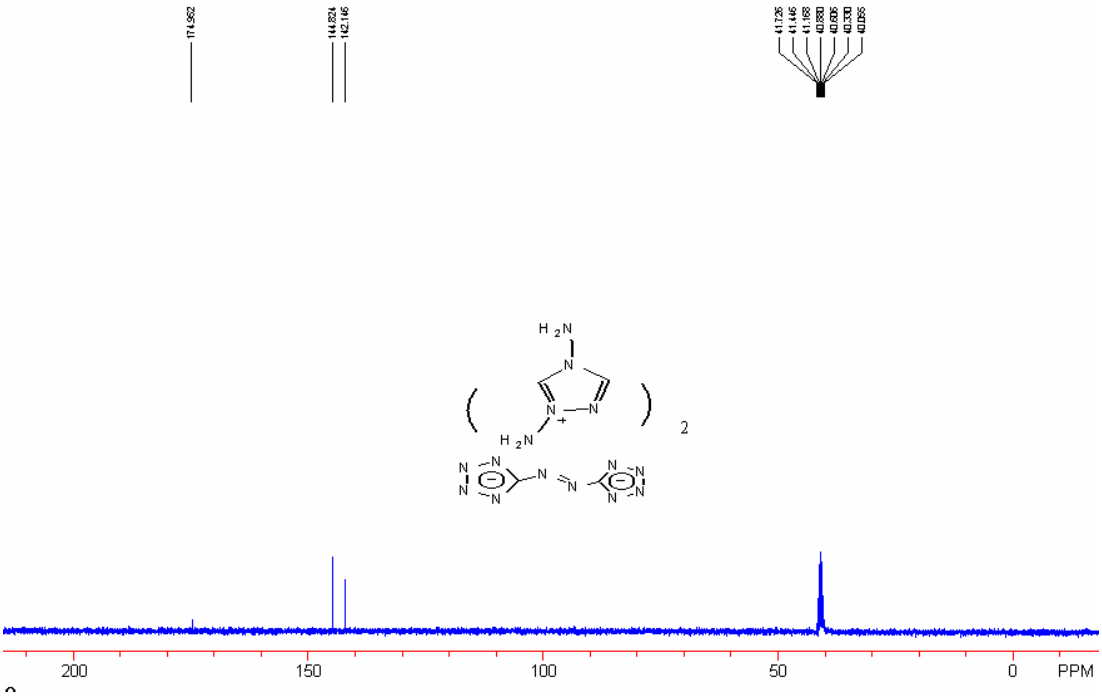


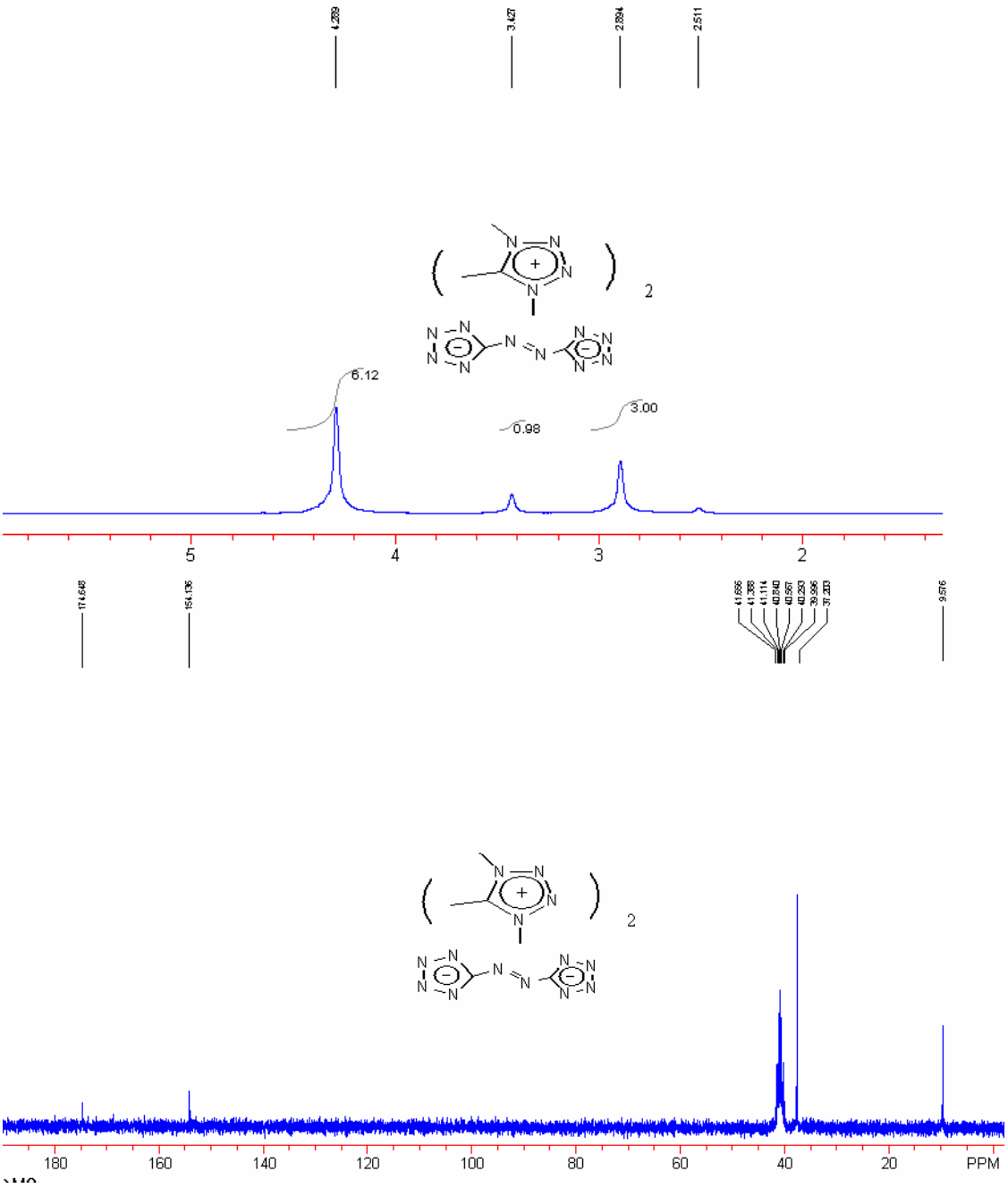


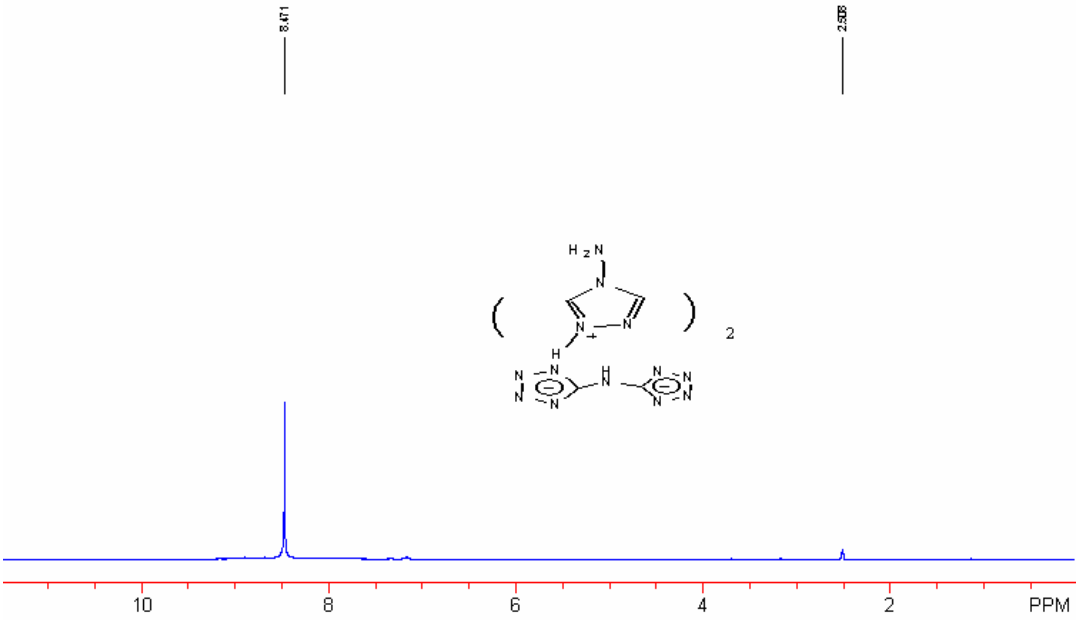


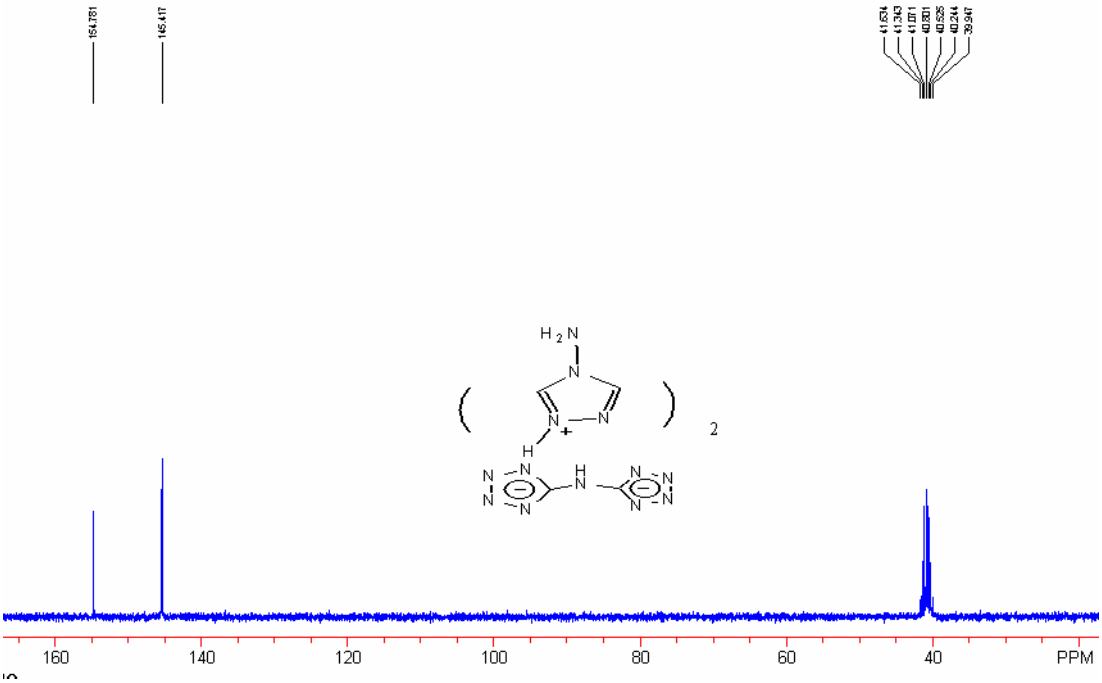


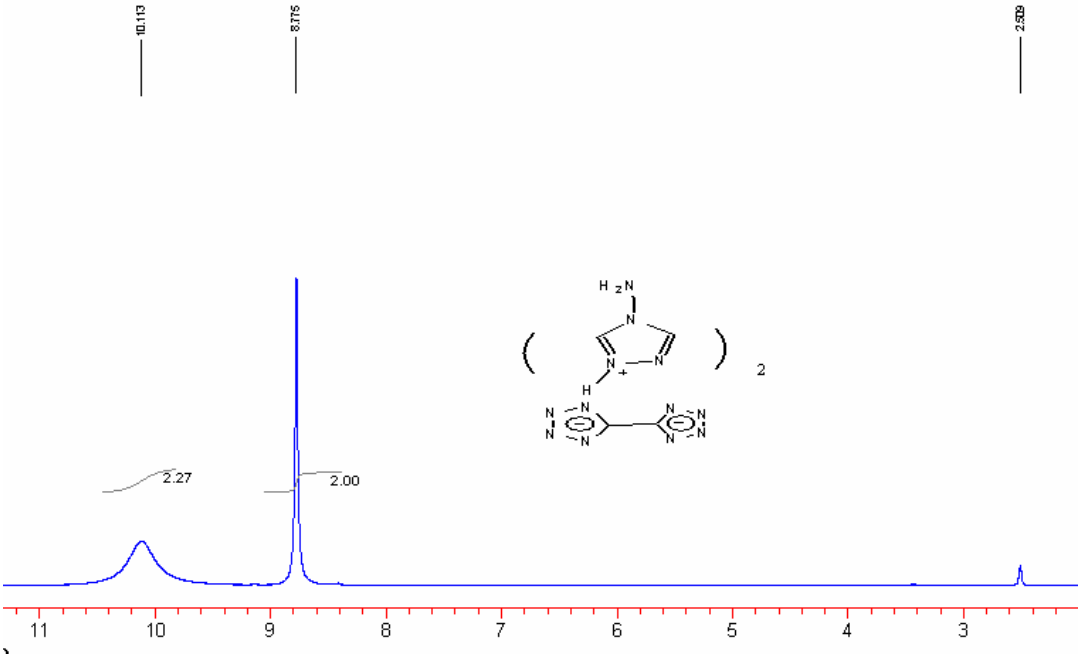












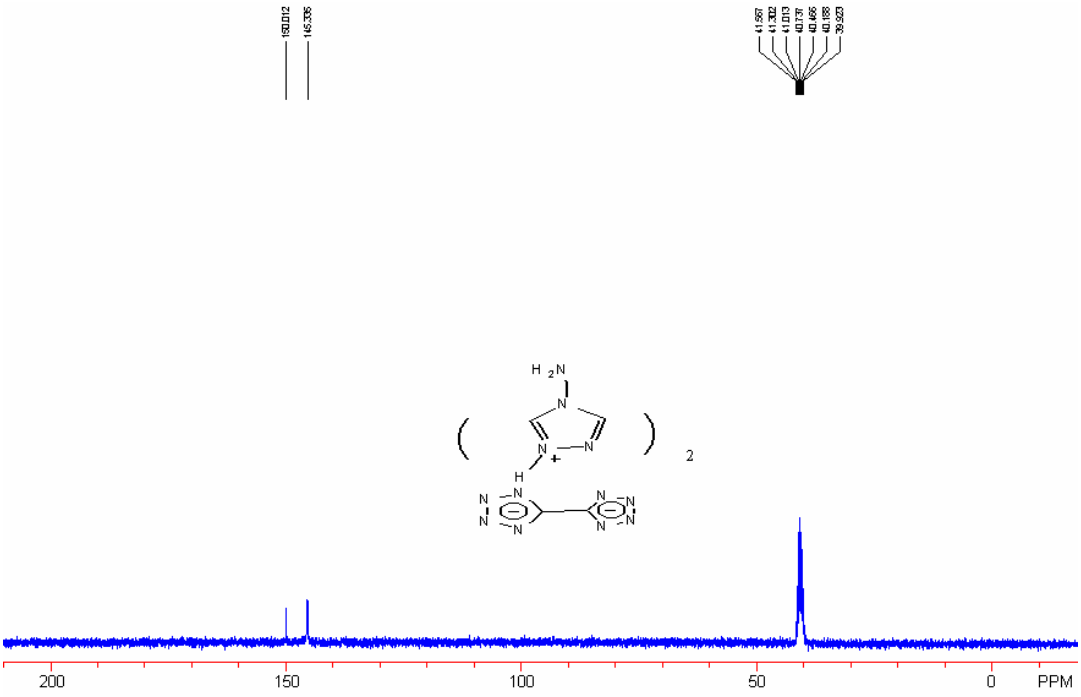


Table 1. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5**.

	x	y	z	U(eq)
H(7A)	3430(50)	273(19)	5550(90)	41
H(7B)	4530(50)	460(20)	3690(90)	41
H(9)	5230(40)	1520(16)	5000	41
H(12)	1690(40)	991(15)	5000	27
H(13A)	550(40)	1965(19)	5000	56
H(13B)	1290(30)	2368(12)	3770(60)	56

Table 2. Hydrogen bonds for **5** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(7)-H(7A)...N(1)#2	0.97(5)	2.16(5)	2.979(5)	140(4)
N(7)-H(7A)...N(1)#3	0.97(5)	2.16(5)	2.979(5)	140(4)
C(9)-H(9)...N(2)#4	0.94(4)	2.33(4)	3.201(5)	155(3)
C(9)-H(9)...N(2)#5	0.94(4)	2.33(4)	3.201(5)	155(3)
C(12)-H(12)...N(6)#2	0.89(4)	2.55(4)	3.363(5)	152(3)
C(12)-H(12)...N(4)#6	0.89(4)	2.47(4)	3.224(5)	142(3)
C(12)-H(12)...N(4)#7	0.89(4)	2.47(4)	3.224(5)	142(3)
C(12)-H(12)...N(6)#3	0.89(4)	2.55(4)	3.363(5)	152(3)
C(13)-H(13A)...N(4)#6	0.88(4)	2.54(5)	3.331(6)	149(4)
C(13)-H(13A)...N(4)#7	0.88(4)	2.54(5)	3.331(6)	149(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 x+0,-y+0,-z+1/2 #3 x,-y,z+1/2

#4 -x+1,y+0,-z+1/2 #5 -x+1,y,z+1/2 #6 -x+0,y+0,-z+1/2

#7 -x,y,z+1/2

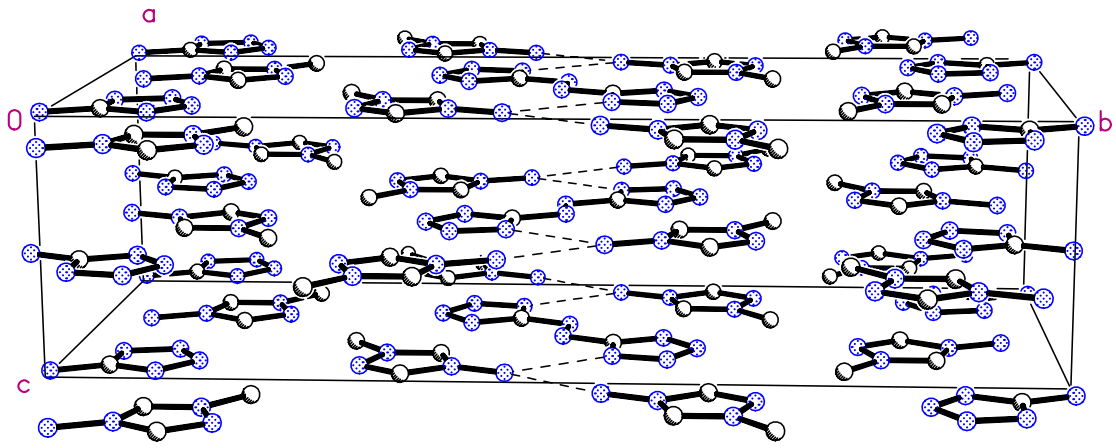


Fig. 1 a packinf diagram, viewed down the a axis, illustrating the layer nature of **5**.

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