Synthesis, single crystal structure and performance of *N*-Substituted Derivatives of dinitroimidazole

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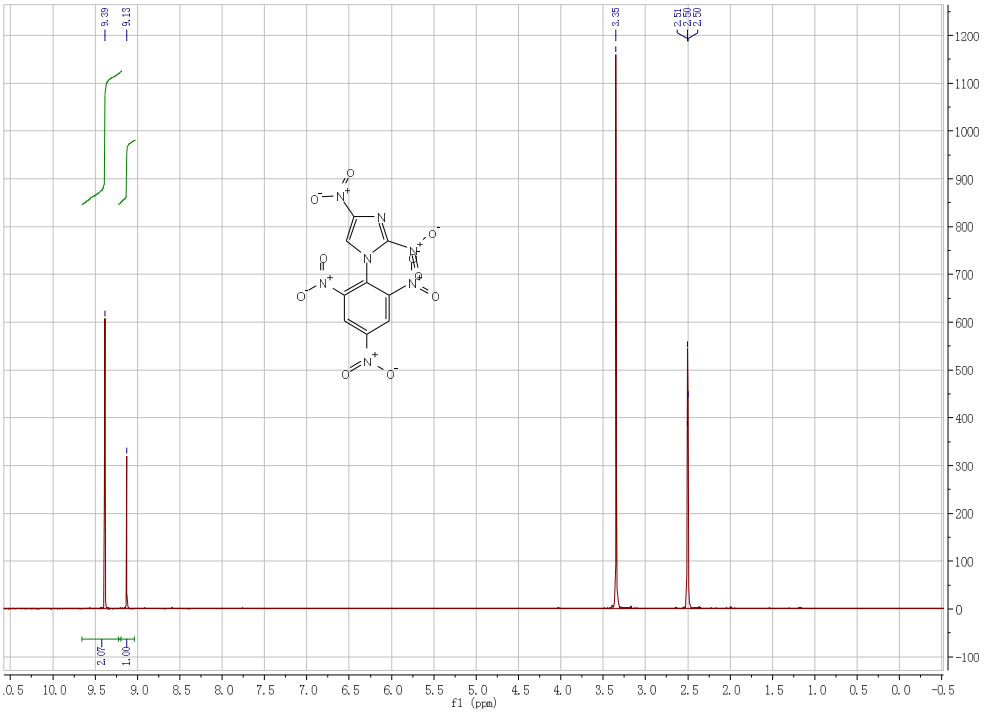
1. Spectroscopic data for dinitroimidazole derivatives:

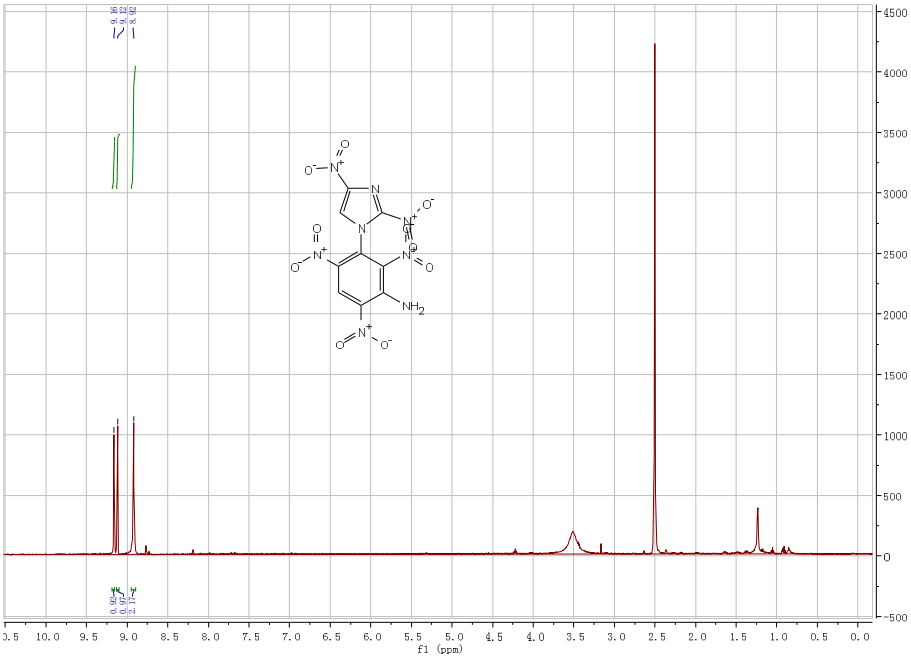
1-(2',4',6'-Trinitrophenyl)-2,4-dinitroimidazole (1)

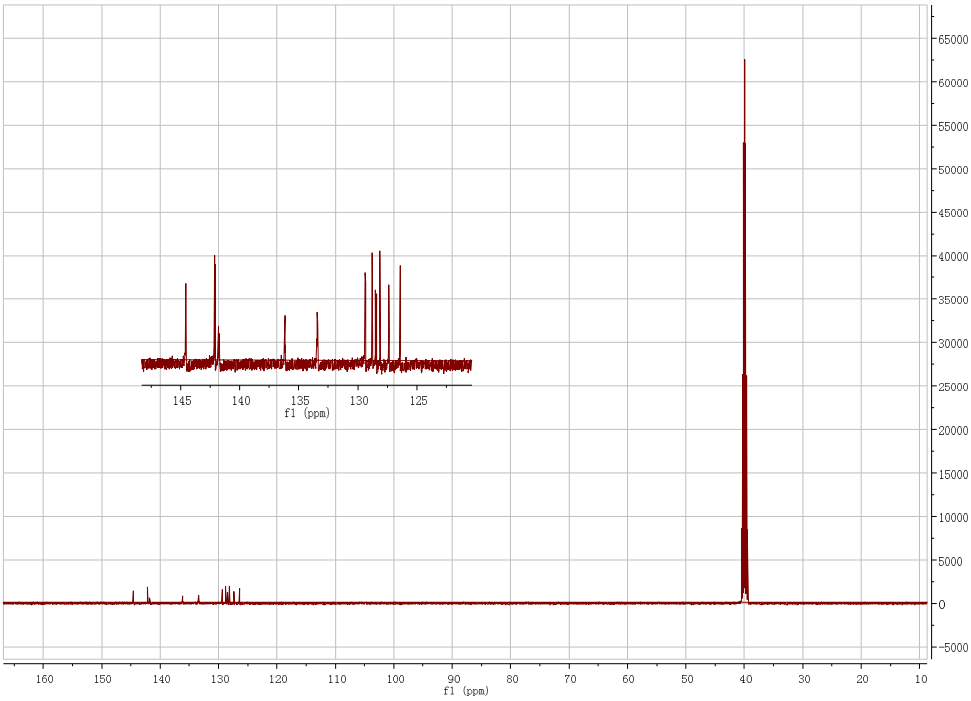
Yield: 57%; m.p. 255-258℃ (237-240℃ [1]); ^{1}H NMR (DMSO-d_6): δ 9.06 (s, 2H), 8.99(s, 1H).



1-(3'-Amino-2',4',6'-Trinitrophenyl)-2,4-Dinitroimidazole (2)

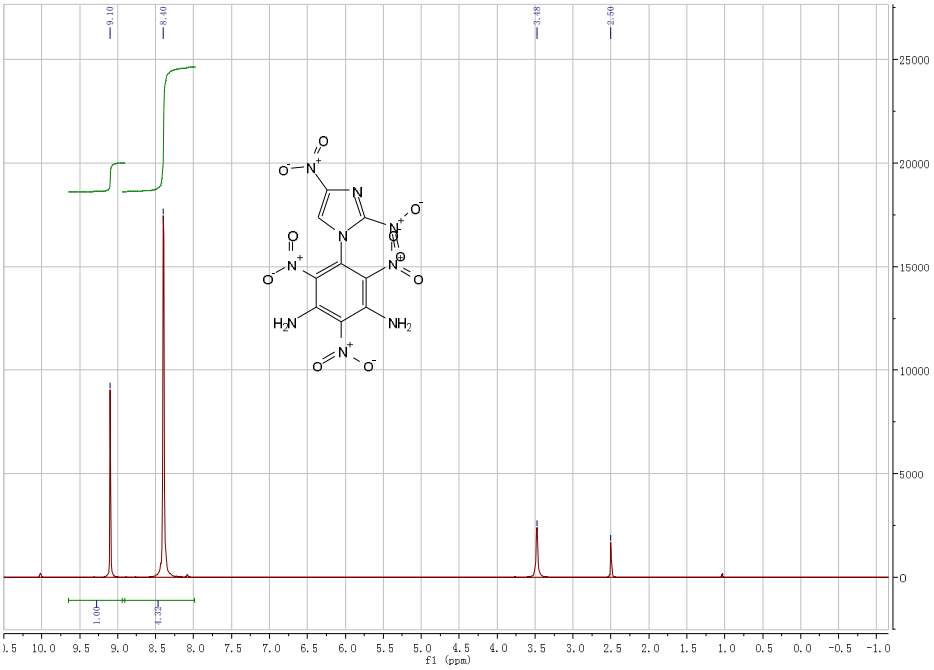
Yield: 50%; m.p. 260-263℃;^{1}H NMR (DMSO-d_6): δ 8.92(s, 2H), 9.12(s, 1H), 9.16 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 125.45, 126.39, 127.14 127.50 127.78, 128.42, 132.46, 135.19, 140.84, 141.14, 143.60; Elemental analysis data obtained for $C_9H_4N_8O_{10}$: Calculated: C, 28.14; H, 1.05; N, 29.17; found: C, 28.22; H, 1.08; N, 29.21%. MS (ESI) m/z : 382.84 (M-H).

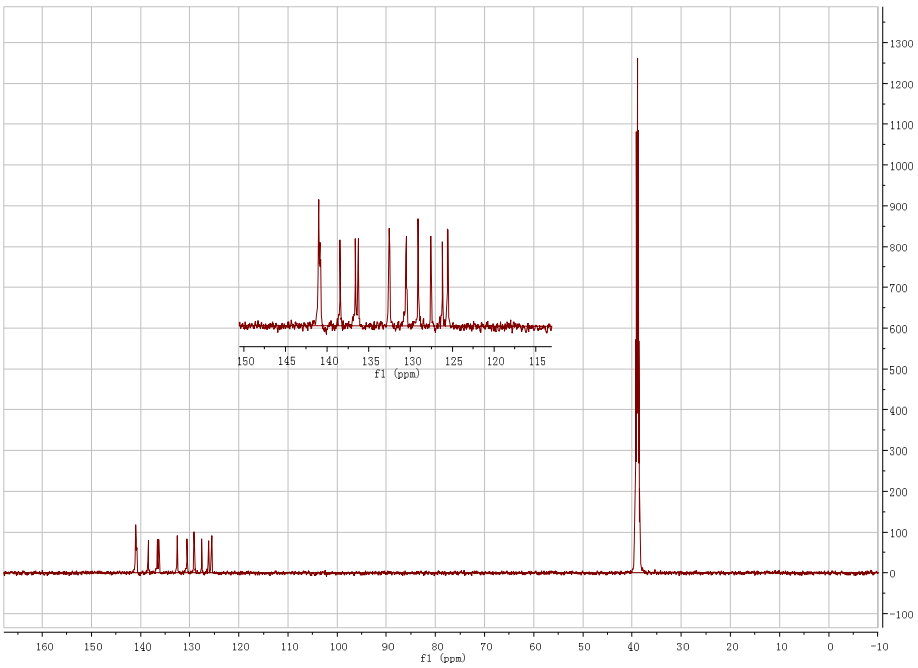




1-(3',5'-diamino-2',4',6'-Trinitrophenyl)-2,4-Dinitroimidazole (3)

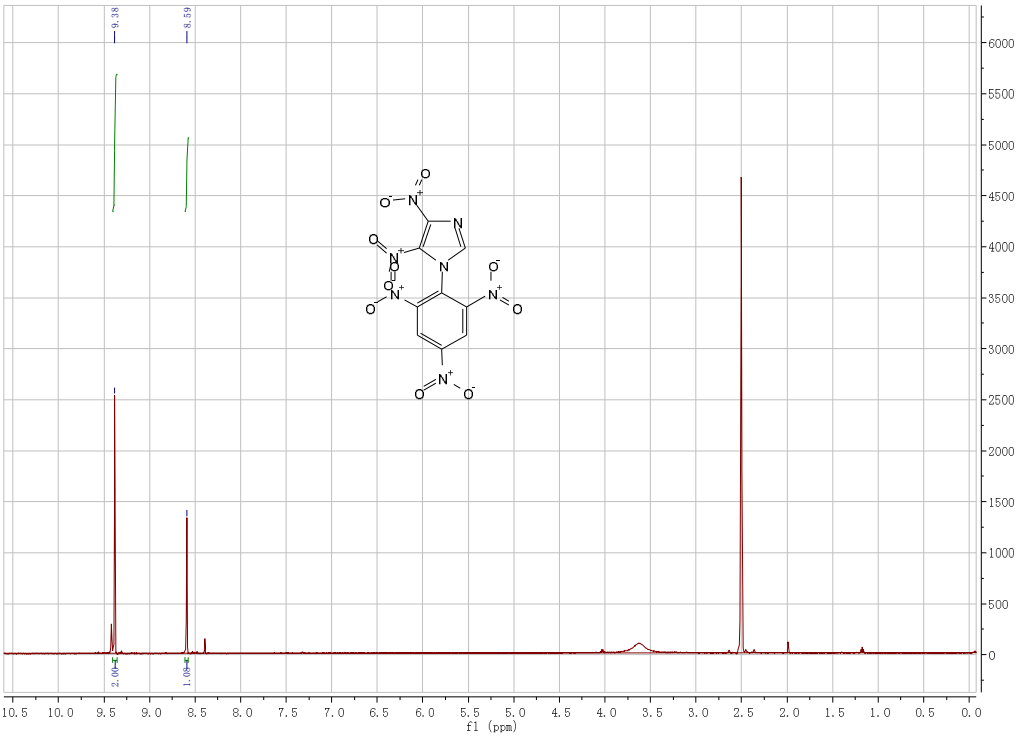
Yield: 78%; m.p. 360-363℃; ^{1}H NMR (DMSO-d_6): δ 8.40 (s, 4H), 9.10 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 121.60, 121.91, 124.76, 126.44, 129.31, 141.58, 143.35; Elemental analysis data obtained for $C_9H_5N_9O_{10}$: Calculated: C, 27.08; H, 1.26; N, 31.58; found: C, 27.11; H, 1.31; N, 31.62%. MS (ESI) m/z: 397.81 (M-H).





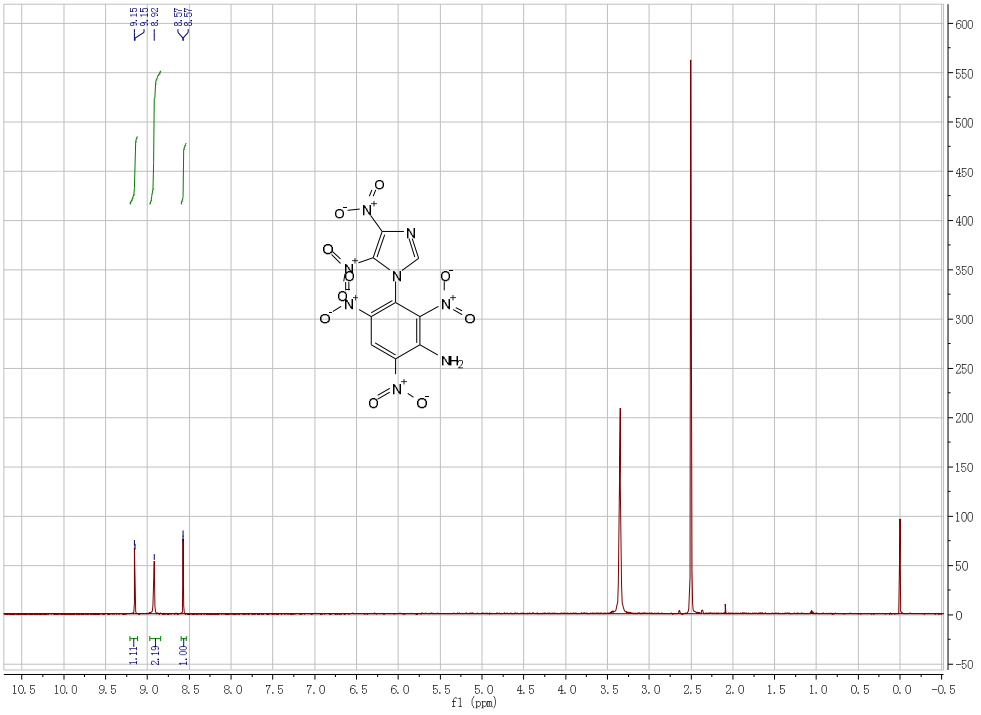
1-(2',4',6'-Trinitrophenyl)-4,5-Dinitroimidazole (4)

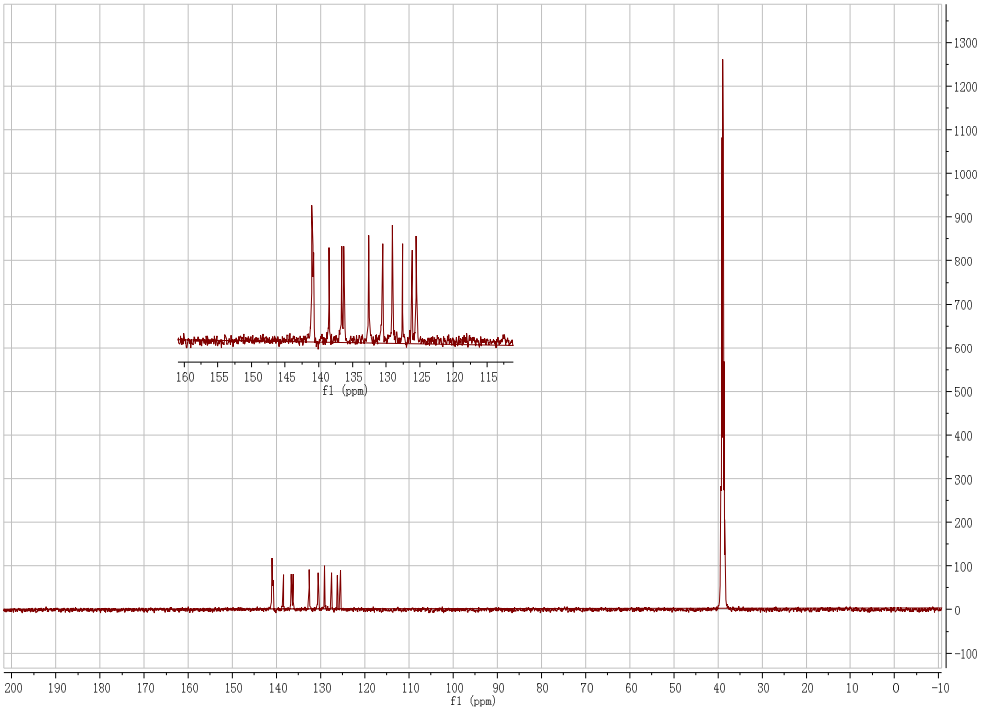
Yield: 65%; m.p. 226-229℃(220-223 ℃ [1]);^{1}H NMR (DMSO-d_6): δ 9.38 (s, 2H), 8.59 (s, 1H).



1-(3'-Amino-2',4',6'-Trinitrophenyl)-4,5-Dinitroimidazole (5)

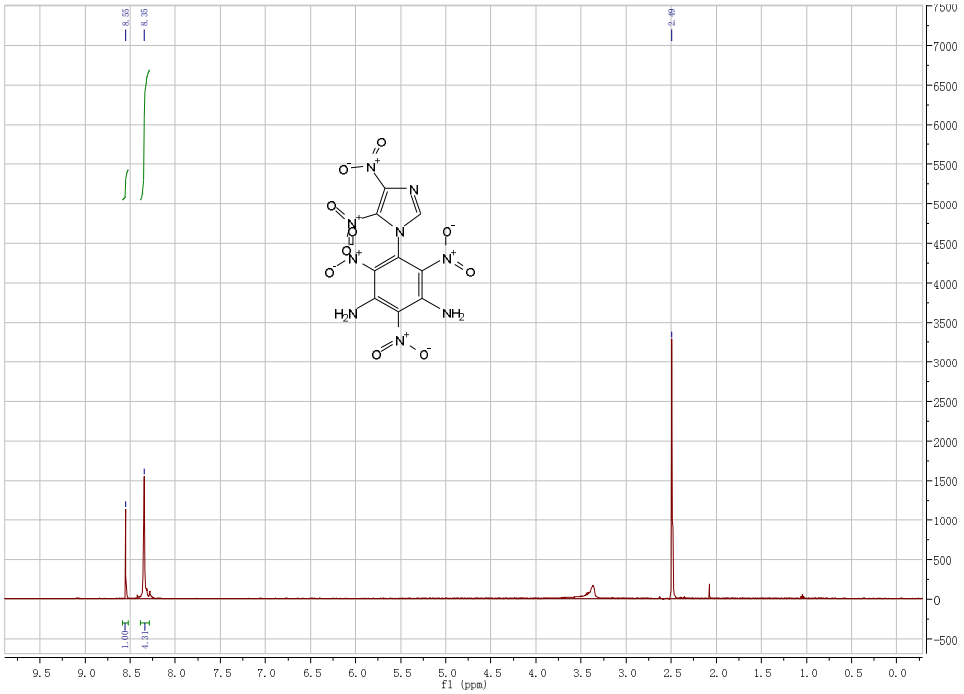
Yield: 61%; m.p. 282-284℃; ^{1}H NMR (DMSO-d_6): δ 8.57 (s, 1H), 8.92 (s, 2H), 9.15 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 125.52, 126.17, 127.56, 129.09, 130.53, 132.56, 136.44, 138.44, 140.93; Elemental analysis data obtained for $C_9H_4N_8O_{10}$: Calculated: C, 28.14; H, 1.05; N, 29.17; found: C, 28.22; H, 1.08; N, 29.21%. MS (ESI) m/z: 382.84 (M-H).

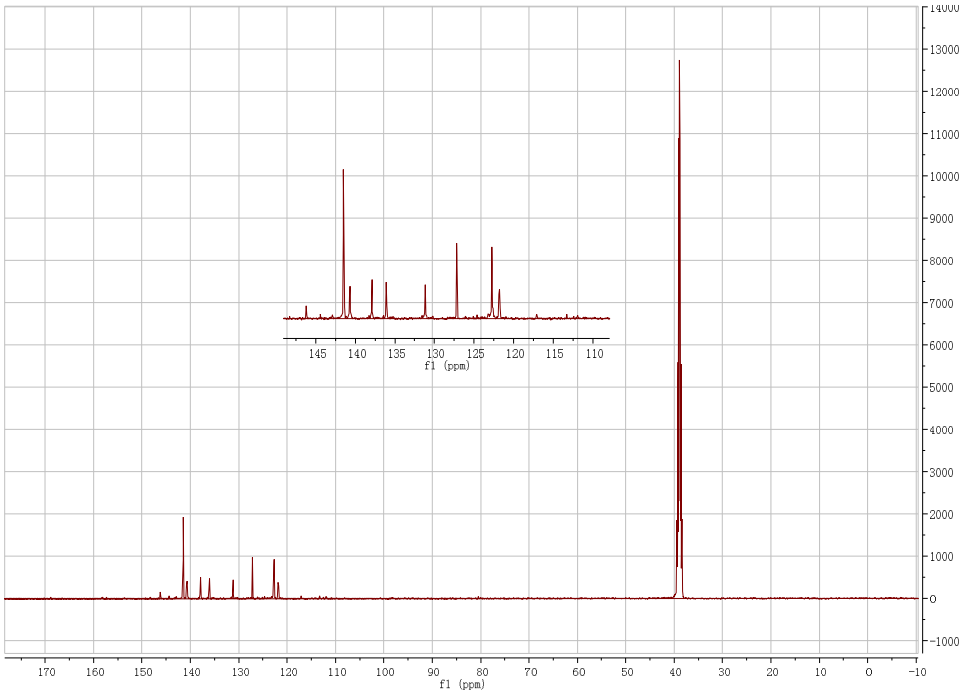




1-(3',5'-diamino-2',4',6'-Trinitrophenyl)-4,5-Dinitroimidazole (6)

Yield: 84%; m.p. 271-274℃; ^{1}H NMR (DMSO-d_6: δ 8.35 (s, 4H), 8.55 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 121.81, 122.73, 127.17, 131.16, 136.07, 137.91, 140.69, 141.47, 146.18; Elemental analysis data obtained for $C_9H_5N_9O_{10}$: Calculated: C, 27.08; H, 1.26; N, 31.58; found: C, 27.11; H, 1.31; N, 31.62%. MS (ESI) m/z: 397.79 (M-H).





Reference

(1) W. S. Wilson. NAVAL AIR WARFARE CENTER WEAPONS DIV CHINA LAKE, 1994.

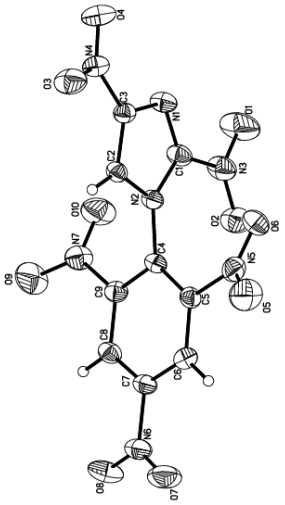


Fig. 1. Molecular structure of 1-(2',4',6'-Trinitrophenyl)-2,4-Dinitroimidazole (1)

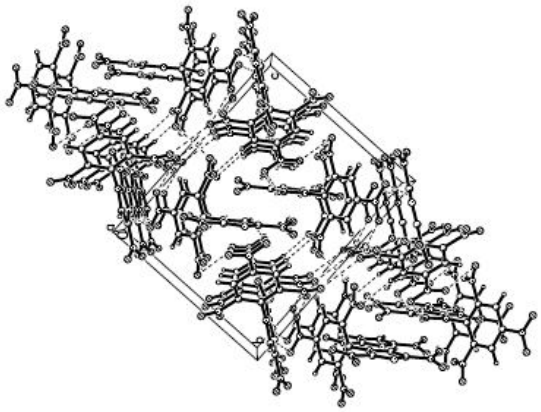


Fig. 2. Crystal packing of 1-(2',4',6'-Trinitrophenyl)-2,4-Dinitroimidazole (1)

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
N(1)- C (1)	1.311(4)	C (3)- N (4)	1.457(3)	N (6)- O (7)	1.212(3)
N(1)- C (3)	1.362(3)	O (3)- N (4)	1.228(3)	N (6)- O (8)	1.223(3)
C(1)- N (2)	1.367(3)	C (4)- C (9)	1.393(4)	N (6)- C (7)	1.478(3)
C(1)- N (3)	1.459(4)	C (4)- C (5)	1.399(4)	C (6)- C (7)	1.386(4)
O(1)- N (3)	1.211(3)	N (4)- O (4)	1.221(3)	C (7)- C (8)	1.391(4)
N(2)- C (2)	1.367(3)	N (5)- O (5)	1.217(4)	N (7)- O (9)	1.207(3)
N (2)- C (4)	1.453(3)	N (5)- O (6)	1.223(3)	N (7)- O (10)	1.220(3)
C (2)- C (3)	1.364(4)	N (5)- C (5)	1.488(3)	N (7)- C (9)	1.500(4)
O (2)- N (3)	1.233(3)	C (5)- C (6)	1.384(4)	C (8)- C (9)	1.390(4)
Angle	(°)	Angle	(°)	Angle	(°)

C (1)- N (1)- C (3)	103.3(2)	C (3)- C (2)- N (2)	105.7(2)	C (4)- C (5)- N (5)	120.3(2)
N (1)- C (1)- N (2)	113.8(2)	N (1)- C (3)- C (2)	111.9(2)	C (6)- C (7)- N (6)	118.8(3)
N (1)- C (1)- N (3)	125.4(2)	N (1)- C (3)- N (4)	122.9(2)	C (8)- C (7)- N (6)	117.7(2)
N (2)- C (1)- N (3)	120.8(2)	C (2)- C (3)- N (4)	125.2(2)	C (8)- C (9)- C (4)	121.7(2)
C (2)- N (2)- C (1)	105.3(2)	C (9)- C (4)- N (2)	119.4(2)	C (8)- C (9)- N (7)	117.1(2)
C (2)- N (2)- C (4)	123.5(2)	C (5)- C (4)- N (2)	121.3(2)	C (4)- C (9)- N (7)	121.2(2)
C (1)- N (2)- C (4)	131.2(2)	C (6)- C (5)- N (5)	117.7(3)		

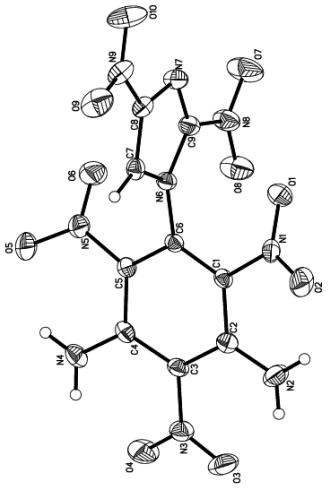


Fig. 3. Molecular structure of 1-(3',5'-diamino-2',4',6'-Trinitrophenyl)-2,4-Dinitroimidazole (3)

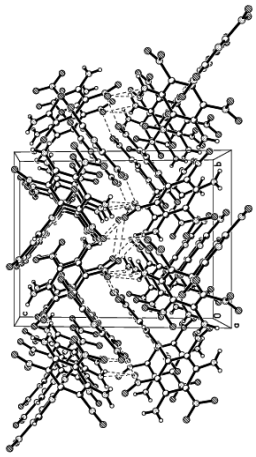


Fig. 4. Crystal packing of 1-(3',5'-diamino-2',4',6'-Trinitrophenyl)-2,4-Dinitroimidazole (3)

Table 2. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
N (1)- O (2)	1.207(3)	C (3)- C (4)	1.425(4)	N (7)- C (9)	1.299(3)
N (1)- O (1)	1.223(3)	N (4)- C (4)	1.323(3)	N (7)- C (8)	1.359(3)
N (1)- C (1)	1.445(3)	C (4)- C (5)	1.432(4)	O (7)- N (8)	1.202(3)
C (1)- C (6)	1.378(3)	C (5)- C (6)	1.380(3)	C (8)- N (9)	1.436(3)

C (1)- C (2)	1.436(3)	C (5)- N (5)	1.454(3)	O (8)- N (8)	1.219(3)
C (2)- N (2)	1.320(3)	N (5)- O (6)	1.214(3)	N (8)- C (9)	1.440(4)
C (2)- C (3)	1.427(4)	N (5)- O (5)	1.232(3)	N (9)- O (10)	1.209(3)
N (3)- O (3)	1.220(3)	N (6)- C (7)	1.363(3)	N (9)- O (9)	1.221(3)
N (3)- O (4)	1.226(3)	N (6)- C (9)	1.365(3)		
N (3)- C (3)	1.443(3)	N (6)- C (6)	1.441(3)		
Angle	(°)	Angle	(°)	Angle	(°)
C (6)-C (1)-N (1)	119.6(2)	C (6)-C (5)-N (5)	118.9(2)	C (9)-N (7)-C (8)	102.3(2)
C (2)-C (1)-N (1)	119.8(2)	C (4)-C (5)-N (5)	120.0(2)	C (8)-C (7)-N (6)	104.1(2)
N (2)-C (2)-C (3)	122.9(3)	C (7)-N (6)-C (9)	106.0(2)	C (7)-C (8)-N (7)	113.5(2)
N (2)-C (2)-C (1)	120.1(2)	C (7)-N (6)-C (6)	122.7(2)	C (7)-C (8)-N (9)	125.2(3)
C (4)-C (3)-N (3)	118.4(2)	C (9)-N (6)-C (6)	131.1(2)	N (7)-C (8)-N (9)	121.2(2)
C (2)-C (3)-N (3)	119.0(2)	C (1)-C (6)-C (5)	121.8(2)	N (7)-C (9)-N (6)	114.1(2)
N (4)-C (4)-C (3)	123.2(2)	C (1)-C (6)-N (6)	119.6(2)	N (7)-C (9)-N (8)	123.9(3)
N (4)-C (4)-C (5)	120.3(2)	C (5)-C (6)-N (6)	117.8(2)	N (6)-C (9)-N (8)	122.0(2)

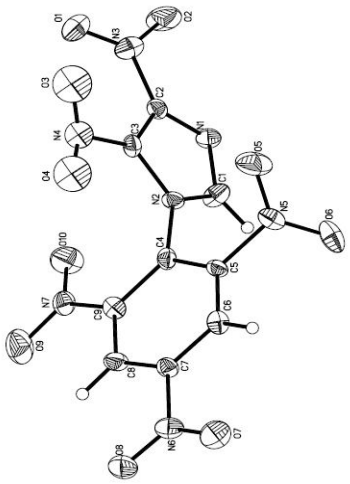


Fig. 5. Molecular structure of 1-(2',4',6'-Trinitrophenyl)-4,5-Dinitroimidazole (4)

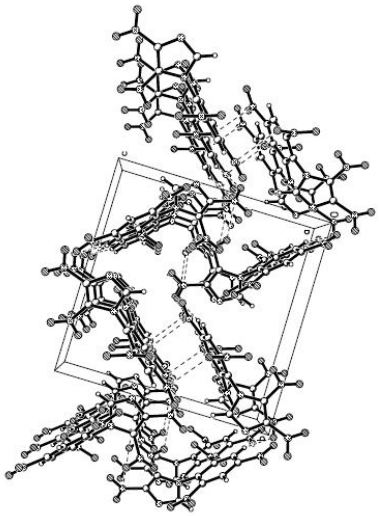


Fig. 6. Crystal packing of 1-(2',4',6'-Trinitrophenyl)-4,5-Dinitroimidazole (4)

Table 3. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
N(1)-C(1)	1.319(7)	C(3)-N(4)	1.500(8)	N(6)-O(7)	1.207(7)
N(1)-C(2)	1.337(7)	O(3)-N(4)	1.098(7)	N(6)-O(8)	1.207(7)
O(1)-N(3)	1.190(7)	N(4)-O(4)	1.024(7)	N(6)-C(7)	1.477(7)
C(1)-N(2)	1.366(7)	C(4)-C(5)	1.398(8)	C(6)-C(7)	1.352(8)
N(2)-C(3)	1.366(7)	C(4)-C(9)	1.436(8)	N(7)-O(10)	1.201(7)
N(2)-C(4)	1.449(7)	N(5)-O(6)	1.224(7)	N(7)-O(9)	1.233(7)
C(2)-C(3)	1.356(8)	N(5)-O(5)	1.227(6)	N(7)-C(9)	1.426(7)
C(2)-N(3)	1.445(7)	N(5)-C(5)	1.470(7)	C(7)-C(8)	1.382(8)
O(2)-N(3)	1.227(7)	C(5)-C(6)	1.364(8)	C(8)-C(9)	1.380(8)
Angle	(°)	Angle	(°)	Angle	(°)
C(1)-N(1)-C(2)	104.7(4)	N(1)-C(2)-C(3)	112.7(5)	N(2)-C(3)-N(4)	121.3(5)
N(1)-C(1)-N(2)	111.0(5)	N(1)-C(2)-N(3)	119.5(5)	C(6)-C(5)-N(5)	118.4(5)
C(1)-N(2)-C(3)	106.9(5)	C(3)-C(2)-N(3)	127.3(5)	C(4)-C(5)-N(5)	119.0(5)
C(1)-N(2)-C(4)	123.9(5)	C(2)-C(3)-N(2)	104.4(5)	C(8)-C(7)-N(6)	117.7(5)
C(3)-N(2)-C(4)	128.4(5)	C(2)-C(3)-N(4)	134.0(5)	C(8)-C(9)-N(7)	120.8(5)

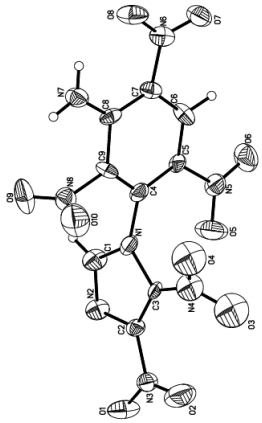


Fig. 7. Molecular structure of 1-(3'-Amino-2',4',6'-Trinitrophenyl)-4,5-Dinitroimidazole (5)

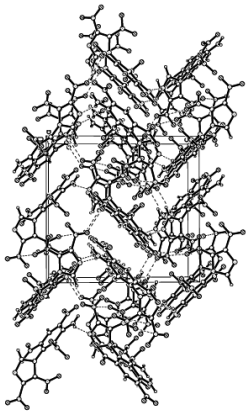


Fig. 8. Crystal packing of 1-(3'-Amino-2',4',6'-Trinitrophenyl)-4,5-Dinitroimidazole (5)

Table 4. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
N (1)- C (1)	1.402(11)	C (3)- N (4)	1.406(13)	C (6)- C (7)	1.409(13)
N (1)- C (3)	1.405(9)	O (3)- N (4)	1.250(12)	N (6)- O (8)	1.214(10)
N (1)- C (4)	1.467(11)	C (4)- C (5)	1.372(12)	N (6)- O (7)	1.232(11)
O (1)- N (3)	1.212(10)	C (4)- C (9)	1.387(12)	N (6)- C (7)	1.476(11)
C (1)- N (2)	1.323(11)	N (4)- O (4)	1.162(12)	N (8)- O (9)	1.185(11)
N (2)- C (2)	1.375(10)	C (5)- C (6)	1.357(12)	N (8)- O (10)	1.241(11)
C (2)- C (3)	1.329(11)	C (5)- N (5)	1.516(11)	N (8)- C (9)	1.440(12)
C (2)- N (3)	1.457(10)	O (5)- N (5)	1.268(12)	C (8)- N (7)	1.335(10)
O (2)- N (3)	1.204(11)	N (5)- O (6)	1.188(10)	C (8)- C (9)	1.470(11)
Angle	(°)	Angle	(°)	Angle	(°)
N (2)- C (2)- N (3)	118.5(8)	N (2)- C (2)- N (3)	118.5(8)	C (6)- C (5)- N (5)	117.5(8)
C (2)- C (3)- N (1)	107.5(8)	C (2)- C (3)- N (1)	107.5(8)	C (4)- C (5)- N (5)	122.3(8)
C (2)- C (3)- N (4)	136.0(8)	C (2)- C (3)- N (4)	136.0(8)	C (8)- C (7)- N (6)	121.4(9)
N (1)- C (3)- N (4)	116.2(8)	N (1)- C (3)- N (4)	116.2(8)	C (6)- C (7)- N (6)	116.9(9)
N (2)- C (2)- N (3)	118.5(8)	C (5)- C (4)- C (9)	118.6(9)	N (7)- C (8)- C (7)	126.5(8)
C (2)- C (3)- N (1)	107.5(8)	C (5)- C (4)- N (1)	123.2(9)	N (7)- C (8)- C (9)	120.4(8)
C (2)- C (3)- N (4)	136.0(8)	C (9)- C (4)- N (1)	118.2(8)	C (4)- C (9)- N (8)	120.0(8)

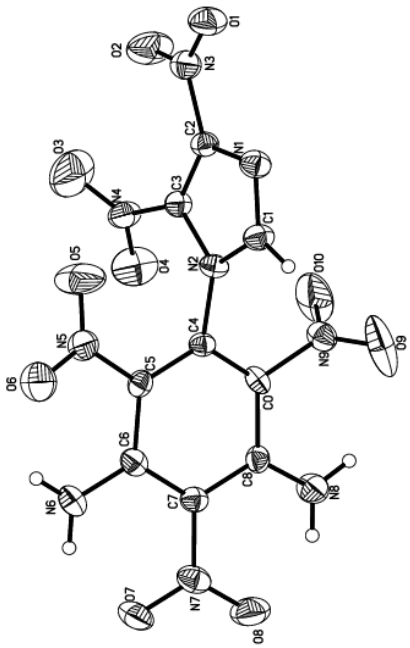


Fig. 9. Molecular structure of 1-(3',5'-diamino-2',4',6'-Trinitrophenyl)-4,5-Dinitroimidazole (6)

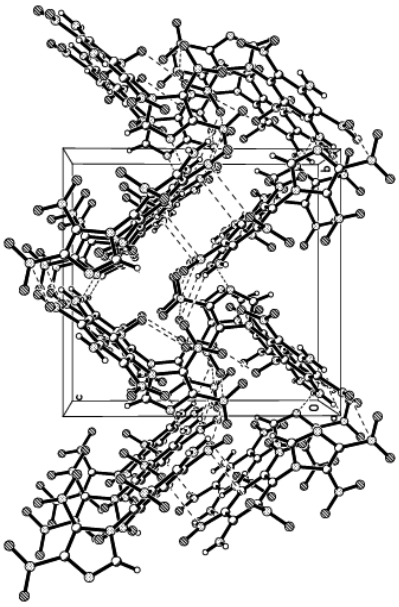


Fig. 10. Crystal packing of 1-(3',5'-diamino-2',4',6'-Trinitrophenyl)-4,5-Dinitroimidazole (6)

Table 5. Selected Bond Lengths (Å) and Bond Angles (°)

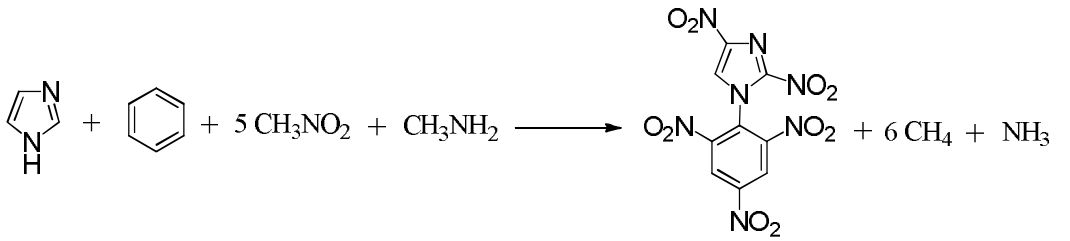
Bond	Dist.	Bond	Dist.	Bond	Dist.
C (0)-C (4)	1.363(7)	C (2)-N (3)	1.472(7)	C (6)-N (6)	1.346(7)
C (0)-C (8)	1.443(8)	O (2)-N (3)	1.211(7)	N (7)-O (8)	1.216(7)
C (0)-N (9)	1.462(7)	C (3)-N (4)	1.463(7)	N (7)-O (7)	1.242(7)
C (1)-N (1)	1.310(7)	O (3)-N (4)	1.195(8)	N (7)-C (7)	1.443(7)
C (1)-N (2)	1.367(7)	C (4)-C (5)	1.392(7)	C (7)-C (8)	1.432(8)
N (1)-C (2)	1.366(7)	N (4)-O (4)	1.173(7)	C (8)-N (8)	1.313(7)
O (1)-N (3)	1.217(6)	C (5)-C (6)	1.436(8)	N (9)-O (10)	1.182(8)
N (2)-C (3)	1.406(7)	C (5)-N (5)	1.451(7)	N (9)-O (9)	1.200(7)
N (2)-C (4)	1.443(7)	N (5)-O (5)	1.187(7)		
C (2)-C (3)	1.345(7)	N (5)-O (6)	1.209(7)		
Angle	(°)	Angle	(°)	Angle	(°)
C (4)-C (0)-N (9)	118.8(5)	C (3)-C (2)-N (3)	128.2(5)	C (6)-C (5)-N (5)	120.8(5)
C (8)-C (0)-N (9)	117.4(5)	N (1)-C (2)-N (3)	119.9(5)	N (6)-C (6)-C (7)	119.9(5)
N (1)-C (1)-N (2)	112.2(5)	C (2)-C (3)-N (2)	105.0(4)	N (6)-C (6)-C (5)	120.8(6)
C (1)-N (1)-C (2)	105.2(4)	C (2)-C (3)-N (4)	134.6(5)	C (6)-C (7)-N (7)	121.8(5)
C (1)-N (2)-C (3)	105.7(4)	N (2)-C (3)-N (4)	120.4(5)	C (8)-C (7)-N (7)	116.7(5)
C (1)-N (2)-C (4)	125.5(4)	C (0)-C (4)-N (2)	116.0(5)	N (8)-C (8)-C (7)	125.1(5)
C (3)-N (2)-C (4)	128.6(5)	C (5)-C (4)-N (2)	122.8(5)	N (8)-C (8)-C (0)	119.7(5)
C (3)-C (2)-N (1)	111.9(4)	C (4)-C (5)-N (5)	120.2(5)	C (7)-C (8)-C (0)	115.1(5)

Table 6. Total energy (E_0) at the B3LYP/6-31G* level and experimental gas phase HOFs for the reference compounds.

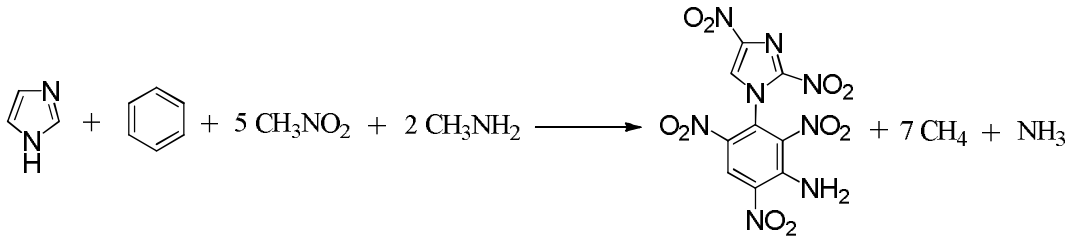
Compd.	E_0 (au)	HOF (kJ/mol)
CH_4	-40.524195	-74.6
NH_3	-56.5577686	-46.1
CH_3NH_2	-95.863686	-22.5
CH_3NO_2	-245.0133753	-80.6
Imidazole	-226.2230978	132.9
Benzene	-232.2582055	82.9

Table 7. Calculated total energies (E_0), gas phase HOFs ($\Delta_f H^0_{Gas}$) for dinitroimidazole derivatives.

Compd	Molecular Formula	M. W. (g/mol)	E_0 (au)	$\Delta_f H^0_{Gas}$ (kF/mol)
1	$C_9H_3N_7O_{10}$	368.9941	-1479.71023	485.1016
2	$C_9H_4N_8O_{10}$	384.005	-1535.082987	213.3052
3	$C_9H_5N_9O_{10}$	399.0159	-1590.45327	180.4869
4	$C_9H_3N_7O_{10}$	368.9941	-1479.700703	277.1873
5	$C_9H_4N_8O_{10}$	384.005	-1535.074468	236.0061
6	$C_9H_5N_9O_{10}$	399.0159	1590.443908	205.3951



(1)



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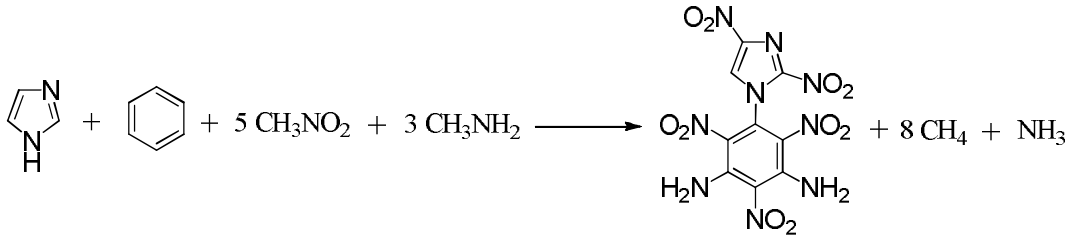

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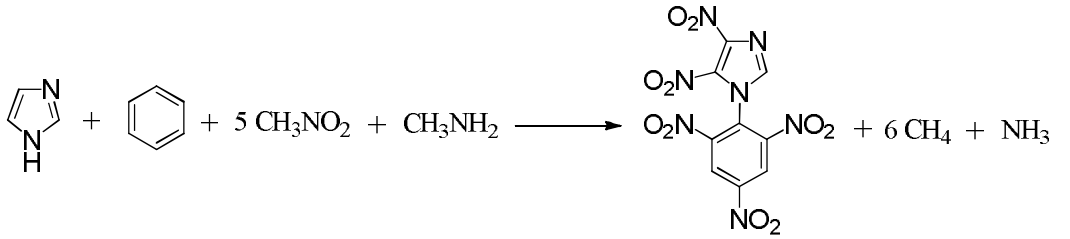

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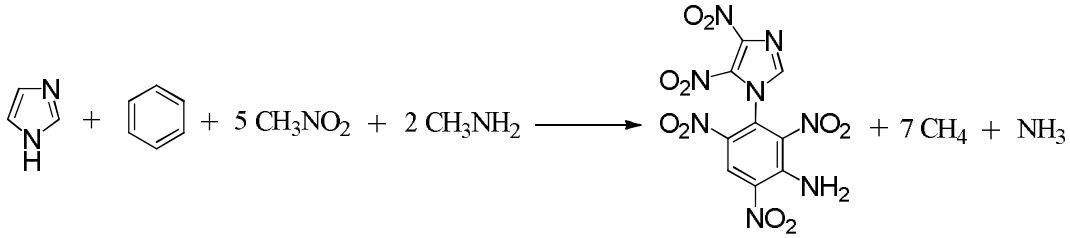

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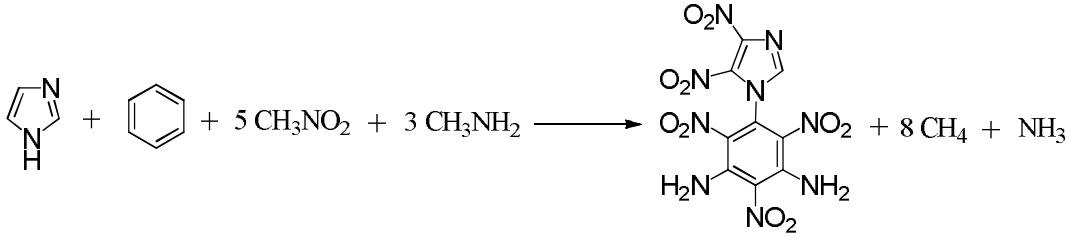

(6)

Fig. 11. Isodesmic reactions for the dinitroimidazole derivatives