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ARTICLE

Mono- and Diiodo-1,2,3-Triazoles and Their Mono Nitro Derivatives

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4-Iodo-1H-1,2,3-triazole (**2**) and 4, 5-diiodo-1H-1,2,3-triazole (**3**) were synthesized using an efficient and viable synthetic route. The N-alkylation of **3** resulted in the formation of two tautomers. The N-alkyl-diiodo-triazoles were nitrated with 100% nitric acid to form monoiodo-mononitro-triazoles. The structures of 2-methyl-4,5-diiodo-1,2,3-triazole (**5**), 1-ethyl-4,5-diiodo-1,2,3-triazole (**6**), 1-methyl-4-nitro-5-iodo-1,2,3-triazole (**8**) and 1-ethyl-4-nitro-5-iodo-1,2,3-triazole (**10**) were confirmed by X-ray crystal analysis. All of the new triazoles were fully characterized via NMR, and infrared spectra, and elemental analyses as well as by their thermal and sensitivity properties. Decomposition products calculated using Cheetah 7 software show that these iodo-nitro triazoles liberate iodine.

Introduction

Iodine has been used as a powerful disinfectant for over 100 years. When in contact with micro-organisms such as bacteria, viruses, fungi and protozoa, iodine is able to rapidly penetrate cell walls and oxidise a number of critical components within the cell. The combined effect of these oxidative reactions is cell death. In aqueous solution, iodine is found as four principal forms: iodine (I_2), hypoiodous acid (HIO), triiodide (I_3^-) and iodate (IO_3-). Both I_2 and HIO are strong antibacterial agents. The I_3^- and IO_3^- species are only present in very low concentrations and are only significant at pH greater than 8.5.[1]

The 1,2,3-triazole ring is a moiety present in anti-allergic, antibacterial, antifungal, anti-virial, and analgesic drugs. Of the two constitutional triazole isomers, 1,2,3-triazole and 1,2,4-triazole, the latter has been extensively investigated for energetic materials applications.[2] Likely because the syntheses of the precursors are more difficult, there are fewer reports dealing with similar applications of 1,2,3-triazole.[3]

In this work an efficient and practical synthesis for 4-iodo-1*H*-1,2,3-triazole (**2**) and 4,5-diiodo-1*H*-1,2,3-triazole (**3**) was developed. A nitro functionality is helpful in enhancing the energy content as well as to attain a better oxygen balance. However, due to the instability of these triazoles in strongly acidic solutions, direct nitration was not possible. Although, the iodo triazoles are less acidic than the parent 1,2,3-triazoles, the alkylation reactions were successful. The resulting N-alkyl triazoles are tautomeric, and can be nitrated using 100% nitric acid. Gaussian 03 calculations were employed to predict the heat of formation values which were used as input parameters for Cheetah 7 calculations to obtain detonation properties and decomposition products.

Results and discussion

Synthesis

Compounds **1** – **11** were synthesized as shown in Scheme 1. 1-Iodo-1,2,3-triazole (**1**) was synthesized based on the literature.[4] 3,5-Dimethyl-1,2,4-triazole, an expensive and not readily available reagent, has been used previously to transform **1** into **2** and **3**.[5] To our delight, we found that this conversion happens by using an inexpensive and readily available reagent, i.e., aqueous ammonia. When 1-iodo-1,2,3-triazole was heated in aqueous ammonia in a thick-walled-pressure tube at 100 °C for 10 – 15 min, ammonium salts of **2** and **3** were obtained.

An aqueous solution of the resulting salts, when acidified with concentrated hydrochloric acid, formed a precipitate which was isolated by filtration and identified as 3,5-diiodo-1*H*-1,2,3-triazole (**3**). 4-Iodo-1*H*-1,2,3-triazole (**2**) was isolated from the filtrate by ether extraction. Because of the low stability of **2** and **3** in acidic solution, direct nitration was not possible. Low temperature alkylation of **3** was accomplished by using potassium carbonate as base and methyl and ethyl iodides as electrophiles. N1- and N2-alkylated products were isolated in excellent yields. Column chromatography (ethyl acetate: hexane) was employed to separate the resulting N-alkyl compounds. By refluxing in 100% nitric acid, nitration of **4**, **5**,

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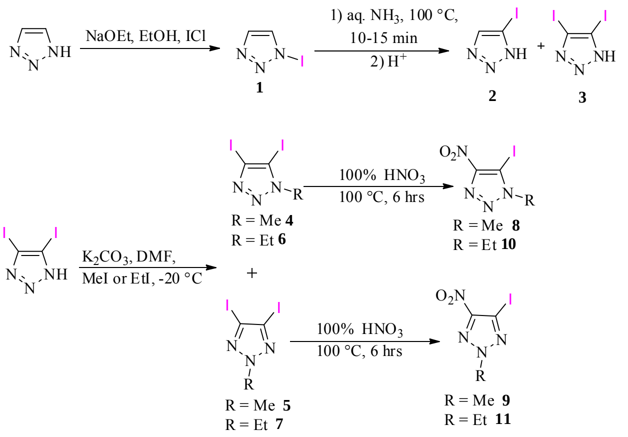
Table 1: Properties of compounds **2–11**

Comp	T_m[a] [°C]	T_d[b] [°C]	d[c] [gcm^{-3}]	$\Delta H_f°$ [d] [kJ mol^{-1}]	$\Delta H_f°$ [kJ g^{-1}]	D[e] [ms^{-1}]	P[f] [GPa]	Iodine [%]
2	110.8	156.7	2.71	430.0	2.2	5112	15.33	65.1
3	-	189.9	3.32	474.4	1.5	4090	11.41	79.1
4	185.7	212.7	3.11	373.1	1.1	3985	10.07	75.8
5	129.7	-	2.90	358.6	1.1	3639	7.91	75.8
6	127.5	170.9	2.81	459.1	1.3	4066	9.96	72.7
7	108.1	-	2.73	443.7	1.3	3926	9.07	72.7
8	98.0	-	2.41	683.1	2.7	6028	21.24	50.0
9	156.0	235.0	2.13	671.1	2.6	5512	16.85	50.0
10	48.3	253.7	2.17	672.5	2.5	5710	20.03	47.4
11	111.2	-	2.11	658.7	2.5	5602	19.12	47.4

[a] melting point; [b] decomposition temperature; [c] density - gas pycnometer 25 °C ; [d] heat of formation - Gaussian 03; [e] detonation velocity - Cheetah 7; [f] detonation pressure - Cheetah 7.

6 and **7** was successful in forming the 4-nitro products. Compounds **2** – **11** were fully characterized with NMR, and IR spectral analysis, DSC and elemental analysis. Single crystal structures were obtained for **5**, **6**, **8** and **10**.



Scheme 1: Synthesis of compounds **1** -**11**

Properties of compounds

The physical properties of **2** – **11** are summarized in Table 1. Heats of formation of all compounds were calculated with the Gaussian 03 program suite using isodesmic reactions[6] (Electronic Supporting Information (ESI) Scheme S1). For these iodine-containing compounds, the (15s, 11p, 6d) basis of Strömberg et al. was augmented with other p shell and the five valence sp exponents optimized resulting in a [5211111111, 411111111, 3111] contraction scheme in conjunction with 6-31+G** for first row and second row elements.[7] Single-point energy (SPE) refinement on the optimized geometries were performed with the use of MP2/6-311++G** level. Corresponding iodine sets were constructed in MP2 method by using all electron calculations and quasi relativistic energy-adjusted spin-orbit-averaged seven-valence-electron effective core potentials (ECPs). All compounds have positive heats of

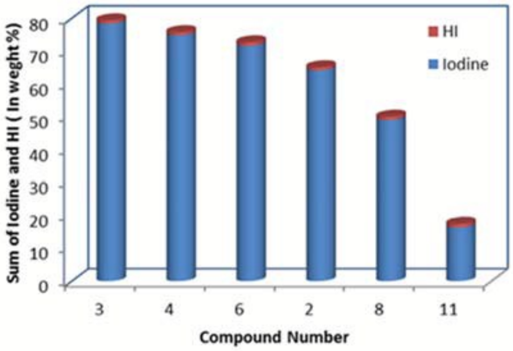


Figure 1. The sums of iodine-containing species in the decomposition products of compounds **2**, **3**, **4**, **6**, **8** and **11** (weight percent).

Table 2. Major decomposition products - Cheetah 7 calculations [wt. % kg kg^{-1}]

comp	N_2 [g]	I_2 [g]	HI [g]	C [s]
2	21.6	64.1	1.0	9.3
3	12.0	78.4	1.0	6.6
4	12.6	74.8	1.0	8.1
6	12.0	71.6	1.1	10.0
8	22.1	49.0	1.0	5.9
11	21.0	16.4	1.1	7.9

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formation. As expected, **8**, **9, 10** and **11** with nitro substituents have higher positive heats of formation. The calculated values for heats of formation and experimental densities were used to predict the detonation velocities (*D*) and detonation pressures (*P*) using the Cheetah 7 program. All of the compounds have low detonation pressures which range from 7.91 to 21.24 GPa and a range of detonation velocities from 3639 to 6028 ms^{-1}.

The decomposition products, I_2 and HI, were predicted using Cheetah 7. As shown in Figure 1, **3** has the highest iodine concentration in its decomposition products at ~79%, followed by **4** at 75%. Each of the isomeric N-alkyl triazole pairs, i.e., **4**, **5** and **6**, **7** as well as **8**, **9** and **10**, **11** give identical calculated decomposition products.

X-ray Crystallography

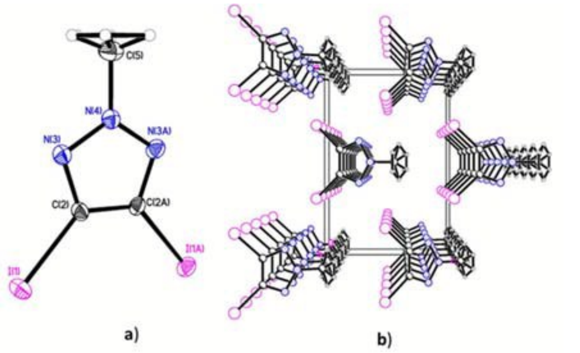

Figure 2: a) Thermal ellipsoid plot (50%) and labeling scheme for **5**. b) Packing diagram of **5** along a axis.

Crystallographic data for **5**, **6**, **8** and **10** are summarized in Table S1 (ESI). Crystals of **5** were obtained by slow evaporation of a saturated solution of the compound in a mixture of ethyl acetate and hexane. The crystals belong to orthorhombic crystal system and are in the Pmn2_1 space group with two molecules per unit cell. The N2-methyl substituent does not appear to hinder strong $\pi - \pi$ stacking interaction between the rings as shown in Figure 2 (b). The carbon- iodine bond length I(1)-C(2) [2.070(5) Å] is comparable to similar bonds in **6** (Figure 3).

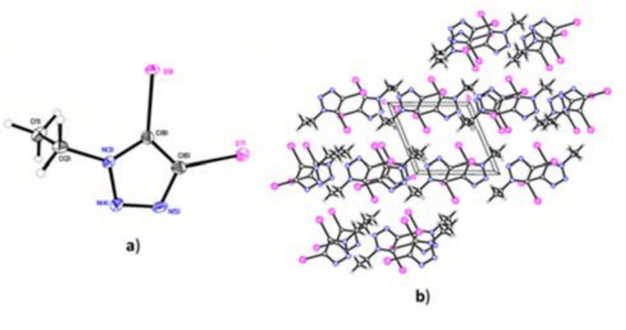

Figure 3. a) Thermal ellipsoid plot (50%) and labeling scheme for **6**. b) Packing diagram of **6** along a axis

Slow evaporation of a saturated solution of **6** in a mixture of ethyl acetate and hexane gave suitable crystals for X-ray crystal structure analysis. There are two molecules in the unit cell in the P-1 space group (Figure 3). Crystal units are packed so as to separate the bulky N-ethyl groups as seen in Fig. 3 (b).

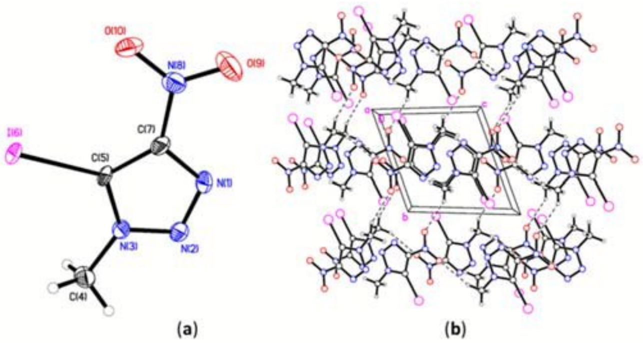

Figure 4. a) Thermal ellipsoid plot (50%) and labeling scheme for **8**. b) Packing diagram of **8** along a axis

Triclinic crystals of **8** were obtained by slow evaporation of a saturated solution in benzene and diethyl ether at room temperature. There are two molecules per unit cell in the crystal which belongs to the P-1 space group. As shown in Figure 4, there are strong intermolecular hydrogen bonding interactions between hydrogen atoms of the methyl group and the oxygen atoms of the nitro group. A nitro group adjacent to a carbon-bearing iodine atom does not appear to influence the carbon iodine bond length C(5)-I(6) [2.072(5) Å].

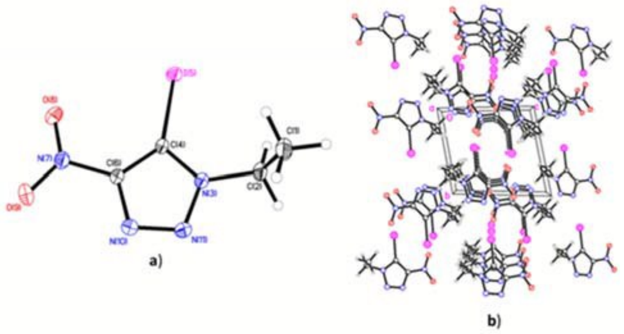

Figure 5. a) Thermal ellipsoid plot (50%) and labeling scheme for **10**. b) Packing diagram of **10** along a axis.

Crystals of **10** suitable for X-ray crystallography were obtained by using a procedure similar to **8**. The triclinic crystals belong to the P-1 space group. The planarity of the ring is preserved in spite of the presence of the bulkier ethyl group. As a result there is strong π–π stacking interaction between the rings (Figure 5).Additionally, intermolecular van der Waals forces of attraction exist between the iodine and the oxygen atoms of the nitro group. The carbon-iodine bond length is similar to that in the other compounds.

Conclusions

4-Iodo-[1*H*]-1,2,3-triazole (**2**) and 4, 5-diiodo-[1*H*]-1,2,3-triazole (**3**) were synthesized using an efficient synthetic route.

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N-alkylation of **3** gave N1- and N2-alkylated isomers in each case. Nitration of these N-alkylated species resulted in iodo triazoles with improved oxygen balances. The iodo triazoles may increase the utility of 1*H*-1, 2, 3-triazoles in synthetic organic chemistry as well as in medicinal chemistry.

Experimental Section

General Methods

^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz (Bruker Avance 300) nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively, by using [D6]DMSO as solvent and locking solvent unless otherwise stated. A 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz was used to obtain ^{15}N spectra.The chemical shifts in ^{1}H and ^{13}C spectra are reported relative to Me_4S, and nitromethane for ^{15}N. The decomposition temperatures (onset) were obtained using a differential scanning calorimeter (DSC) (Model Q 10, TA Instruments Co.) at a scanning rate of 5 °C per minute in closed aluminum containers with a small hole in the lids. IR spectra were recorded using KBr pellets on a BIORAD model 3000 FTS spectrometer. Densities were determined at room temperature employing a Micromeritics AccuPyic 1330 gas pycnometer. Elemental analyses were carried out using an Exeter CE-440 elemental analyzer.

X-ray Crystallography

Colorless plate crystals of dimensions 0.399 x 0.206 x 0.018 mm^3 for **5**, 0.316 x 0.115 x 0.104 mm^3 for **6**, 0.223 x 0.150 x 0.037 mm^3 for **8,** and 0.174 x 0.077 x 0.014 mm^3 for **10** were mounted on MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation (λ = 0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 150(2) K during data collection.

Data collection was performed and the unit cell was initially refined using *APEX3* [v2014.3-0].[8] Data reduction was performed using *SAINT* [v7.68A][9] and *XPREP* [v2014/2].[10] Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2008/1].[11] The structure was solved and refined with the aid of the programs SHELXL-2014/7 within WingX.[12, 13] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

4-Iodo-[1*H*]-1,2,3-triazole (2) and 4,5-diiodo-[1*H*]-1,2,3-triazole (3).

1-Iodo-1,2,3-triazole [4] (0.06 mol, 11g) was supended in 15 % aqueous ammonia (10 mL) and heated with occasional shaking at 100 °C in a thick-walled pressure tube. After 10-15 minutes, heating was stopped when a clear solution was obtained. After cooling the tube, the aqueous ammonia was evaporated by blowing air over the solution and the residue was taken up in water (100 mL). The solution was acidified with concentrated HCl to pH 3 to obtain an off-white precipitate which was filtered and washed with cold water. The compound was identified as 4,5-diiodo-[1*H*]-1,2,3-triazole (**3**). The filtrate was extracted with diethyl ether which was evaporated using a rotary evporator and the residue was dried in vacuo. The compound was identified as 4-iodo-1,2,3-triazole (**2**).

2: Yield 33.3%. (3.9 g). T_m = 110.8 °C, T_{dec} (onset) = 156. 6 ^{o}C; IR (KBr) υ 3429, 3115, 2962, 2916, 1633, 1504, 1445, 1300, 1224, 1178, 1136, 1074, 927, 864, 817, 636 cm^{-1} ; ^{1}H NMR δ 15.4 (broad, NH), 8.0 (ring – CH) ; ^{13}C NMR δ 135.9, 89.4; elemental analysis: (%) calculated for $C_2H_2IN_3$ (194.96): C, 12.32; H, 1.03; N, 21.55; found C, 12.15; H, 1.03; N, 21.15.

3: Yield 25%. T_{dec} (onset) = 189. 9 ^{o}C; IR (KBr) υ 3430, 3121, 2943, 2827, 1718, 1629, 1556, 1503, 1444, 1332, 1284, 1179, 1091, 1008, 979, 804, 458 cm^{-1} ; ^{1}H NMR δ 15.6 (broad, NH) ; ^{13}C NMR δ 104.2; elemental analysis: (%) calculated for $C_2H\,I_2\,N_3$ (320.86): C, 7.49; H, 0.31; N, 13.10; found C, 7.65; H, 0.24; N, 13.10.

1-Methyl-4,5-diiodo-1,2,3-triazole (4) and 2-methyl-4,5-diiodo-1,2,3-triazole (5).

4,5-Diiodo-1,2,3-[1*H*]-triazole (14.6 mmol, 4.7 g) was dissolved in DMF (5 mL) and potassium carbonate (23.15 mmol, 3.2g) was added. The mixture was cooled to -20 °C in an ice-salt bath. Iodomethane (21.8 mmol, 1.36 mL) was added to the cooled mixture and stirred for two hours. An off-white precipitate was formed which was filtered and washed with water. Analysis by TLC indicated the mixture contained two constituents which were separated using column chromatography [eluent - hexane: ethyl acetate (2:8)]. Yield = 82% (4.7 g).

4: Yield 48 %. T_m = 185.7 °C, T_{dec} (onset) = 212.7 ^{o}C; IR (KBr) υ 2924, 1421, 1383, 1265, 1195, 1084, 1028, 983, 709 cm^{-1}; ^{1}H NMR δ 4.1 (methyl, H), 8.0; ^{13}C NMR δ 102.7, 95.3; ^{15}N NMR δ –0.5, -19.9, -133.7; elemental analysis: (%) calculated for $C_3H_3I_2N_3$ (334.88): C, 10.76; H, 0.90; N, 12.55; found C, 11.10; H, 0.91; N, 12.31.

5: Yield 52 %, T_m = 129.7 °C; IR (KBr) υ 2925, 2854, 1638, 1438, 1413, 1365, 1292, 1018, 716, 644, 448 cm^{-1}; ^{1}H NMR δ 15.4 (broad, NH), 4.1 (methyl – H) ; ^{13}C NMR δ 104.3, 42.3; ^{15}N NMR δ –39.5, -117.1; elemental analysis: (%) calculated for $C_3H_3I_2N_3$ (334.88): C, 10.76; H, 0.90; N, 12.55; found C, 10.78; H, 0.88; N, 12.21.

1-Ethyl-4,5-diiodo-1,2,3-triazole (6) and 2-ethyl-4,5-diiodo-1,2,3-triazole (7).

N-ethylation of 4,5-diiodo-1,2,3-triazole was carried out using the procedure used for **4** and **5**. Yield 85%. The two isomers **6** and **7** were separated using silica gel column chromatography. [Eluent – hexane: ethyl acetate (1:9)]

6: Yield 47%. T_m = 127.5 °C, T_d = 170.9 °C ; IR (KBr) υ 2992, 2975, 2955, 2932, 1631, 1531, 1418, 1438, 1431, 1404, 1376, 1340, 1296, 1238, 1097, 989, 1045, 989, 958, 785, 683 cm^{-1} ; ^{1}H NMR δ 4.4 (CH_2), 1.4 (CH_3) ; ^{13}C NMR δ 102.9, 93.9, 15.1; elemental analysis: (%) calculated for $C_4H_5I_2N_3$ (348.91): C, 13.77; H, 1.44; N, 12.04; found C, 13.67; H, 1.42; N, 11.52.

7: Yield 47%. T_m = 108.1 °C ; IR (KBr) υ 2981, 2926, 2852, 1443, 1386, 1361, 1330, 1084, 1016, 964, 795, 690, 657, 430 cm^{-1} ; ^{1}H NMR δ 4.4 (CH_2), 1.4 (CH_3) ; ^{13}C NMR δ 104.4, 50.7, 14.5; ^{15}N NMR δ –1.8, -19.5, -121.9; elemental analysis:

(%) calculated for $C_4H_5I_2N_3$ (348.91): C, 13.77; H, 1.44; N, 12.04; found C, 13.98; H, 1.44; N, 12.04.

1-Methyl-4-nitro-5-iodo-1,2,3-triazole (8).

1-Methyl-4,5-diiodo-1,2,3-triazole (1 g, 3 mmol) was added portion wise to 10 mL of 100% nitric acid and the mixture was heated at reflux for six hours. After cooling to room temperature the mixture was poured onto crushed ice to give a pale yellow precipitate which was filtered, and washed with cold water (10 mL x 3) to obtain **8.**

8: Yield 62 %. T_m = 98.0 °C ; IR (KBr) υ 2924, 2853, 1539, 1435, 1377, 1300, 1267, 1219, 1097, 1045, 831, 717, 435 cm^{-1} ; ^1H NMR δ 4.1(CH_3); ^{13}C NMR δ 155.3, 88.3, 38.6; ^{15}N NMR δ -11.6, -25.2, -35.0, -128.4; elemental analysis: (%) calculated for $C_3H_3IN_4O_2$ (253.99): C, 14.19; H, 1.19; N, 22.06; found C, 14.49; H, 1.22; N, 21.63.

2-Methyl-4-nitro-5-iodo-1,2,3-triazole (9).

Compound **9** was prepared following a procedure similar to that for **8** by using 2-methyl-4, 5-diiodo-1,2,3-triazole (1 g, 3 mmol).

9: Yield 63.3 %. T_m = 156.0 °C, T_d = 235.0 °C; IR (KBr) υ 2924, 2853, 1633, 1541, 1416, 1362, 1331, 1085, 831, 725, 644 cm^{-1} ; ^1H NMR δ 4.2 (CH_3); ^{13}C NMR δ 154.3, 91.4, 38.6; ^{15}N NMR δ -26.4, -31.5, -49.8, -123.0; elemental analysis: (%) calculated for $C_3H_3IN_4O_2$ (253.99): C, 14.19; H, 1.19; N, 22.06; found C, 14.63; H, 1.23; N, 20.91.

1-Ethyl-4-nitro-5-iodo-1, 2, 3-triazole (10).

Compound **10** was prepared following a procedure similar to that for **8** by using 1-ethyl-4, 5-diiodo-1, 2, 3-triazole (1 g, 2.9 mmol).

10: Yield 63 %. T_m = 111.2 °C, T_d = °C, T_d = 235.0 °C; IR (KBr) υ 1537, 1431, 1387, 1325, 1095, 1072, 968, 827, 650, 571, 474, 426 cm^{-1} ; ^1H NMR δ 4.5(CH_3), 1.4 (CH_2); ^{13}C NMR δ 154.2, 91.4, 51.8, 13.8; elemental analysis: (%) calculated for $C_4H_5IN_4O_2$ (268.01): C, 17.93; H, 1.88; N, 20.90; found C, 18.14; H, 1.87; N, 20.66

2-Ethyl-4-nitro-5-iodo-1, 2, 3-triazole (11).

Compound **11** was prepared following a procedure similar to **8** by using 2-ethyl-4, 5-diiodo-1, 2, 3-triazole (1 g, 2.9 mmol). **11**: Yield 64 %. Tm = 111.2 °C, Td = °C; IR (KBr) υ 2992, 2924, 1635, 1538, 1484, 1440, 1410, 1374, 1295, 1255, 1186, 1105, 1043, 958, 833, 692 cm-1 ; 1H NMR δ 4.5(CH3), 1.4 (CH2); 13C NMR δ 155.3, 87.0, 47.2, 14.4; ^{15}N NMR δ -26.3, -34.0, -52.1, -111.5 elemental analysis: (%) calculated for C4H5IN4O2 (268.01): C, 17.93; H, 1.88; N, 20.90; found C, 17.99; H, 1.84; N, 20.50

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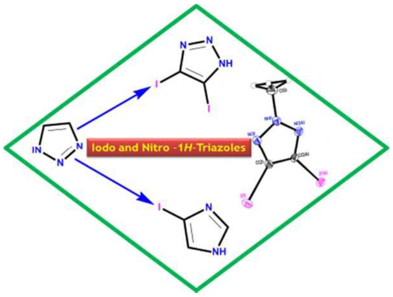

TOC

An efficient synthetic route to mono and diiodo-1*H*-1,2,3-triazoles