An Efficient Route to 1,3,5-Triazido-2,4,6-tricyanobenzene

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Dedicated to Professor Wolfgang Beck on the occasion of his 80th birthday

An efficient synthetic route starting from 1,3,5-trimethylbenzene is described for binary 1,3,5-triazido-2,4,6-tricyanobenzene. Besides 1,3,5-triazido-2,4,6-tricyanobenzene, all intermediates have been isolated and fully characterized.

Key words: Polyfunctional Aromatic Compounds, Nitriles, Azides

Introduction

Benzonitriles and organic azides are of particular importance as components of dyes, herbicides, natural products, and drugs [1 – 6]. For example, it is possible to convert the nitrile group into a variety of other functional groups. Therefore benzonitriles are important intermediates for the synthesis of biologically important structures such as benzoic acid derivatives, benzyl amines, benzyl amides, and heterocyclic compounds. Due to the diverse applications of benzonitrile numerous synthetic possibilities have been developed. In particular, the Rosenmund-von-Braun reaction [7] (reaction of aryl halides with copper(I) cyanide) and the Sandmeyer reaction [8] (reaction of arene-diazonium salts with copper(I) cyanide) are used. The problem of both methods is the formation of stoichiometric amounts of heavy metal salts. Therefore, today aryl cyanides are produced primarily by the ammoxidation of the corresponding toluenes [9, 10]. This process requires harsh reaction conditions and shows a lack of tolerance of other functional groups.

Another way to generate the nitrile group is the stepwise construction of a CN moiety by application of a series of classical organic synthesis steps as shown in Scheme 1. Here we report on the stepwise synthesis and full characterization of binary 1,3,5-triazido-2,4,6-tricyanobenzene.

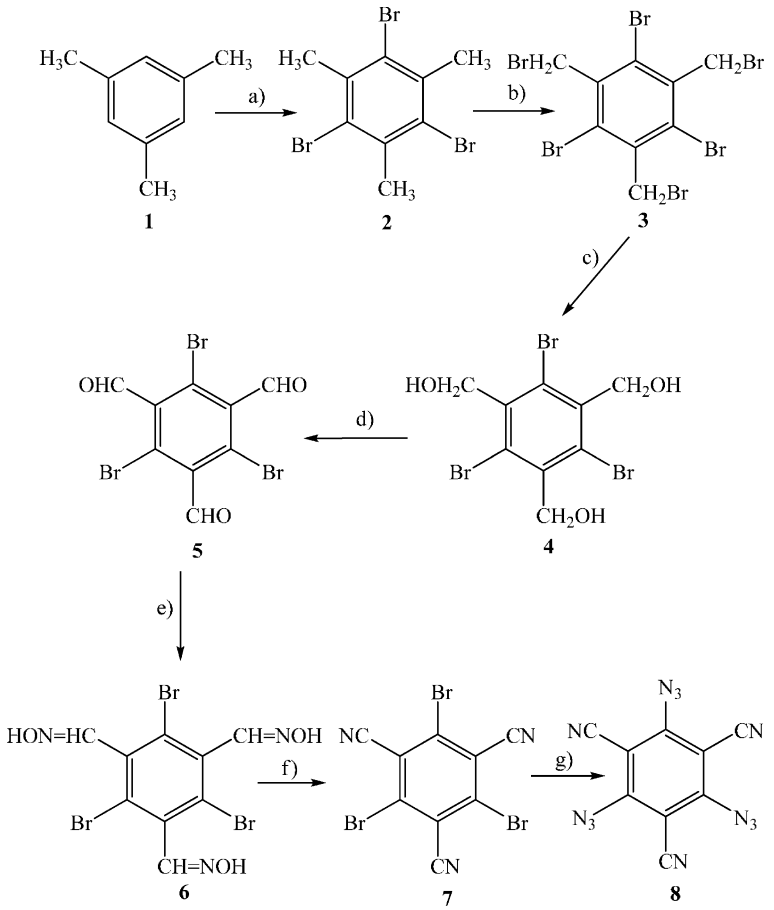
Results and Discussion

Synthesis

As starting material for the synthesis of 1,3,5-tribromo-2,4,6-trimethylbenzene (**2**), commercially available 1,3,5-trimethylbenzene (**1**) was used. Different bromination reactions were attempted [11 – 17], however, the utilization of $Br_2/AlBr_3$ gave the best results (Scheme 1). For this reason, 1,3,5-trimethylbenzene (**1**) was dropped slowly at 0 °C to a mixture of bromine and aluminum bromide [12] to obtain 1,3,5-tribromo-2,4,6-trimethylbenzene (**2**).

Bromination of the methyl groups of **2** leads to 1,3,5-tribromo-2,4,6-tris(bromomethyl)benzene (**3**) [12 – 20]. To a solution of **2** in 1,2-dibromoethane bromine is slowly added drop wise, and the reaction mixture is heated. The beginning of the radical chain reaction is indicated by the resulting hydrogen bromide gas. The product **3** precipitates and can be filtered and purified. By means of NMR spectroscopy the progress of the reaction is easily followed.

Starting with **3**, 1,3,5-tribromo-2,4,6-tris(hydroxymethyl)benzene (**4**) can be synthesized in a two-step reaction [12, 13]. A suspension of **3** and potassium acetate in DMF is heated. After purification, the substitution product in which the bromomethyl groups were exchanged by acetoxymethyl groups is hydrolyzed to



Scheme 1. Stepwise preparation of 1,3,5-triazido-2,4,6-tricyanobenzene. a) Br_2, $AlBr_3$, 0 °C → 20 °C, 12 h; b) Br_2, 1,2-dibromo-ethane, Δ, 20 h; c) 1. KOAc, DMF, 80 °C, 20 h, 2. KOH, H_2O, 90 °C, 20 h; d) NaOCl, KBr, TEMPO (2,2,6,6-tetramethyl-piperidin-1-oxyl), DCM (CH_2Cl_2)/H_2O, r. t., 3 d; e) NaOAc, H_2N-OH·H_2O, EtOH, 60 °C, 2 h; f) Ac_2O, Δ, 6 h; g) NaN_3, CH_3CN, Δ, 1 h.

the desired product by heating in potassium hydroxide solution. After cooling, the suspension is neutralized, and the resulting product **4** is filtered off.

2,4,6-Tribromo-1,3,5-benzenetricarbaldehyde (**5**) can be generated by selective oxidation of **4**. As oxidizing agents chromium(VI) reagents (chromium trioxide, chromic acid, chromates), manganese(IV) oxide, halogen compounds (chlorine, hypochloric acid) and dimethyl sulfoxide are commonly used [21]. Compound **4** was suspended in a mixture of water/dichloromethane, and NaOCl and KBr were added besides TEMPO (2,2,6,6-tetramethyl-piperidin-1-oxyl). The suspension was stirred for 2 days. The resulting compound **5** is soluble in dichloromethane in contrast to **4**. One advantage of the oxidation with TEMPO is that over-oxidation during the long reaction time is not possible. Another advantage is the possibility to recover the unreacted starting material by filtering.

2,4,6-Tribromo-1,3,5-tris(hydroxyiminomethyl)-benzene (**6**) is easily synthesized from compound **5** by addition of hydroxylamine. It was found that the reaction proceeds most efficiently in the presence of an acid. Therefore we used hydroxylamine hydrochloride. In the ^{13}C NMR spectra the carbon resonance signals of the *C*HO group in **5** and the *C*HN group in **6** shows a significant upfield shift from $\delta = 192.9$ to 147.5 ppm. The quaternary ring carbon atoms, however, show similar chemical shifts (136.7 and 123.4 ppm in **5** *vs.* 134.7 and 125.6 ppm in **6**). The ^1H NMR spectrum

of **5** shows a typical signal for aldehydes (C*H*O) at 10.07 ppm, whereas for **6** two resonances [11.79 ppm (C*H*N) and 8.07 (NO*H*)] are obtained.

1,3,5-Tribromo-2,4,6-tricyanobenzene (**7**) is obtained by dehydration of the oxime group which can be achieved by dehydrating agents such as carbon disulfide [22], thionyl chloride in dichloromethane [23], pyridine and trifluoroacetic anhydride in 1,4-dioxane [24], pyridine and methanesulfonyl chloride [25]. In the synthetic route applied, the aldoxime was heated with acetic anhydride [26]. After purification the corresponding colorless nitrile compound (**7**) is obtained. IR spectroscopy provides a simple way to detect the dehydration of the hydroxyimino groups in **6** to the cyano groups in **7**. The product shows the typical CN stretching vibration at $\nu = 2232\,\mathrm{cm}^{-1}$. ^{13}C NMR spectroscopy can also be used to study the transformation of **6** to **7** as illustrated by a significant upfield shift from $\delta = 147.5$ in **6** (R-*C*H=NOH) to 115.0 ppm in **7** (R-*C*N).

Finally, 1,3,5-triazido-2,4,6-tricyanobenzene (**8**) is obtained by a halogen/pseudohalogen exchange reaction. Compound **7** and sodium azide are heated in acetonitrile [26]. 1,3,5-Triazido-2,4,6-tricyanobenzene (**8**) represents a thermally stable binary CN compound with two different alternating functional groups. Although an organic azide, it is neither heat (<160 °C) nor shock sensitive, but at temperatures above 160 °C it decomposes violently.

It is known that organic azides, in order to be non-explosive, should have a smaller number of nitrogen atoms compared to the number of carbon atoms, and the quotient of the number of carbon and nitrogen atoms should be larger than three [27]. For triazide **8** with the chemical formula C_9N_{12} both conditions are not fulfilled. The number of nitrogen atoms significantly exceeds the number of carbon atoms, and the quotient is only 0.75.

Substitution of all three bromine atoms in **7** by azido groups in **8** leads to a significant change in the chemical shifts of the resonance signals in the ^{13}C NMR spectra $\delta = 136.0$, 117.0 and 115.0 ppm in **7** *vs.* 149.7, 110.2 and 95.6 ppm in **8**. The vibrational spectrum of the triazide **8** features the presence of covalently bonded azido ligands by the strong asymmetrical stretching modes in the range $2300-2000\,\mathrm{cm}^{-1}$ (besides ν_{CN}), the symmetrical stretching modes at $1400-1200\,\mathrm{cm}^{-1}$ and the deformation modes at $700-600\,\mathrm{cm}^{-1}$ [5]. The presence of more than one azido/cyano ligand results in in-phase and out-of-phase coupling giving rise to strong and very broad asymmetric stretching modes of the azide groups.

Table 1. Crystallographic details of **3**, **4** and **8**.

	3	**4**	**8**
Chem. Formula	$C_9\,H_6\,Br_6$	$C_9\,H_{10}\,Br_3\,O_{3,5}$	C_9N_{12}
M_r, g mol^{-1}	593.6	413.9	276.2
Color	colorless	colorless	brown
Crystal system	triclinic	tetragonal	orthorhombic
Space group	$P\bar{1}$	$I\bar{4}2d$	$P2_12_12_1$
a, Å	4.769(4)	8.821(5)	5.970(4)
b, Å	9.405(7)	8.821(5)	11.318(7)
c, Å	15.12(1)	30.67(2)	16.878(12)
α, deg	84.74(3)	90	90
β, deg	86.96(3)	90	90
γ, deg	79.99(3)	90	90
V, Å^3	664.7(9)	2386(2)	1140(1)
Z	2	8	4
$\rho_{calc.}$, g cm^{-3}	2.97	2.30	1.61
T, K		173(2)	
Radiation; λ, Å		MoK_α; 0.71073	
μ(MoK_α), mm^{-1}	18.1	10.1	0.1
F(000), e	540	1576	552
Refl. measd./	10038/	7095/	8563/
indep./	4641/	1915/	3757/
R_{int}	0.037	0.030	0.034
Refl. with $I > 2\sigma(I)$	3341	1685	3143
Parameters	136	82	190
R_1 (F) [$F^2 > 2\sigma(F^2)$]	0.0350	0.0215	0.0384
wR_2 (F^2) (all data)	0.0733	0.0457	0.0950
GooF	0.926	1.053	1.003
$\Delta\rho_{max/min}$, e Å^{-3}	0.64/−1.15	0.39/−0.43	0.30/−0.18
CCDC	880714	880713	880712

X-Ray crystallography

The structures of compounds **3**, **4** and **8** have been determined. Table 1 presents the X-ray crystallographic data. X-ray quality crystals were selected in Kel-F-oil (Riedel deHaen) or Fomblin YR-1800 (Alfa Aesar) at ambient temperature. All samples were cooled to –100(2) °C during measurements. The molecular structures of **3**, **4** and **8** are shown in Figs. 1–3, respectively, along with selected bond lengths and angles. We want to focus the discussion on the target molecule, the triazido species **8**.

Compound **8** crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units per cell. The asymmetric unit consists of one almost C_{3h}-symmetric molecule. There are no significant intermolecular interactions within the unit cell. The molecules are stacked parallel to each other. As shown on numerous occa-

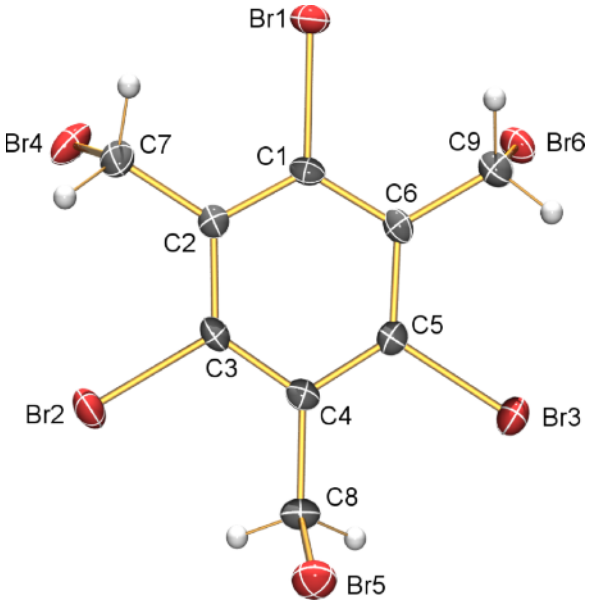


Fig. 1 (color online). ORTEP drawing of the molecular structure of 1,3,5-tribromo-2,4,6-tris(bromomethyl)-benzene (**3**) in the crystal. Ellipsoids are drawn with 50% probability at 173 K. Selected bond lengths (Å) and angles (deg): Br1–C1 1.908(3), Br2–C3 1.910(3), Br3–C5 1.907(3), Br4–C7 1.963(3), Br5–C8 1.962(3), Br6–C9 1.968(3); C2–C1–C6 123.5(3), C2–C1–Br1 118.5(2), C6–C1–Br1 118.0(2), C4–C3–C2 123.9(3), C4–C3–Br2 117.9(2), C2–C3–Br2 118.2(2), C4–C5–Br3 118.1(2), C6–C5–Br3 118.4(2), C2–C7–Br4 109.8(2), C4–C8–Br5 108.6(2), C6–C9–Br6 110.5(2).

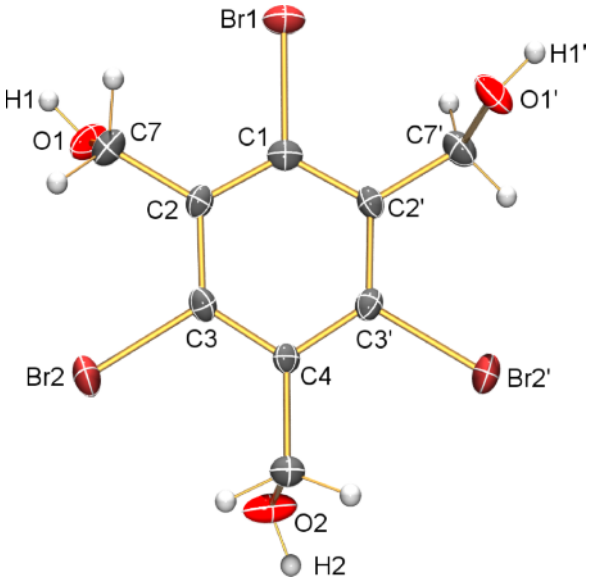


Fig. 2 (color online). ORTEP drawing of the molecular structure of 1,3,5-tribromo-2,4,6-tris(hydroxymethyl)-benzene (**4**) in the crystal (50% probability allipsoids at 173 K). Selected bond lengths (Å) and angles (deg): Br1–C1 1.902(6), Br2–C3 1.899(6), Br3–C5 1.893(6), C7–O1 1.431(8), C9–O3 1.422(8); C2–C1–Br1 117.6(4), C6–C1–Br1 118.0(4), C4–C3–Br2 118.4(4), C2–C3–Br2 118.6(4), C4–C5–Br3 118.4(4), C6–C5–Br3 118.5(4), O1–C7–C2 110.3(5), O3–C9–C6 110.2(5).

sions, covalently bound azide groups display a *trans*-bent configuration with a N_α–N_β–N_γ bond angle of 166 – 168 °C and a formally sp^2-hybridized N_α atom (*e. g.* N5–N4–C2 122.5(1)°) [27b]. The N_α–N_β bonds range between 1.23–1.25 Å (average 1.243 Å), and an average N_β–N_γ bond length of 1.115 Å is found, in accord with our expectation [27b].

Conclusion

Binary 1,3,5-triazido-2,4,6-tricyanobenzene was obtained in a novel seven-step synthetic protocol. This efficient synthetic route starts from 1,3,5-trimethylbenzene and leads *via* successive introduction of functional groups such as -CHO, -CHOH, -CHNOH, and finally -CN to the product. It is interesting to note that the binary CN compound, triazide **8**, possesses formal $(C_3N_4)_3$ stoichiometry and might be used as precursor for CN-based materials.

Experimental Section

Unless otherwise described, all manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk techniques. All chemicals were commercially available and used as received. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker spectrometers Avance 250, 300, or 500. The ^{1}H and ^{13}C NMR chemical shifts (δ values in ppm) were referenced to the solvent signals (^{1}H: $\delta(CDCl_3) = 7.25$, δ ([D$_6$]DMSO) = 2.49; ^{13}C: δ ($CDCl_3$) = 77.0, δ ([D$_6$]DMSO) = 39.5 ppm). IR spectra: Nicolet 6700 FT-IR with Smart Endurance ATR device or Nicolet 380 FT-IR with Smart Orbit ATR module. Raman spectra: Bruker Vertex 70 FT-IR with RAM II FT-Raman module, equipped with an Nd:YAG laser (1064 nm). Mass spectra: Finnigan MAT 95-XP from Thermo Electron. CHN analyses: Analysator Flash EA 1112 from Thermo Quest. DSC measurements: Thermoanalytical measurements were performed with a Mettler-Toledo DSC 823e instrument. Two point calibrations with In (m. p. 156.6 °C) and Zn (m. p. 419.6 °C) were carried out. About 2 – 6 mg of the samples were weighed and contained in sealed aluminum crucibles. They were studied in the temperature range of 25 – 500 °C with a heating rate of 5 °C min^{-1}; throughout this process the

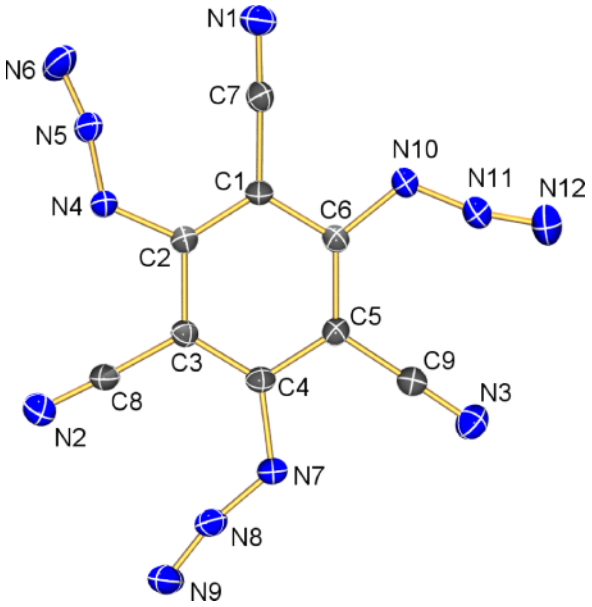


Fig. 3 (color online). ORTEP drawing of the molecular structure of 1,3,5-triazido-2,4,6-tricyanobenzene (**8**) in the crystal (50 % probability allipsoids at 173 K). Selected bond lengths (Å) and angles (deg): C1–C2 1.397(2), C1–C6 1.409(2), C1–C7 1.441(2), C2–N4 1.393(2), C4–N7 1.388(2), C6–N10 1.396(2), C7–N1 1.142(2), N4–N5 1.237(2), N5–N6 1.110(2), N7–N8 1.250(2), N8–N9 1.115(2), N10–N11 1.244(2), N11–N12 1.120(2); N4–C2–C1 126.7 (1), N4–C2–C3 112.5(1), N1–C7–C1 175.9(1), N2–C8–C3 177.1(1), N3–C9–C5 178.8(2), N5–N4–C2 122.5(1), N6–N5–N4 166.7(1), N8–N7–C4 120.5(1), N9–N8–N7 168.6(1), N11–N10–C6 120.7(1), N12–N11–N10 168.2(2).

furnance was flushed with dry nitrogen. For the evaluation of the output the STAR^e software was employed.

*1,3,5-Tribromo-2,4,6-trimethylbenzene (**2**)*

To a 1-L 3-necked flask containing aluminum bromide (0.27 g, 0.001 mol) and bromine (96 g, 0.6 mol) fitted with appropriate vents to accommodate the large quantities of HBr gas produced in this reaction, 1,3,5-trimethylbenzene (12 g, 0.1 mol) is added slowly within 1.5 h at 0 °C. Then the mixture is allowed to warm to room temperature and stirred for 2 d. After the addition of 50 mL of water, the crude product is filtered, washed with water and recrystallized from $CHCl_3$ to give colorless fine needles (23 g, 65 %). – DSC: onset 226 °C, 330 °C (dec.). – $C_9H_9Br_3$: calcd. C 30.29, H 2.54; found C 30.31, H 2.25. – ^{13}C NMR ($CDCl_3$, 63 MHz, 25 °C): $\delta = 137.0$ (s, C_{quart}, 3C), 124.0 (s, C_{quart}, 3C), 26.3 (s, CH_3, 3C). – ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta = 2.68$ (s, CH_3, 9H). – IR (ATR, cm^{-1}): $\nu = 1539$ (w), 1375 (w), 1349 (m), 1269 (w), 1017 (w), 949 (s), 646 (s). – Raman (400 mW, 1000 scans, cm^{-1}): $\nu = 2924$ (7), 1543 (2), 1384 (3), 1301 (2), 1058 (1), 955 (1), 589 (6), 339 (1), 233 (10), 153 (5).

*1,3,5-Tribromo-2,4,6-tris(bromomethyl)benzene (**3**)*

To 1,3,5-tribromo-2,4,6-trimethylbenzene (35.7 g, 0.1 mol) in 150 mL of 1,2-dibromoethane in a 1-L flask equipped with a reflux condenser is added bromine (48 g, 0.3 mol) over a period of 30 min at room temperature. The mixture is heated to reflux for 20 h. Upon cooling the reaction mixture to r. t. the product precipitates. The crude product is filtered, washed with a small amount of 1,2-dibromoethane and recrystallized from $CHCl_3$ to give a colorless powder (56 g, 96 %). – DSC: onset 227 °C, 331 °C (dec.). – ^{13}C NMR ($CDCl_3$, 63 MHz, 25 °C): $\delta = 138.3$ (s, C_{quart}, 3C), 125.1(s, C_{quart}, 3C), 37.0 (s, CH_2, 3C). – ^{1}H NMR ($CDCl_3$, 250 MHz, 25 °C): $\delta = 4.94$ (s, CH_2, 6H). – IR (ATR, cm^{-1}): $\nu = 1532$ (m), 1430 (m), 1368 (s), 1300 (w), 1213 (s), 962 (s), 971 (s), 864 (s), 737 (w), 686 (w), 649 (s), 614 (m), 595 (m), 536 (s). – Raman (400 mW, 1034 scans, cm^{-1}): $\nu = 3046$ (1), 2994 (5), 2923 (6), 1536 (7), 1432 (1), 1379 (3), 1301 (7), 1216 (7), 644 (2), 616 (3), 537 (7), 394 (1), 305 (1), 232 (10), 156 (4), 109 (2). – MS: m/z (%) = 594 (0.2) $[M]^+$, 514 (7) $[M–Br]^+$, 435 (100) $[M–2Br]^+$, 353 (20) $[M–3Br]^+$. – HRMS (EI): $m/z = 593.54910$ (calcd. 593.55029 for $C_9H_6{}^{79}Br_3^{81}Br_3$).

*1,3,5-Tribromo-2,4,6-tris(hydroxymethyl)benzene (**4**)*

To 150 mL of DMF are added 1,3,5-tribromo-2,4,6-tris(bromomethyl)benzene (14.9 g, 0.025 mol) and KOAc (14.7 g, 0.150 mol). The mixture is heated to 80 °C for 20 h and then cooled to r. t., treated with 100 mL of water, poured into CH_2Cl_2, and extracted. The organic layer is washed with water, dried with Na_2SO_4. After evaporation of the solvent, to the residue is added aq. KOH (14 g, 0.250 mol) and the mixture stirred and heated to 90 °C for 24 h. The reaction mixture is cooled, neutralized, and the colorless solid filtered off and washed with small amounts of MeOH and Et_2O to give the final product (9.2 g, 92 %). – DSC: onset 262 °C, 314 °C (dec). – ^{13}C NMR ([D$_6$]DMSO, 63 MHz, 25 °C): $\delta = 139.6$ (s, C_{quart}, 3C), 128.5 (s, C_{quart}, 3C), 65.4 (s, CH_2, 3C). – ^{1}H NMR ([D$_6$]DMSO, 250 MHz, 25 °C): $\delta = 5.24$ (t, $^3J = 5.12$ Hz, OH, 3H), 4.88 (d, $^3J = 5.12$ Hz, CH_2, 6H). – IR (ATR, cm^{-1}): $\nu = 3153$ (m), 1538 (m), 1369 (m), 1302 (w), 1219 (w), 1035 (s), 1020 (s), 1000 (s), 943 (s). – Raman (400 mW, 1803 scans, cm^{-1}): $\nu = 2962$ (1), 2905 (1), 1541 (4), 1484 (1), 1372 (1), 1285 (3), 1066 (1), 1040 (1), 571 (2), 412 (1), 233 (10), 155 (4). – MS: m/z (%) = 403 (100) $[M]^+$, 405 (99) $[M]^+$, 401 (29) $[M]^+$. – HRMS (EI): $m/z = 403.80728$ (calcd. 403.80759 for $C_9H_6O_3^{79}Br_2^{81}Br_1$).

*2,4,6-Tribromo-1,3,5-benzenetricarbaldehyde (**5**)*

To a solution of 1,3,5-tribromo-2,4,6-tris(hydroxymethyl)benzene (4 g, 10 mmol) in 50 mL of CH_2Cl_2 are added 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (48 mg, 0.3 mmol) and KBr (360 mg, 3 mmol) in 5 mL of water. To this two-phase system NaOCl (2.2 g, 30 mmol) in water is added at 0 °C over 30 min. After the addition is complete the reaction mixture is allowed to warm to r. t. and stirred for 3 d. The suspension is filtered, the filtrate poured into CH_2Cl_2 and extracted. The organic layer is washed with water and dried with Na_2SO_4. After evaporation of the solvent, the residue is recrystallized from EtOH to give a colorless solid (0.79 g, 20 %). – DSC: onset 245 °C, 285 °C (dec). – $C_9H_3Br_3O_3$: calcd. C 27.10, H 0.76; found C 27.48, H 0.87. – ^{13}CNMR ([D$_6$]DMSO, 63 MHz, 25 °C): $\delta = 192.9$ (s, CHO, 3C), 136.7 (s, C_{quart}, 3C), 123.4 (s, C_{quart}, 3C). – ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 25 °C): $\delta = 10.07$ (s, CHO, 3H). – IR (ATR, cm^{-1}): $\nu = 2890$ (w), 1696 (vs), 1525 (s), 1332 (w), 1261 (w), 987 (m), 940 (s), 799 (m). – Raman (400 mW, 1000 scans, cm^{-1}): $\nu = 2920$ (3), 1703 (9), 1531 (5), 1378 (1), 1277 (2), 546 (1), 234 (10), 153 (2).

*2,4,6-Tribromo-1,3,5-tri(hydroxyiminomethyl)benzene (**6**)*

To a solution of 2,4,6-tribromo-1,3,5-benzenetricarbaldehyde (4 g, 10 mmol) in 50 mL of EtOH are added NaOAc (4.9 g, 60 mmol) and hydroxylammonium chloride (4.2 g, 60 mmol). The mixture is heated to 60 °C for 2 h, cooled and poured into ice water. The crude product is filtered, washed with EtOH and dried in a vacuum (3.04 g, 69 %). – DSC: onset 150 °C, 229 °C (dec). – $C_9H_6Br_3N_3O_3$: calcd. C 24.35, H 1.36, N 9.47; found C 24.10, H 1.65, N 8.39. – ^{13}C NMR ([D$_6$]DMSO, 63 MHz, 25 °C): $\delta = 147.5$ (s, HCN, 3C), 134.7 (s, C_{quart}, 3C), 125.6 (s, C_{quart}, 3C). – ^{1}H NMR ([D$_6$]DMSO, 250 MHz, 25 °C): $\delta = 11.79$ (s, HCN, 3H), 8.07 (s, OH, 3H). – IR (ATR, cm^{-1}): $\nu = 3270$ (br), 1610 (w), 1530 (w), 1441 (w), 1291 (w), 1265 (w), 1026 (m), 973 (s), 914 (s), 661 (m), 563 (w), 545 (w). – Raman (400 mW, 1000 scans, cm^{-1}): $\nu = 2928$ (1), 2236 (10), 1537 (2), 1294 (3), 524 (1), 295 (1), 240 (1), 156 (2).

*1,3,5-Tribromo-2,4,6-tricyanobenzene (**7**)*

A solution of 2,4,6-tribromo-1,3,5-tri(hydroxyiminomethyl)benzene (4.4 g, 10 mmol) in 50 mL of acetic anhydride is heated to reflux for 6 h. The solvent is removed *in vacuo* resulting in a brown residue. The crude product is recrystallized from benzene to give a colorless solid (2.4 g, 62 %). – DSC: 359 °C (dec.).– ^{13}C NMR ([D$_6$]DMSO, 63 MHz, 25 °C): $\delta = 136.0$ s, $C_{quart.}$, 3C), 117.0 (s, $C_{quart.}$, 3C), 115.0 (s, $C_{quart.}$, 3C). – IR (ATR, cm^{-1}): $\nu = 2232$ (w), 1532 (s), 1353 (s), 1137 (m), 1011 (m), 969 (m), 678 (s). – MS: *m/z* (%) = 389 (100) [M]$^+$, 391 (97) [M]$^+$, 387 (32) [M]$^+$. – HRMS (EI): $m/z = 388.76152$ (calcd. 388.76164 for $C_9N_3^{79}Br_2^{81}Br_1$).

*1,3,5-Triazido-2,4,6-tricyanobenzene (**8**)*

1,3,5-Tribromo-2,4,6-tricyanobenzene (255 mg, 1 mmol) and sodium azide (215 mg, 3.3 mmol) are heated in 25 mL of acetonitrile for 1 h under reflux. A color change from yellow to orange-brown can be noted. The hot suspension is filtered and freed from the precipitate of NaCl. Upon cooling to 5 °C brown needles precipitate. The product is filtered and dried in a vacuum (215 mg, 78 %). – DSC: 161 °C (dec). – C_9N_{12}: calcd. C 39.14, N 60.86; found C 39.09, N 60.91. – ^{13}C NMR ([D$_6$]DMSO, 75 MHz, 25 °C): $\delta = 149.7$ (s, C_{quart}, 3C), 110.2 (s, C_{quart}, 3C), 95.6 (s, C_{quart}, 3C). – IR (ATR, cm^{-1}): $\nu = 2228$ (w), 2170 (m, sh), 2114 (st, br), 1547 (s), 1404 (s), 1267 (s), 873 (m), 758 (w), 626 (w). – Raman (200 mW, 1500 scans, cm^{-1}): $\nu = 2234$ (10), 2128 (1), 1552 (4), 1408 (3), 1296 (2).

X-Ray structure determinations

X-Ray quality crystals of different samples were selected in Fomblin 1800 oil (Alfa Aesar) at ambient temperatures. All measurements were carried out at 173(2) K. The data were collected on a Bruker-Nonius Apex X8 CCD diffractometer using graphite-monochromatized Mo K_α radiation. The structures were solved by Direct Methods (SHELXS-97 [28]) and refined by full-matrix least-squares procedures (SHELXL-97 [29]). Semiemperical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the refinements at calculated positions using a riding model.

CCDC 880712 (**8**), 880713 (**4**), and 880714 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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