Synthesis A. Bodzioch et al. Paper

Efficient Synthesis of Bis(dibromomethyl)arenes as Important Precursors of Synthetically Useful Dialdehydes

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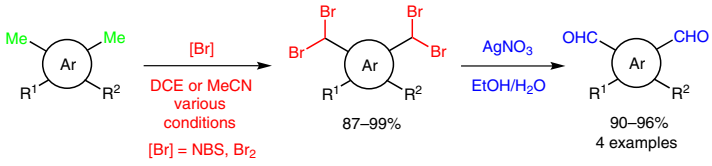

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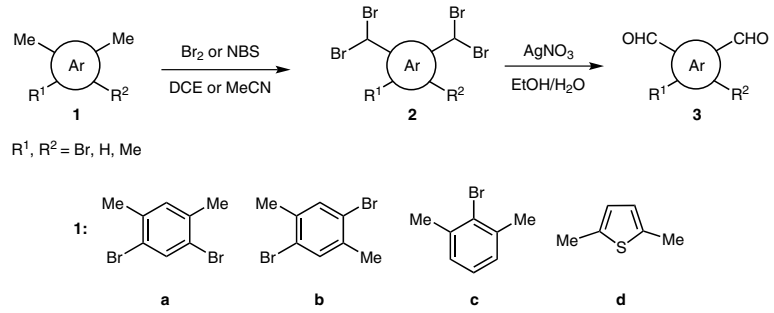
Abstract This work presents an efficient synthesis of bis(dibromomethyl)benzenes and a bis(dibromomethyl)thiophene as precursors of aromatic dialdehydes by bromination of dimethyl-substituted arenes under various reaction conditions (yields up to 99%). Several new variants of this reaction, including the use of *N*-bromosuccinimide (NBS) and bromine, and various solvents to replace carbon tetrachloride, benzene and carbon disulfide, were also tested. In the optimised protocols, the inconvenient solvents were replaced by 1,2-dichloroethane (DCE) and/or acetonitrile. In the DCE protocols, we reduced reaction times 24–32-fold, reduced the amount of NBS a fewfold and lowered power consumption relative to the literature protocols. The procedures also allowed elimination of long-lasting incandescent irradiation (100–500 W). The replacement of NBS by bromine led to a further reduction in the amount of brominating agent. The obtained bromo derivatives were efficiently converted into the corresponding dialdehydes (90–96%), which in turn are useful in materials chemistry.

Key words bis(dibromination), dialdehydes, radical reaction, solvents, bromine, *N*-bromosuccinimide

The aim of our present research was the synthesis of bis(dibromomethyl)aromatic derivatives **2** and aromatic dialdehydes **3**, as precursors of more complex, π-conjugated compounds, useful as optoelectronic materials. Isomeric dibromoxylenes **1a** and **1b**, monobromoxylene **1c** and 2,5-dimethylthiophene (**1d**) represent substrates for the corresponding bis(dibromomethyl)benzenes **2a**–**c** and 3,4-dibromo-2,5-bis(dibromomethyl)thiophene (**2d**) which can be further hydrolysed to the corresponding aromatic dialdehydes **3** with an aqueous ethanolic solution of silver nitrate (Scheme 1).

The dibromination of methyl groups in arenes is a known process;[1a–c] however, the reaction procedures are often inconvenient and have not been optimised. They usually require long reaction times in refluxing, toxic solvents (CCl_4, benzene, CS_2), use of a large excess of non-optimised amounts of brominating agents, and long-lasting UV or incandescent irradiation that leads to high power consumption. The aromatic dialdehydes **3** constitute useful compounds for the preparation of more complex molecules, which have been successfully used as optoelectronic materials, such as dibenz[*a*,*j*]anthracene,[1a] 2,3,6,7-tetraphenylanthracene,[2] dibenzo[*d*,*d′*]benzo[1,2-*a*:4,5-*a′*]dicycloheptenes[1b] and poly(*p*-phenylenevinylene) derivatives.[3] Dialdehydes **3** have also been applied in the synthesis of spindle-type chromophores for nonlinear, optical materials[4,5] and dithienothiophene-based polymers as promising materials for electrochromic displays and inks.[6] Both dibromodialdehyde isomers **3a** and **3b** have very recently been applied by our group in the synthesis of positional isomers of higher analogues of *o*-bromo(hetero)acenaldehydes.[7] Biological applications of dialdehydes **3** include the synthesis of cephalostatin analogues[8] and an *o*-quinone derivative of benzo[*a*]pyrene as an active carcinogenic metabolite of the parent polycyclic aromatic hydrocarbons.[9]

Synthesis of the precursor bis(dibromomethyl)benzenes **2a**–**c** has been limited to two methods involving perbromination of single isomers of the corresponding dibromoxylene **1a** and bromoxylene **1c** with *N*-bromosuccinimide (NBS) and dibromoxylene **1b** with bromine.[1a–c,8,10] Thus, bis(dibromination) of **1a** with a large excess (19 equiv) of NBS in refluxing carbon tetrachloride for 9 hours under incandescent irradiation (100 W) gave the desired 1,5-dibro-



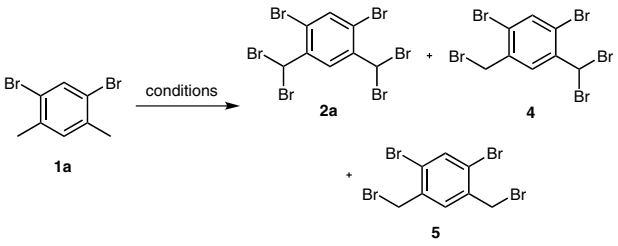
Scheme 1 Bis(dibromination) of methyl groups in arenes **1**

mo-2,4-bis(dibromomethyl)benzene (**2a**) in 88% yield.[1a] The bis(dibromination) reaction of 1,4-dibromo-2,5-dimethylbenzene (**1b**) with bromine in refluxing carbon tetrachloride, under irradiation with a high-power 500 W incandescent lamp for 4 hours, gave 1,4-dibromo-2,5-bis(dibromomethyl)benzene (**2b**) in 89% yield.[1b] Synthesis of 2-bromo-1,3-bis(dibromomethyl)benezene (**2c**) required conducting the reaction with 12 equivalents of NBS in refluxing benzene and incandescent irradiation for an extended 8 days.[8,10] On the other hand, bis(dibromination) of **1a** in refluxing carbon tetrachloride was achieved using only 4 equivalents of NBS.[1c] Bromination of 2,5-dimethylthiophene (**1d**) with bromine in the inconvenient solvent carbon disulfide afforded 3,4-dibromo-2,5-bis(dibromomethyl)thiophene (**2d**) in 71% yield.[1d]

In our studies, we optimised reaction conditions for the bromination of **1** in solvents other than carbon tetrachloride (bp 76.7 °C) (Scheme 1). It turned out that acetonitrile (bp 82 °C), considered as a preferred and usable solvent in the Pfizer solvent selection guide,[11] worked well in the case of isomeric **1a** and **1b**. In other cases, acetonitrile resulted in failure and only 1,2-dichloroethane (DCE) gave high yields of the final brominated products. As brominating agents, we used NBS and bromine. In the case of NBS, solvents (such as DCE, MeCN and benzene) in the presence or absence of radical initiators could be employed. We first attempted the bromination reaction of **1a** and **1b** in benzene to achieve only 65% and 81% yield of **2a** and **2b**, respectively (Table 1, entry 1, and Table 2, entry 2; see also Supporting Information).

In our next attempts, we applied DCE as a solvent and benzoyl peroxide as a radical initiator. Surprisingly, following the literature procedure[12] of refluxing **1a** with 3 equivalents of NBS for 2.5 hours, we obtained mainly 1,5-dibromo-2-(bromomethyl)-4-(dibromomethyl)benzene (**4**) (so far unknown) instead of the expected 1,5-dibromo-2,4-bis(bromomethyl)benzene (**5**). After 5.5 hours, an additional product appeared on TLC, which was identified by ^{1}H NMR spectroscopy as 1,5-dibromo-2,4-bis(dibromomethyl)benzene (**2a**) (see Table S1 in Supporting Information). Further increase in the amount of NBS (6.5 equiv) gave, after 6 hours, **4** in 44% and **2a** in only 56% NMR yield. Prolongation of the reaction time to 12 hours resulted in an increased NMR yield of the tetrabrominated product **2a** to 70% (see Table S1 in Supporting Information). Finally, the full conversion of **1a** into **2a** was achieved using 8 equivalents of NBS within 4.5 hours (Table 1, entry 3). The same reaction conditions were applied to the synthesis of the second isomer, 1,4-dibromo-2,5-bis(dibromomethyl)benzene (**2b**), which was obtained in high yield (94%) by the reaction of 1,4-dibromo-2,5-dimethylbenzene (**1b**) with 8 equivalents of NBS in refluxing DCE and in the presence of benzoyl peroxide (Table 2, entry 3). Bromination of isomers **1a** and **1b** with NBS in refluxing acetonitrile[11] in the presence of benzoyl peroxide provided **2a** and **2b** in almost quantitative yields (Tables 1 and 2, entry 4); however, both reactions required use of the optimised 14 equivalents of

Table 1 Optimisation of the Bromination of **1a**

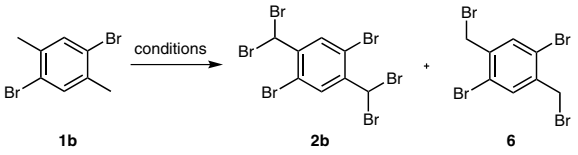


Entry	Reaction conditions	Yield (%) of **2a**	Yield (%) of **4**	Yield (%) of **5**
1	NBS (12 equiv), AIBN, benzene, 100 W lamp, reflux, 6 d	65	0	12
2	NBS (3 equiv), benzoyl peroxide, DCE, reflux, 5.5 h	6[a]	57[a]	37[a]
3	NBS (8 equiv), benzoyl peroxide, DCE, reflux, 4.5 h	97	0	0
4	NBS (14 equiv), benzoyl peroxide, MeCN, reflux, 16 h	96	0	0
5	Br_2 (5 equiv), DCE, 100 W lamp, reflux, 8 h	87	0	0

[a] Yield based on ^{1}H NMR spectra.

NBS and prolongation of the reaction time to 15–16 hours. Bromination of xylene derivatives **1a** and **1b** carried out in acetone, methanol and alkyl acetates[13] did not proceed. Bromination of **1b** according to the literature protocol[13a] with NBS (4.4 equiv) and AIBN (4 mol%) in refluxing ethyl acetate using a 100 W incandescent lamp for 16 hours led to symmetrical dibrominated product **6** only. Further increase in the amount of NBS to 8.8 equivalents and the reaction time to 48 hours did not lead to formation of the bis(dibrominated) product **2b**. Instead, a competitive α-keto bromination of ethyl acetate with bromine occurred.

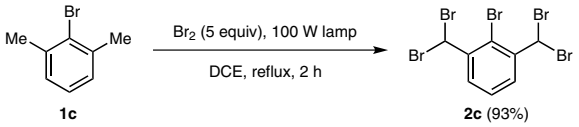
Table 2 Optimisation of the Bromination of **1b**



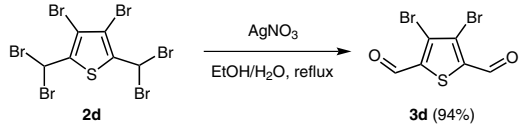
Entry	Reaction conditions	Yield (%) of **2b**	Yield (%) of **6**
1	NBS (8 equiv), AIBN, benzene, reflux, 18 d	80	11
2	NBS (8 equiv), AIBN, benzene, 100 W lamp, reflux, 4 d	81	0
3	NBS (8 equiv), benzoyl peroxide, DCE, reflux, 4 h	94	0
4	NBS (14 equiv), benzoyl peroxide, MeCN, reflux, 15 h	95	0
5	Br_2 (5 equiv), DCE, 100 W lamp, reflux, 4 h	93	0

Alternatively, we used bromine in DCE for the synthesis of bis(dibrominated) products **2** from dimethylbenzenes **1a–c** and dimethylthiophene **1d**. Thus, bromination of **1a** with bromine in boiling DCE, supported by a 100 W incandescent lamp, gave **2a** in 87% isolated yield (Table 1, entry 5). The same reaction conditions applied to the more reactive isomer **1b** afforded **2b** in 93% yield within 4 hours (Lit.[1b] 500 W, 89% yield) (Table 2, entry 5).

Synthesis of 2-bromo-1,3-bis(dibromomethyl)benzene (**2c**) has been realised by reaction of 2-bromo-1,3-dimethylbenzene (**1c**) with bromine (Scheme 2). In contrast to the literature, this reaction in DCE gave **2c** in high yield (93%) in a short reaction time (2 h instead of 8 d[10]) and allowed avoidance of a large excess (12 equiv) of brominating agent (NBS).[8,10] On the other hand, the same reaction in acetonitrile, instead of DCE, did not provide the desired product **2c**.



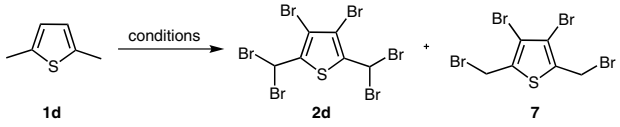
Scheme 2 Bromination of 2-bromo-1,3-dimethylbenzene (**1c**)



Scheme 3 Synthesis of 3,4-dibromo-2,5-thiophenedicarbaldehyde (**3d**) from **2d**

Bromination of 2,5-dimethylthiophene (**1d**) with bromine (5 equiv) in refluxing DCE for 16 hours afforded 3,4-dibromo-2,5-bis(dibromomethyl)thiophene (**2d**) accompanied by 3,4-dibromo-2,5-bis(bromomethyl)thiophene (**7**) (Table 3, entry 1).[14] Only the application of an additional 2.5 equivalents of bromine resulted in the formation of the desired **2d** in almost quantitative yield after 32 hours (Table 3, entry 2). Notably, the bromination of **1d** with 7 equivalents of bromine in dichloromethane for 18 hours without irradiation did not afford the expected hexabrominated product **2d**, but only tetrabrominated **7** in 88% yield.[14]

Table 3 Optimisation of the Bromination of **1d**



Entry	Reaction conditions	Yield (%) of **2d**	Yield (%) of **7**
1	Br_2 (5 equiv), DCE, 100 W lamp, reflux, 16 h	35	65
2	Br_2 (7.5 equiv), DCE, 100 W lamp, reflux, 32 h	99	0

Summing up our results on the bromination of dimethylarenes, we noticed that the efficiency of bromination depended on the kind and amount of brominating agent. Even under the optimised reaction conditions, we had to use larger amounts of NBS than bromine.

The final step of the synthesis required the conversion of bromides **2** into the corresponding dialdehydes **3** (Scheme 1). We applied the literature procedure which involves hydrolysis of a dibromomethyl moiety to an aldehyde group with an aqueous ethanolic solution of silver nitrate. In the case of **2a–c**, we obtained the dialdehydes **3a–c** in yields which were comparable to those reported in the literature (93–94%).[1a,b,8] 3,4-Dibromo-2,5-thiophenedicarbaldehyde (**3d**) was obtained from **2d** in the same manner, in 94% yield (Scheme 3). The direct 2,5-diformylation of the corresponding 2,5-dilithiothiophene with *N*-formylpiperidine provided **3d** in only 54–80% yield.[9,15]

X-ray crystal structure analysis was performed at room temperature for crystals of two final products, namely dialdehydes **3a** and **3b**, and of one of the starting materials, namely **1b** (Figure 1). The structural assignment based on

X-ray analysis, carried out by us for the first time, for a crystal of **3a** shows that this compound crystallises in the monoclinic $P2_1/c$ space group with one symmetry-independent, practically planar molecule (Figure 1, c) in the unit cell. In the crystal structure the molecules are connected by the C3–H3···O2^{i} hydrogen bond [C3–H3 = 0.93 Å, H3···O2 = 2.41 Å, C3···O2 = 3.319(9) Å and C3–H3···O2 = 167°, symmetry code (i) 1 + *x*, *y*, –1 + *z*] into a simple *C*(6) chain. Two such chains are linked by a halogen···halogen interaction of type I [i.e., C4–Br2···Br2^{ii}, Br2···Br2 = 3.591(1) Å, C4–Br2···Br2^{ii} = C4^{ii}–Br2^{ii}···Br2 = 139.31°, symmetry code (ii) 2 – *x*, –*y*, –*z*], so generating a one-dimensional framework in the form of an infinite tape built up from rings consisting of 18 atoms (Figure 1, d). There are no directional interactions between the molecules of adjacent tapes. This may be because the substituents at positions 1 (formyl group) and 2 (Br atom) do not participate in the formation of these interactions.

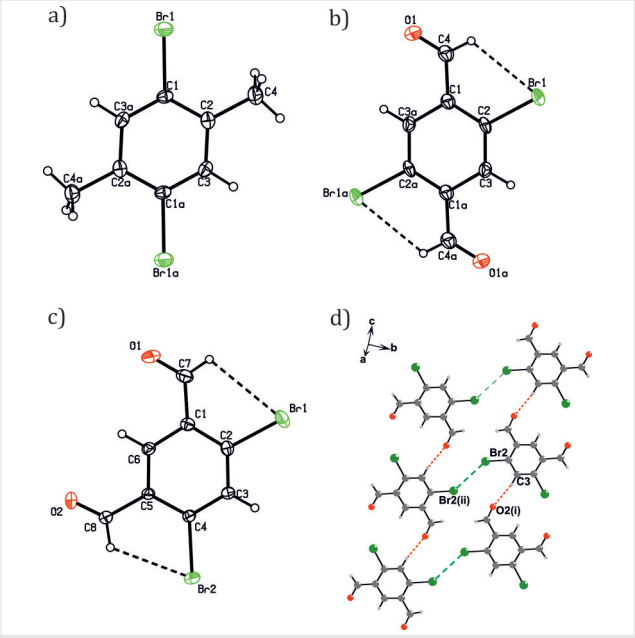


Figure 1 Views of molecules of **1b** (a), **3b** (b) and **3a** (c) with the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level; black dashed lines depict the intramolecular C–H···Br hydrogen bonds. (d) Part of the crystal structure of **3a** showing the C–H···O and Br···Br interactions (red and green dashed lines, respectively) linking the molecules into a tape built up from 18-membered rings.

In conclusion, we have presented optimised and efficient protocols for the preparation of bis(dibromomethyl)-substituted arenes **2** as synthetically useful precursors of the corresponding dialdehydes **3**. In the syntheses, we replaced inconvenient carbon tetrachloride, benzene and carbon disulfide by DCE, which allowed an efficient synthesis of **2**. Compared to the literature methods, we obtained the desired products **2a**–**d** in higher yields (up to 99%), in much shorter reaction times (hours versus days) and lower power consumption using optimised amounts of *N*-bromosuccinimide. The replacement of NBS by bromine allowed a further reduction in the amount of brominating agent. Alternative procedures using the preferable acetonitrile only worked well for the formation of **2a** and **2b**. All presented protocols enable efficient syntheses of aromatic dialdehydes **3** as substrates for biologically active compounds and materials for optoelectronic devices.

^{1}H NMR (500 or 200 MHz) and ^{13}C NMR (125 or 50 MHz) spectra were recorded with a Bruker AV-III-500 or a Bruker AV-200 spectrometer. IR spectra were recorded with an ATI Mattson Infinity FTIR 60 spectrophotometer. The mass spectra of pure compounds were obtained using a Finnigan MAT 95 spectrometer. Melting points were determined using a Boetius apparatus. Column chromatography was performed on Merck silica gel 60 (F254, 270–400 mesh).

General Procedures for the Synthesis of 2a and 2b

Variant A (NBS, Acetonitrile)

To a stirred solution of dibromodimethylbenzene **1a** or **1b** (3.33 g, 12.6 mmol) in MeCN (120 mL), benzoyl peroxide (65 mg, 0.26 mmol) and NBS (17.9 g, 100.8 mmol) were added in a single portion. The mixture was heated to reflux and an additional portion of benzoyl peroxide (184 mg, 0.74 mmol) was added. The reaction mixture was stirred at reflux for 8 h, then an additional portion of NBS (13.4 g) was added and reflux was continued for 8 h. After cooling, the precipitated solids were filtered off and rinsed with hexane (150 mL). The combined filtrates were concentrated under reduced pressure and purified by flash column chromatography (petroleum ether) to give **2a** (6.99 g, 96% yield) or **2b** (6.84 g, 95% yield).

Variant B (NBS, 1,2-Dichloroethane)

To a stirred solution of dibromodimethylbenzene **1a** or **1b** (3.25 g, 12.3 mmol) in DCE (120 mL), benzoyl peroxide (63 mg, 0.26 mmol) and NBS (17.5 g, 98.4 mmol) were added in a single portion. The mixture was heated to reflux and an additional portion of benzoyl peroxide (180 mg, 0.74 mmol) was added. The reaction mixture was stirred at reflux for 4.5 h and then cooled to room temperature. The precipitated solids were filtered off and rinsed with hexane (150 mL). The combined filtrates were concentrated under reduced pressure and purified by flash column chromatography (petroleum ether) to give **2a** (6.94 g, 97% yield) or **2b** (6.7 g, 94%).

Variant C (Br_2, 1,2-Dichloroethane, Light)

Dibromodimethylbenzene **1a** or **1b** (3.76 g, 14 mmol) was dissolved in DCE (40 mL) under reflux and then Br_2 (10.9 g, 3.5 mL, 71 mmol) was added dropwise to the solution. The resulting mixture was refluxed under incandescent irradiation (100 W) for 8 h (for **1a**) or 4 h (for **1b**). After cooling to room temperature, the reaction mixture was quenched with an aqueous solution of $NaHSO_3$. The organic layer was dried over $MgSO_4$ and evaporated to dryness to give **2a** (7.06 g, 87% yield) or **2b** (7.55 g, 93% yield).

1,5-Dibromo-2,4-bis(dibromomethyl)benzene (2a)

White solid; mp 122–123 °C (from hexane) (Lit.[1a] 115–118 °C).

IR (KBr): 3434, 3083, 3024, 3014, 1582, 1541, 1452, 1423, 1366, 1255, 1148, 1050, 980, 899, 868, 769, 719, 689, 654, 618, 594, 554 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (s, 1 H, ArH), 7.70 (s, 1 H, ArH), 6.96 (s, 2 H, $CHBr_2$).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.2, 135.7, 133.5, 121.2, 37.7.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_8H_4Br_6$: 573.54139; found: 573.54176.

Anal. Calcd for $C_8H_4Br_6$: C, 16.58; H, 0.70. Found: C, 16.71; H, 0.67.

1,4-Dibromo-2,5-bis(dibromomethyl)benzene (2b)

White solid; mp 168–170 °C (from hexane) (Lit.[1b] 176–178 °C).

IR (KBr): 3434, 3011, 1646, 1359, 1287, 1216, 1153, 1058, 893, 807, 700, 661, 554 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (s, 2 H, ArH), 6.93 (s, 2 H, $CHBr_2$).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.8, 135.8, 120.3, 38.0.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_8H_4Br_6$: 573.54139; found: 573.54065.

Anal. Calcd for $C_8H_4Br_6$: C, 16.58; H, 0.70. Found: C, 16.75; H, 0.72.

1,5-Dibromo-2-(bromomethyl)-4-(dibromomethyl)benzene (4)

To a solution of 1,5-dibromo-2,4-dimethylbenzene (**1a**; 3.25 g, 12.3 mmol) in DCE (120 mL), benzoyl peroxide (63 mg, 0.26 mmol) and NBS (7.5 g, 42.1 mmol) were added in a single portion. The mixture was heated to reflux and an additional portion of benzoyl peroxide (180 mg, 0.74 mmol) was added. The reaction mixture was stirred at reflux for 2 h and then cooled to room temperature. The precipitated solid was filtered off and rinsed with hexane (150 mL). The combined filtrates were concentrated under reduced pressure and purified by flash column chromatography (petroleum ether) to give **4** as a white solid (3.17 g, 52% yield); mp 101–102 °C (from hexane).

IR (KBr): 3452, 3080, 3011, 1581, 1458, 1433, 1365, 1245, 1210, 1149, 1056, 972, 905, 874, 760, 723, 694, 593 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09 (s, 1 H, ArH), 7.76 (s, 1 H, ArH), 6.96 (s, 1 H, $CHBr_2$), 4.57 (s, 2 H, CH_2Br).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.4, 138.0, 136.5, 133.1, 126.1, 119.9, 38.0, 31.7.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_8H_5Br_5$: 495.63086; found: 495.63126.

Anal. Calcd for $C_8H_5Br_5$: C, 19.19; H, 0.70. Found: C, 19.23; H, 0.97.

2-Bromo-1,3-bis(dibromomethyl)benzene (2c)

To a solution of 2-bromo-1,3-dimethylbenzene (**1c**;[15] 1.00 g, 5.4 mmol) in refluxing DCE (40 mL), Br_2 (1.38 mL, 27 mmol) was added dropwise. The resulting mixture was refluxed under incandescent irradiation (100 W) for 2 h. After cooling to room temperature, the reaction mixture was quenched with an aqueous solution of $NaHSO_3$. The organic layer was dried over $MgSO_4$ and evaporated to dryness to give **2c** (2.5 g, 93% yield) as a white solid; mp 151–152 °C (from EtOH) (Lit.[9] 150–151 °C).

IR (KBr): 3024, 1420, 1254, 1149, 1022, 937, 721, 625 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09 (d, J_{HH} = 7.7 Hz, 2 H, ArH), 7.57 (t, J_{HH} = 7.9 Hz, 1 H, ArH), 7.18 (s, 2 H, $CHBr_2$).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.7, 132.5, 129.1, 39.4.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_8H_5Br_5$: 495.63087; found: 495.63109.

Anal. Calcd for $C_8H_5Br_5$: C, 19.19; H, 1.01. Found: C, 19.23; H, 0.98.

3,4-Dibromo-2,5-bis(dibromomethyl)thiophene (2d)

A solution of 2,5-dimethylthiophene (**1d**; 1.00 g, 8.9 mmol) in refluxing DCE (40 mL) was treated dropwise with Br_2 (7.11 g, 2.28 mL, 44.5 mmol) over 40 min. The resulting mixture was refluxed under incandescent irradiation (100 W) for 16 h. Then, an additional amount of Br_2 (3.55 g, 1.14 mL, 22.3 mmol) was added and refluxing was continued for 16 h. After cooling to room temperature, the reaction mixture was quenched with an aqueous solution of $NaHSO_3$. The organic layer was dried over $MgSO_4$ and evaporated to dryness to give **2d** (5.17 g, 99% yield) as a light yellow solid.

IR (KBr): 2980, 1318, 1186, 1162, 1122, 870, 784, 685, 631 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.91 (s, $CHBr_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.3, 112.5, 30.2.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_6H_2SBr_6$: 579.49781; found: 579.49858.

Anal. Calcd for $C_6H_2SBr_6$: C, 12.31; H, 0.34; S, 5.48. Found: C, 12.43; H, 0.32; S, 5.19.

3,4-Dibromo-2,5-thiophenedicarbaldehyde (3d)

To a solution of **2d** (302 mg, 0.516 mmol) in EtOH (10 mL) was added a solution of $AgNO_3$ (369 mg, 2.17 mmol) in water (4 mL). The resulting mixture was heated at reflux under argon for 40 min. The solution was allowed to cool; AgBr was filtered off and washed with EtOH (2 × 5 mL). The solvent was evaporated and the residue was purified by recrystallisation (from hexane) to give **3d** (146 mg, 94% yield) as a white solid; mp 230–231 °C (from EtOH).

IR (KBr): 3304, 2938, 2836, 1660, 1444, 1329, 1307, 1208, 1170, 1087, 1056, 985, 904, 777, 683 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.07 (s, CHO).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 183.2, 142.1, 123.6.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_6H_2O_2SBr_2$: 295.81425; found: 295.81346.

Anal. Calcd for $C_6H_2O_2SBr_2$: C, 24.19; H, 0.68; S, 10.74. Found: C, 24.23; H, 0.72; S, 10.68.

Crystal Structure Data for 1,4-Dibromo-2,5-dimethylbenzene (1b)

$C_8H_8Br_2$, *M* = 263.96, monoclinic, space group $P2_1/n$ (No. 14), *a* = 6.3264(4) Å, *b* = 10.6529(6) Å, *c* = 6.5012(5) Å, *β* = 97.757(7)°, *V* = 430.47(5) Å^3, *Z* = 2, T = 290(2) K, D_{calcd} = 2.036 g·cm^{-3}, Mo Kα radiation, $2\theta_{max}$ = 50.30°, 8072 reflections collected, 770 reflections unique and 686 reflections with $I > 2\sigma(I)$. Final GOF = 1.129, R_1 = 0.0333 and wR_2 = 0.0747 for 686 reflections and 48 parameters.

Crystal Structure Data for 4,6-Dibromo-1,3-benzenedicarbaldehyde (3a)

$C_8H_4Br_2O_2$, *M* = 291.93, monoclinic, space group $P2_1/c$ (No. 14), *a* = 3.9947(2) Å, *b* = 33.386(2) Å, *c* = 6.3449(5) Å, *β* = 92.227(5)°, *V* = 845.56(9) Å^3, *Z* = 4, T = 290(2) K, D_{calcd} = 2.293 g·cm^{-3}, Mo Kα radiation, $2\theta_{max}$ = 50.38°, 14951 reflections collected, 1513 reflections unique and 1311 reflections with $I > 2\sigma(I)$. Final GOF = 1.209, R_1 = 0.0576 and wR_2 = 0.1217 for 1311 reflections and 115 parameters.

Crystal Structure Data for 2,5-Dibromo-1,4-benzenedicarbaldehyde (3b)

$C_8H_4Br_2O_2$, *M* = 291.93, triclinic, space group $P\bar{1}$ (No. 2), *a* = 4.0109(5) Å, *b* = 6.2592(9) Å, *c* = 8.7639(12) Å, *α* = 72.851(13)°, *β* = 81.962(11)°, *γ* = 85.694(11)°, *V* = 207.93(5) Å^3, *Z* = 1, *T* = 290(2) K, D_{calcd} = 2.331 g·cm^{-3}, Mo Kα radiation, $2\theta_{max}$ = 50.34°, 2851 reflections collected, 744 reflections unique and 552 reflections with $I > 2\sigma(I)$. Final GOF = 0.946, R_1 = 0.0368 and wR_2 = 0.0805 for 552 reflections and 58 parameters.

Diffraction data were collected using an Oxford Diffraction Xcalibur™ 3 diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELX-97.[16] The non-hydrogen atoms were refined anisotropically. All aromatic and methyl (in **1b**) H atoms were positioned geometrically and constrained to ride on their parent atoms, with U_{iso}(H) values of 1.2 U_{eq}($C_{aromatic}$) and 1.5 U_{eq}(C_{methyl}). The formyl H atoms (in **3a** and **3b**) were located in difference maps and refined with U_{iso}(H) set at 1.2 U_{eq}(C). CCDC 1454291 (**1b**), CCDC 1454292 (**3a**) and CCDC 1454293 (**3b**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561651.

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