




Short Note

2,3,4,5,6-Pentabromobenzoic Acid

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Abstract: Pentabromobenzoate is a useful fragment in organic synthesis and in coordination chemistry. Among known synthetic approaches to pentabromobenzoic acid (PBA), we have assessed and identified exhaustive bromination of benzoic acid by using 1,3-dibromoisocyanuric acid in concentrated H₂SO₄ solution as the most efficient method for the preparation of PBA on a multigram scale. As the crude bromination product is typically contaminated with 3,4,5,6-tetrabromobenzoic acid (TBA) and pentabromobenzene, C₆Br₅H, a simple purification protocol for preparation of analytically pure PBA has been developed. The molecular structure and crystal packing of PBA established by single-crystal X-ray diffractometry suggests a pattern of H-bonding and halogen bonding in solid state.

Keywords: perbromination; benzoic acid; dibromoisocyanuric acid; electrophilic bromination; perhalogenated benzoic acids



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1. Introduction

Perhalogenated benzoic acids are important compounds which have a variety of practical applications. Perfluorobenzoic acid, for example, owing to its availability and low cost, is most commonly used as a building block in coordination chemistry [1,2], physiologically active compounds [3,4], luminescence [5], optical materials [6,7], and numerous other applications [8]. In contrast, other perhalogenated benzoic acids are poorly studied, despite the fact that these compounds were described in the literature [9–11] a few decades ago. This is likely due to limited industrial applications and poor availability of chloro-, bromo-, and iodo-derivatives due to their relatively difficult syntheses.

In continuation of our work on the design of new lanthanide luminescent coordination compounds [11–14], we have tested PBA and found that it is a promising ligand. One may expect the corresponding complexes to be highly luminescent due to two simultaneous effects: one is the «heavy atom» effect, and another is due to multi-photon relaxation suppression. As for the other possible points of interest, the occurrence of halogen-bonding in such complexes, is potentially appealing from the viewpoints of both supramolecular and structural chemistry.

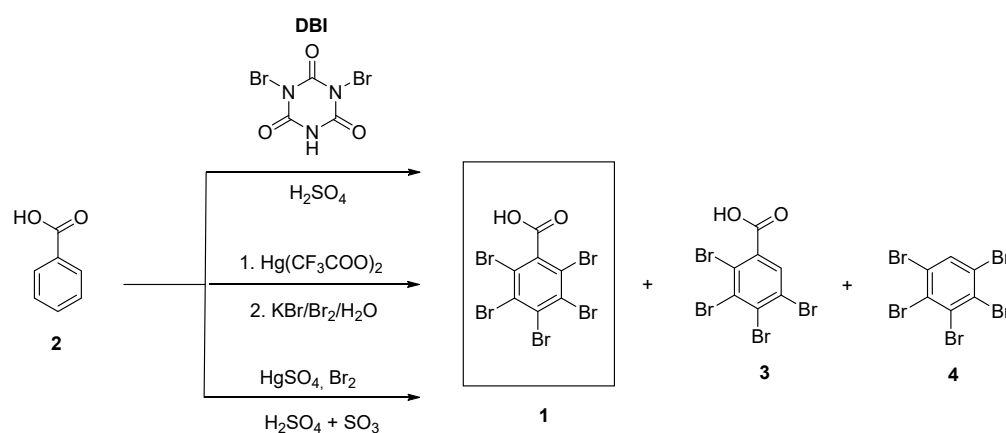
The synthesis of PBA, described in 1969 by Gottardi [15], did not work well: upon numerous trials, we failed to obtain PBA of appropriate purity due to insufficient detail in relation to purification reported in the published procedure. The material was typically contaminated with 3,4,5,6-tetrabromobenzoic acid and other impurities; sadly, our repeated attempts to purify it by using suggested protocols [15] failed.

In this communication, we report a reliable straightforward synthetic protocol for the preparation of PBA from benzoic acid, as well as the key bromination reagent dibromoisocyanuric acid (1,3-dibromo-1,3,5-triazinane-2,4,6-trione, DBI). Additionally, we have developed an effective purification procedure, which allows us to obtain analytically pure PBA in an acceptable yield.

2. Results and Discussion

The first historical synthesis of PBA (**1**) was described in 1869 by Reinecke [16], who discovered that extended heating of 3,4,5-tribromobenzoic acid with an excess of bromine at 200 °C led to the formation of a small amount of **1**. As most of the acid **1** undergoes decarboxylation under such conditions, pentabrombenzene (**4**) was isolated as a major product, making this method unsuitable for practical preparation of target PBA.

The first practical preparative synthesis of **1** was developed by W.Gottardi [17], who introduced dibromoisocyanuric acid (DBI) as a powerful electrophilic brominating agent for deactivated aromatic compounds (Scheme 1). Benzoic acid (**2**) was brominated by 2.5 equivalents of DBI in concentrated H₂SO₄ at room temperature for 1 h, affording the target compound **1** in 92% isolated yield after a simple work-up. This method was slightly improved upon and reported a year later [15]. Both publications by Gottardi feature a melting point for compound identification without providing other types of characterization data.



Scheme 1. Known synthetic pathways to PBA, **1**.

A completely different approach to **1** was proposed by G. Deacon et al. [18,19]. Benzoic acid (**2**) was first mercurated exhaustively via heating with the excess of molten Hg(CF₃COO)₂, and the resulting permercurated compound C₆(HgCF₃COO)₅COOH was digested by heating with KBr/Br₂ in aqueous solution. In this way, the overall yield of compound **1** was moderate, and considerable amounts of other less brominated byproducts were also isolated. Obviously, due to the toxicity of mercury compounds and the unfavorable stoichiometry of mercury cleavage reaction, this atom-wasteful approach is impractical.

Other attempts to brominate benzoic acid (**2**) directly in the presence of Hg²⁺ catalyst were made [20]. Heating of benzoic acid in 30% oleum at 45–50 °C in the presence of HgSO₄ and Br₂ for 2.5 h afforded, after laborious workup, acid **1** in 66% isolated yield. The most valuable part of this report is a detailed description of isolation and purification procedure, which was very useful for the development of our improved synthesis of PBA. The information on other more exotic approaches to acid **1** can be found elsewhere [21].

When we assessed various options for the preparation of PBA, bromination by DBI was identified as the most suitable alternative. Unfortunately, when following Gottardi's method [15,17] the acid **1** obtained was impure. As the impurities, identified by mass-spectroscopy, were mainly cyanuric acid, acid **3** and the bromide **4** a simple separation technique leading to pure **1** was adopted. In the first step, the by-product cyanuric acid was removed due to its insolubility in diethyl ether Et₂O, as follows: crude mixture of the products including brominated acids **1** and **3** was obtained by quenching the reaction mixture. Excess ice was air-dried on a glass sintered filter and extracted by small portions of Et₂O. Three extractions are usually sufficient to dissolve all brominated products while cyanuric acid remains on the filter. The ether extracts, upon evaporation, gave a crude mixture of acids which was boiled with an excess of 5% Na₂CO₃ aqueous

solution. The suspension was filtered quickly while hot, and the insoluble matter (mainly **4**) was discarded. The clear solution was cooled down, and a crystalline precipitate of sodium 2,3,4,5,6-pentabromobenzoate was filtered off. At this stage, most of acid **3** was removed in the form of its water-soluble sodium salt. Since it was established that traces of **4** co-precipitate with sodium 2,3,4,5,6-pentabromobenzoate, this salt was acidified with HCl and the slightly impure acid **1** was finally recrystallized from toluene. After cooling, analytically pure X-ray-quality crystals of the target product **1** were obtained in good yield: 61%. This practical preparation of **1** can easily be reproduced on a multi-gram scale; if required, multiple batches of crude acid can be combined and then purified in one run.

The purity of the acid **1** was confirmed by a number of analytical methods, including mass-spectroscopy, elemental analysis and ^{13}C -NMR. Single crystals of **1** suitable for X-ray crystallography were obtained via slow crystallization from toluene. The molecular structure of **1** is presented in Figure 1, whereby molecules of **1** form pseudo-centrosymmetric dimers, as shown in Figure 2, such that a dihedral angle between the two aromatic rings is about 1.5 degrees. Remarkably, in the structure of **1**, the C1–C2 distance is 1.52 (Table 1), i.e., somewhat longer than the mean $\text{C}_{\text{Ph}}\text{--C}_{\text{COO}^-}$ distance of 1.498 Å, deduced by an analysis of all structures of phenyl-substituted carboxylic acids and ethers published in the Cambridge Structural Base (CCDC) to date. This may suggest significant steric hindrance caused by the bulky bromines [22] in the ortho-positions and the O–H...O H-bonding (Table 2). Moreover, the analysis of crystal packing reveals the presence of a weak Br...O interaction (the Br1...O4 distance is 3.25 Å; the Br9...O2 distance is 3.36 Å), as illustrated in Figure 3.

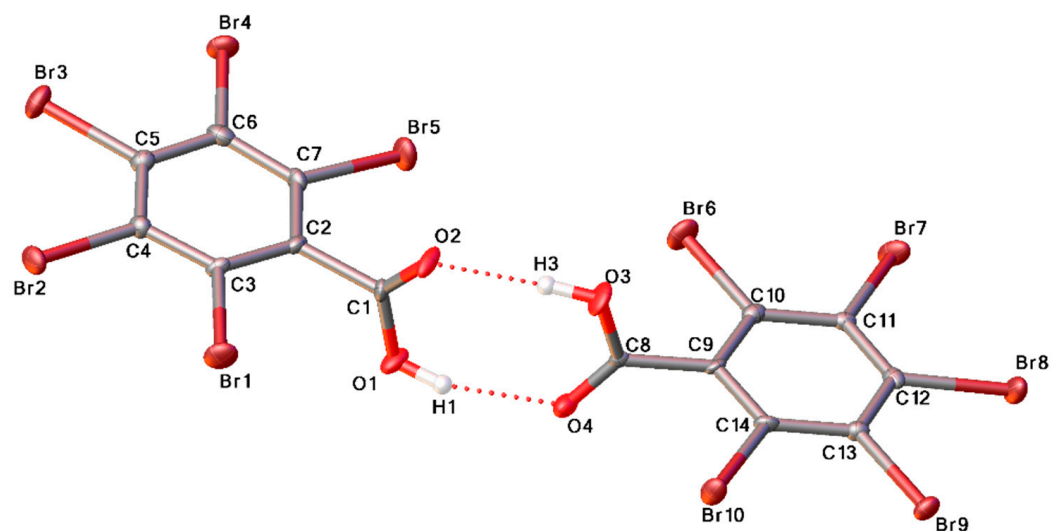


Figure 1. General view of the asymmetric unit of **1** with the thermal ellipsoids presented at 50% probability. Hydrogen O–H...O bonds are illustrated with dotted lines.

Table 1. List of bond lengths for **1**.

Bond	Length, Å	Bond	Length, Å
Br1–C3	1.877 (8)	Br10–C14	1.871 (8)
Br2–C4	1.875 (10)	Br9–C13	1.883 (9)
Br3–C5	1.892 (9)	Br8–C12	1.904 (9)
Br4–C6	1.865 (9)	Br7–C11	1.874 (9)
Br5–C7	1.889 (10)	Br6–C10	1.870 (9)
O1–C1	1.316 (11)	O3–C8	1.319 (12)
O2–C1	1.189 (11)	O4–C8	1.215 (11)
C1–C2	1.525 (13)	C8–C9	1.486 (13)
C2–C3	1.389 (12)	C9–C14	1.381 (12)
C2–C7	1.389 (13)	C9–C10	1.404 (12)
C3–C4	1.388 (13)	C14–C13	1.407 (13)

Table 1. Cont.

Bond	Length, Å	Bond	Length, Å
C4–C5	1.376 (13)	C13–C12	1.395 (12)
C5–C6	1.401 (14)	C12–C11	1.366 (13)
C6–C7	1.375 (14)	C11–C10	1.408 (13)

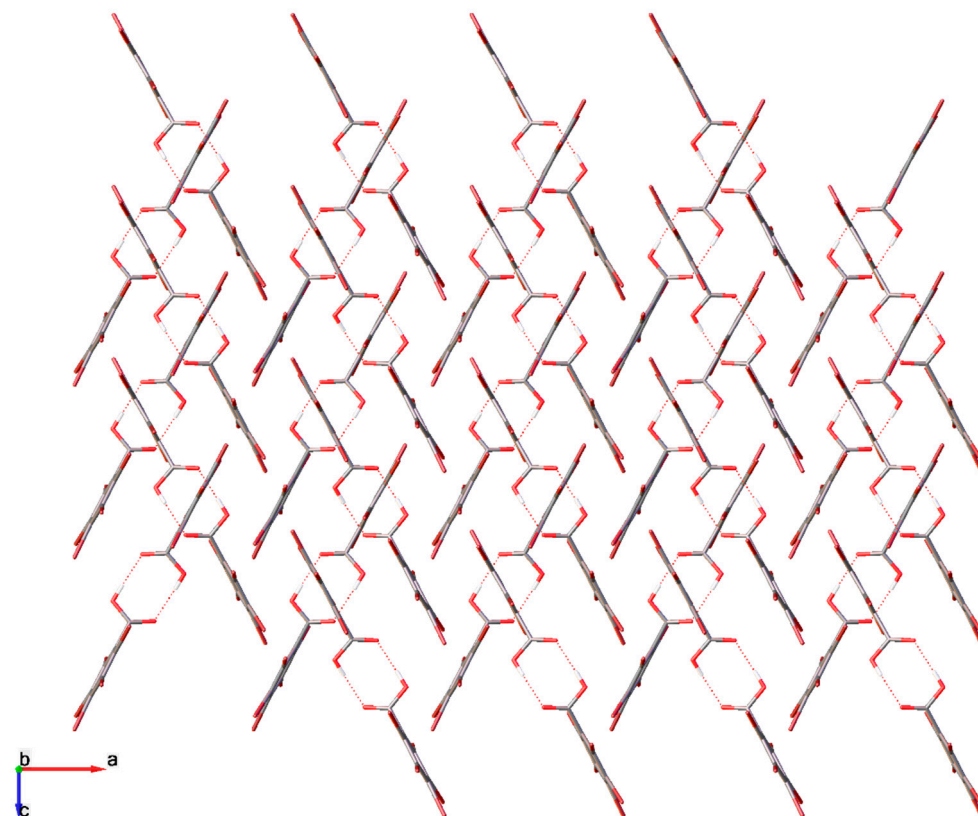


Figure 2. Crystal packing of **1** along (010) plane. Hydrogen O–H...O bonds are illustrated with dotted lines.

Table 2. List of hydrogen bonds present in the crystal of **1** and their geometrical parameters.

Bond	O...O, Å	∠O–H...O, °
O1–H1...O4	2.707	158.9
O3–H3...O2	2.678	176.7

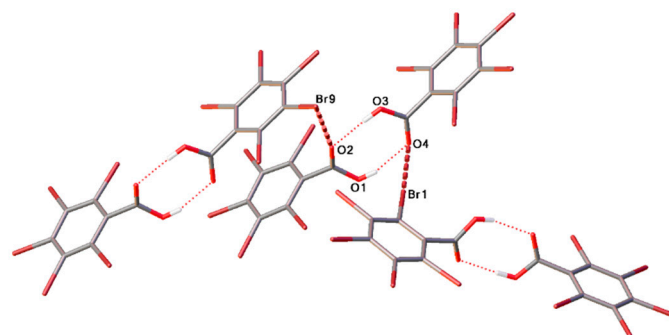


Figure 3. Crystal packing of **1**. Hydrogen O–H...O bonds are illustrated with dotted lines and Br...O contacts are illustrated with dashed lines.

The IR spectrum of **1** (Figure 4) contains bands of OH vibrations (broad band 3400–2900 cm^{-1}), strong band ν C=O (1711 cm^{-1} , lit. 1715 cm^{-1} [18]), ν (C–O) 1249 (lit. 1241) cm^{-1} , C=C (benzene ring) 1553–1317 cm^{-1} .

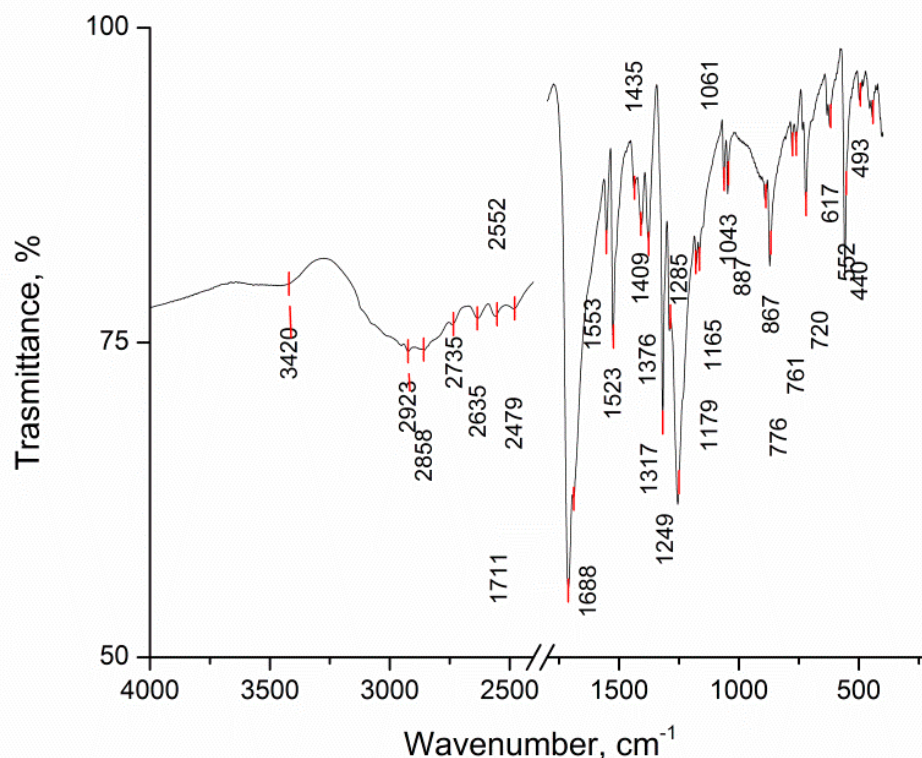


Figure 4. FT-IR spectrum of acid **1**.

In conclusion, we have shown that PBA prepared via bromination of benzoic acid with 1,3-dibromoisocyanic acid in H_2SO_4 is impure. A reliable purification protocol for PBA has been developed. The molecular structure and intermolecular interaction in solid 2,3,4,5,6-pentabromobenzoic acid have been confirmed via X-ray crystallography.

3. Materials and Methods

All reagents were purchased from Aldrich (St. Louis, MO, USA) and were used without further purification. Concentrated sulfuric acid, 98% ($d = 1.84 \text{ g/mL}$) was purchased from Component-Reactive (Moscow, Russian Federation). DBI was prepared and identified according procedure described in SI (Scheme 1, Figure S1). Elemental analysis was performed by the Laboratory of Microanalysis of Nesmeyanov Institute of Organoelement compounds (Moscow, Russian Federation). The melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^1H and ^{13}C -NMR spectra were acquired using a Bruker AV-300 instrument (Bruker AXS Handheld Inc., Kennewick, WA, USA) operated at 300 and 75.5 MHz, respectively, in $\text{DMSO-}d_6$ solution. Mass-spectra were recorded on a Bruker Maxis TOF instrument (Bruker Daltonic GmbH, Bremen, Germany), operated in negative mode, with ESI ionization. FTIR spectra were recorded in KBr pellets on a Perkin Elmer Spectrum One instrument (Santa Barbara, CA, USA). Single X-ray diffraction analysis was carried out on a Bruker D8 Quest diffractometer (Bruker AXS Handheld Inc., Kennewick, WA, USA), $\text{MoK}\alpha$ radiation, ω and φ -scan mode. The structure was solved with direct methods and refined via a least-squares method in the full-matrix anisotropic approximation on F^2 . All hydrogen atoms were located from an electron-difference map and refined within a riding model. All calculations were performed using the SHELXTL [23,24] and Olex2 [25] software packages. Crystal Data for $\text{C}_7\text{HBr}_5\text{O}_2$ ($M = 516.63 \text{ g/mol}$): orthorhombic, space group $\text{Pna}2_1$ (no. 33), $a = 17.288(5) \text{ \AA}$, $b = 15.298(3) \text{ \AA}$, $c = 8.315(2) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 2198.9(10) \text{ \AA}^3$, $Z = 8$, $T = 115(2) \text{ K}$, $\mu(\text{MoK}\alpha) = 18.244 \text{ mm}^{-1}$,

$D_{\text{calc}} = 3.121 \text{ g/cm}^3$, 16949 reflections measured ($3.56^\circ \leq 2\Theta \leq 54.00^\circ$), 4797 unique ($R_{\text{int}} = 0.0840$, $R_{\text{sigma}} = 0.0861$), which were used in all calculations. The final R_1 was 0.0449 ($I > 2\sigma(I)$) and wR_2 was 0.1043 (all data). Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 2196019, which is available free of charge at www.ccdc.cam.ac.uk (accessed on 12 August 2022).

Synthesis of pentabromobenzoic acid (1).

Benzoic acid (1.5 g, 12.4 mmol) was dissolved in 30 g (16.5 mL) of conc. H_2SO_4 with vigorous magnetic stirring. Separately, DBI (9 g, 34.4 mmol) solution in 150 g (81.5 mL) of conc. H_2SO_4 was prepared. It is important to dissolve all solid material in both flasks without external heating. Sometimes it takes 20–30 min to obtain a clear solution at room temperature. The DBI solution then was added to a well-stirred solution of benzoic acid rather quickly (1–2 min), and the resulting mixture was stirred at room temperature for an additional 30 min with protection from moisture (CaCl_2 drying tube). The mixture gradually transformed into a light-yellow paste due to the formation of thick precipitate; some heat was also evolved, but external cooling was not necessary for small uploads. The reaction mixture was poured on 500 g of crushed ice, stirred for 30 min and filtered of a glass frit. White precipitate was washed using cold water ($3 \times 20 \text{ mL}$) with suction and dried in air (1–2 days) directly in the filtering funnel. The coarsely ground cake was extracted on filter with 4 portions of ether (30 mL each). The clear filtrate was evaporated under diminished pressure (10 torr), and yielded white crystalline solid. The residue on filter consists mainly of isocyanuric acid, which is insoluble in ether, and was discarded.

Crude 2,3,4,5,6-pentabromobenzoic acid was heated to boiling point with 20 mL of 5% Na_2CO_3 aqueous solution; the alkali (pH~ 8–9) hot solution was filtered rapidly from insoluble salt of tetrabromobenzoic acid and hexabromobenzene and cooled in an ice bath. Thick paste of sodium pentabromobenzoate was filtered, and crystals were washed with a small amount (5 mL) of cold 5% Na_2CO_3 solution and dried in air. A suspension of the sodium salt in 10 mL of water was acidified with 35% HCl solution until pH~1 was achieved. Precipitate of free acid was filtered, and it was washed with 5 mL of cold water and dried in air. Finally, the acid was recrystallized from hot toluene (35 mL on 4 g of the crude product). The yield was 3.1 g (61%) of pure 2,3,4,5,6-pentabromobenzoic acid as colorless crystals.

Mp 265–266 °C (lit. 265–268 °C, [15]). Anal. calcd. for $\text{C}_7\text{HBr}_5\text{O}_2$ (516.60): C, 16.27; H, 0.20; Br 77.35. Found: C, 16.31; H, 0.23; Br 77.98%. IR spectrum, ν , cm^{-1} : 3400–2900 (broad), 3420 (vw), 2923 (vw), 2858 (vw), 2735 (vw), 2635 (vw), 2552 (vw), 2479 (vw), 1711 (vs), 1688 (sh), 1553 (w), 1523 (m), 1435 (vw), 1409 (w), 1376 (w), 1317 (s), 1285 (vw), 1249 (vs), 1179 (vw), 1165 (vw), 1061 (w), 1043 (vw), 887 (vw), 867 (m), 776 (vw), 761 (vw), 720 (m), 617 (w), 552 (s), 493 (vw), 440 (vw). $^1\text{H-NMR}$ (ppm): δ 13.89 (v. broad, 1H, $-\text{COOH}$). $^{13}\text{C-NMR}$ (ppm): δ 165.62, 140.45, 129.29, 128.51, 120.51. HRMS (ESI-TOF), m/z : calcd. for $\text{C}_7\text{HBr}_5\text{O}_2 [\text{M}]^+$, 516.6016, found, 516.5748. (See also Figures S2 and S3).

Supplementary Materials: Detailed procedure for preparation DBI; Scheme S1: Preparation of 1,3-dibromoisocyanuric acid (DBI); Figure S1: FT-IR spectrum of DBI; Figure S2: $^{13}\text{C-NMR}$ spectrum of compound 1; Figure S3: HR mass-spectrum of the compound 1 [26–29].

Author Contributions: I.V.T.—project administration, funding acquisition, supervision, writing—original draft preparation; T.S.V.—investigation; V.E.G.—investigation, writing—original draft preparation; Y.A.B.—investigation, writing—original draft preparation. S.R.Z.—investigation. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Han, L.-J.; Kong, Y.-J.; Xu, Y.-Y.; Huang, M.-M. A Zn-Based Coordination Compound for Fluorescence Detection of Fe³⁺, Cu²⁺, Ni²⁺ and CrO₄²⁻ Ions. *Polyhedron* **2021**, *193*, 114868. [[CrossRef](#)]
2. Shmelev, M.A.; Gogoleva, N.V.; Kuznetsova, G.N.; Kiskin, M.A.; Voronina, Y.K.; Yakushev, I.A.; Ivanova, T.M.; Nelyubina, Y.V.; Sidorov, A.A.; Eremenko, I.L. Cd(II) and Cd(II)–Eu(III) Complexes with Pentafluorobenzoic Acid Anions and N-Donor Ligands: Synthesis and Structures. *Russ. J. Coord. Chem.* **2020**, *46*, 557–572. [[CrossRef](#)]
3. Cox, B.; Duffy, J.; Zdorichenko, V.; Bellanger, C.; Hurcum, J.; Laleu, B.; Booker-Milburn, K.I.; Elliott, L.D.; Robertson-Ralph, M.; Swain, C.J.; et al. Escaping from Flatland: Antimalarial Activity of Sp³-Rich Bridged Pyrrolidine Derivatives. *ACS Med. Chem. Lett.* **2020**, *11*, 2497–2503. [[CrossRef](#)]
4. Černý, I.; Buděšínský, M.; Pouzar, V.; Vyklický, V.; Krausová, B.; Vyklický, L. Neuroactive Steroids with Perfluorobenzoyl Group. *Steroids* **2012**, *77*, 1233–1241. [[CrossRef](#)]
5. Shmelev, M.A.; Kiskin, M.A.; Voronina, J.K.; Babeshkin, K.A.; Efimov, N.N.; Varaksina, E.A.; Korshunov, V.M.; Taydakov, I.V.; Gogoleva, N.V.; Sidorov, A.A.; et al. Molecular and Polymer Ln₂M₂ (Ln = Eu, Gd, Tb, Dy; M = Zn, Cd) Complexes with Pentafluorobenzoate Anions: The Role of Temperature and Stacking Effects in the Structure; Magnetic and Luminescent Properties. *Materials* **2020**, *13*, 5689. [[CrossRef](#)]
6. Zhang, H.; Xiao, H.; Liu, F.; Huo, F.; He, Y.; Chen, Z.; Liu, X.; Bo, S.; Qiu, L.; Zhen, Z. Synthesis of Novel Nonlinear Optical Chromophores: Achieving Enhanced Electro-Optic Activity and Thermal Stability by Introducing Rigid Steric Hindrance Groups into the Julolidine Donor. *J. Mater. Chem. C* **2017**, *5*, 1675–1684. [[CrossRef](#)]
7. Wu, W.; Huang, Q.; Zhong, C.; Ye, C.; Qin, J.; Li, Z. Second-Order Nonlinear Optical (NLO) Polymers Containing Perfluoroaromatic Rings as Isolation Groups with Ar/ArF Self-Assembly Effect: Enhanced NLO Coefficient and Stability. *Polymer* **2013**, *54*, 5655–5664. [[CrossRef](#)]
8. Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H.-Z.; Liu, L. Copper-Catalyzed Decarboxylative Cross-Coupling of Potassium Polyfluorobenzoates with Aryl Iodides and Bromides. *Angew. Chem. Int. Ed.* **2009**, *48*, 9350–9354. [[CrossRef](#)]
9. Mattern, D.L. Direct Aromatic Periodination. *J. Org. Chem.* **1984**, *49*, 3051–3053. [[CrossRef](#)]
10. Pearson, D.E.; Cowan, D.; Beckler, J.D. A Study of the Entrainment Method for Making Grignard Reagents. *J. Org. Chem.* **1959**, *24*, 504–509. [[CrossRef](#)]
11. Taydakov, I.V.; Kiskin, M.A. On the Hydrolysis of Diethyl 2-(Perfluorophenyl)Malonate. *Beilstein J. Org. Chem.* **2020**, *16*, 1863–1868. [[CrossRef](#)] [[PubMed](#)]
12. Lutoshkin, M.A.; Taydakov, I.V. Selenoyl-Trifluoroacetone: Synthesis, Properties, and Complexation Ability towards Trivalent Rare-Earth Ions. *Polyhedron* **2021**, *207*, 115383. [[CrossRef](#)]
13. Gusev, A.; Kiskin, M.; Lutsenko, I.; Svetogorov, R.; Veber, S.; Minakova, O.; Korshunov, V.; Taydakov, I.; Linert, W. Triazole-Based Lanthanide(III) Adducts: Photo- and Thermochromic Luminescence. *J. Lumin.* **2021**, *238*, 118305. [[CrossRef](#)]
14. Belousov, Y.A.; Drozdov, A.A.; Taydakov, I.V.; Marchetti, F.; Pettinari, R.; Pettinari, C. Lanthanide Azolecarboxylate Compounds: Structure, Luminescent Properties and Applications. *Coord. Chem. Rev.* **2021**, *445*, 214084. [[CrossRef](#)]
15. Gottardi, W. Über Bromierungen mit Dibromoisocyanursäure unter ionischen Bedingungen, 2. Mitt.: Perbromierungen. *Mon. Chem.* **1969**, *100*, 42–50. [[CrossRef](#)]
16. Reinecke, A. Ueber Mono-, Tri-Und Pentabrombenzoesäure. *Z. Fur Chem.* **1869**, *5*, 109–111.
17. Gottardi, W. Über Bromierungen mit Dibromoisocyanursäure unter ionischen Bedingungen, 1. Mitt.: Monobromierungen. *Mon. Chem.* **1968**, *99*, 815–822. [[CrossRef](#)]
18. Deacon, G.B.; Farquharson, G.J. Permercurated Arenes. *J. Organomet. Chem.* **1974**, *67*, C1–C3. [[CrossRef](#)]
19. Deacon, G.; Farquharson, G. Synthesis and Bromodemercuration of Some Permercurated Arenes. *Aust. J. Chem.* **1976**, *29*, 627. [[CrossRef](#)]
20. Shishkin, V.N.; Bolusheva, I.Y.; Lapin, K.K.; Tanaseichuk, B.S. Polybrominated Aromatic Compounds VI. Exhaustive Bromination in the Ring of Deactivated Aromatic Compounds. *J. Org. Chem. USSR* **1991**, *27*, 1303–1308.
21. Mongin, F.; Marzi, E.; Schlosser, M. Extensive Halogen Scrambling and Buttressing Effects Encountered upon Treatment of Oligobromoarenes with Bases. *Eur. J. Org. Chem.* **2001**, *2001*, 2771–2777. [[CrossRef](#)]
22. Kumagai, H.; Kawata, S. 4,4'-Bipyridine-1,1'-Dium 2,3,5,6-Tetrabromoterephthalate Dihydrate. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2011**, *67*, o2636. [[CrossRef](#)] [[PubMed](#)]
23. Sheldrick, G.M. SHELXT—Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8. [[CrossRef](#)] [[PubMed](#)]
24. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8. [[CrossRef](#)] [[PubMed](#)]

25. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339–341. [[CrossRef](#)]
26. Demko, Z.P.; Bartsch, M.; Sharpless, K.B. Primary Amides. A General Nitrogen Source for Catalytic Asymmetric Aminohydroxylation of Olefins. *Org. Lett.* **2000**, *2*, 2221–2223. [[CrossRef](#)]
27. Gottardi, W. Über die Reaktion von Brom mit Alkalicyanuraten. *Monatshefte für Chemie* **1967**, *98*, 507–512. [[CrossRef](#)]
28. Petterson, R.C.; Grzeskowiak, U.; Jules, L.H. N-Halogen Compounds. II. ^{1,2} The N—Cl Stretching Band in Some N-Chloroamides. The Structure of Trichloroisocyanuric Acid. *J. Org. Chem.* **1960**, *25*, 1595–1598. [[CrossRef](#)]
29. Gottardi, W. Zur Chemie der Bromisocyanursäuren: Eigenschaften und Reaktionen der Dibromisocyanursäure. *Mon. Chem.* **1977**, *108*, 1067–1084. [[CrossRef](#)]