Synthesis and characterization of tetraphenylammonium salts

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Abstract

The phenyl (Ph) group is a representative substituent in the field of organic chemistry as benzene (the parent molecule) is of fundamental importance. Simple Ph-substituted compounds of common chemical elements are well known. However, extensive structural characterization of tetraphenylammonium (Ph_4N^+) salts has not been reported. Herein, the synthesis of Ph_4N^+ salts and their characterization data including the ^1H - and ^{13}C -nuclear magnetic resonance (NMR) spectra and the single-crystal X-ray structure have been presented. An intermolecular radical coupling reaction between an aryl radical and a triarylammoniumyl radical cation was conducted to synthesize the target moieties. The Ph_4N^+ salts described herein are the simplest tetraarylammonium (Ar_4N^+) salts known. The results reported herein can potentially help access the otherwise inaccessible non-bridged Ar_4N^+ salts, a new class of rigid and sterically hindered organic cations.

Introduction

The elements in groups 13 (B and Al), 14 (C and Si), and 15 (N and P) typically form tetrahedral ions or molecules of the general formula $\text{R}_4\text{Z}^{0\pm 1}$, when four identical substituents (R_4) are attached to the central element (Z). The charge on the atom Z depends on the group to which it belongs: -1 , 0 , and $+1$ for groups 13, 14, and 15, respectively. Compounds of type $\text{R}_4\text{Z}^{0\pm 1}$, bearing simple R substituents, are of special importance and considered benchmark compounds. The structural features, physical properties, and chemical reactivities of the other derivatives belonging to this class of compounds were compared with those of the benchmark compounds for a deeper understanding of the compound characteristics. Therefore, for a long time, organic chemists have focused on synthesizing such $\text{R}_4\text{Z}^{0\pm 1}$ compounds bearing simple R substituents. The compounds of the general formula $\text{R}_4\text{Z}^{0\pm 1}$ ($\text{R} = \text{Ph}$ (Ph_4B^- , Ph_4Al^- , Ph_4C , Ph_4Si , and Ph_4P^+ ; Fig. 1))^{1–6} are known since long. Ph_4Si was identified more than 130 years ago. The fundamental properties of these $\text{Ph}_4\text{Z}^{0\pm 1}$ compounds have been studied extensively over a long period of time. The results serve as references during the study of the corresponding tetraaryl-substituted compounds ($\text{Ar}_4\text{Z}^{0\pm 1}$). Quantum chemical calculations have been conducted for Ph_4N^+ .⁷ However, the experimental properties of this simple organic cation remain largely unknown. Though several researchers have reported the application prospects of the Ph_4N^+ salts (Supplementary Table 1), the synthetic route followed, and the compound characteristics have not been reported.

It has been reported that the pentatritiated tetraphenylammonium salts (**1**; Fig. 2a) can be formed following the nuclear-chemical method via the tritium β -decay of hexatritiated benzene (C_6T_6).^{8,9} The isomorphic co-crystallization data and the radioactivity-based yields have been documented. However, the detailed synthetic procedure and data from experiments conducted for structure identification have not been reported. Bridged Ar_4N^+ salts are structurally similar to the Ph_4N^+ salts. In 1963, Nesmeyanov synthesized the (*N,N*-diphenyl)carbazolium salts (**2**; Fig. 2b) as the first examples of this class of

compounds.¹⁰ The key reaction step affording **2** from precursor **3** was the intramolecular *N*-arylation of triarylamine. The step proceeded via the decomposition of the spatially proximal aryldiazonium moiety. This process resulted in the formation of a 5-membered ring containing a nitrogen atom bearing four aromatic rings. Following the success of the method, a similar cyclization strategy was followed for the synthesis of various (*N,N*-diaryl)carbazolium salts^{11–16} (such as **4** and **5**; Fig. 2c), and sulfide- or amide-bridged Ar₄N⁺ salts (**6**¹⁷ and **7**¹⁸, respectively). Recently, the quaternary ammonium structure of **2** was confirmed using the single-crystal X-ray diffraction technique.^{13,16} However, none of these bridged Ar₄N⁺ salts could be converted to Ph₄N⁺ salts, as there is a dearth of efficient methods that can be used to remove the bridge moieties.¹⁷

Ar₄N⁺ is a promising organic cation that can be used for developing surfactants, supporting electrolytes, phase-transfer catalysts, and anion-exchange membranes.¹³ Also, it is potentially useful for industrial and biological studies. The wide application range of the cation can be attributed to the high chemical stability^{14,15} and unique rigid structure of the organic cation. Although the bridged Ar₄N⁺ cations represented by **2** have been studied and characterized, non-bridged Ar₄N⁺ cations have not been explored because of synthetic limitations. Herein, we report a novel synthetic strategy for the preparation of Ph₄N⁺ salts. This is the first report where the results of structural characteristics of the cation have been reported.

Results And Discussion

Synthetic strategy. The direct *N*-phenylation of triphenylamine (**8**; Fig. 3a) using a Ph cation (or its synthetic equivalent) to form Ph₄N⁺ is difficult because **8** is weakly nucleophilic (indicated by the low p*K*_{aH} value (−3.91)¹⁹ recorded during *N*-protonation). Ph₄N⁺ salts could not be obtained by reacting **8** with a phenyldiazonium unit.¹⁰ The *N*-phenylation of **8** using diphenyliodonium²⁰ or the *in-situ*-generated benzyne²¹ unit was also unsuccessful. We designed the triarylammuniumyl salt (**9**; Fig. 3b) as a novel precursor that could be used for the synthesis of Ph₄N⁺ to address the problem of low reactivity of **8**. In general, triarylamines can be oxidized to form the corresponding radical cations (referred to as triarylammuniumyls) that exhibit high reactivity. Triphenylammuniumyl easily dimerizes via the *para* positions of the Ph groups following the process of intermolecular radical coupling to afford tetraphenylbenzidine.²² The results obtained from quantum chemical calculations revealed that the singly occupied molecular orbital of triphenylammuniumyl was spread over all the Ph rings and the central nitrogen atom.²³ Therefore, we expected that the intermolecular radical coupling reaction involving a triphenylammuniumyl unit and an aryl radical occurs via the nitrogen atom if the Ph group is hindered by steric protection. The *tert*-butyl and bromo groups were selected as the bulky protecting groups of **9** at the *meta*- and *para*-positions, respectively. These groups can exert a large extent of steric hindrance and can be removed at the later stages of the synthetic procedure.

Synthesis. The starting material used for the synthesis of the target was tris[(3,5-di-*tert*-butyl)phenyl]amine (**10**; Fig. 4), which was prepared over three steps starting from benzene: Friedel–Crafts reaction, dealkylative bromination, and palladium-catalyzed amination.^{24,25} The *para*-brominated compound **11** was formed in 81% yield when **10** was treated with *N*-bromosuccinimide (NBS). The triarylamine **11** was then activated to form the triarylammoniumyl salt **9** following the one-electron oxidation process using AgBF₄.²⁶ It was isolated as a monohydrate in 93% yield. Similar to other triarylammoniumyl salts,²² **9** was a blue solid. The color could be attributed to the absorption over the visible region ($\lambda_{\text{max}} = 797 \text{ nm}$ in *o*-dichlorobenzene). Following this, we investigated the key intermolecular radical coupling reactions. Bis(3,5-di-*tert*-butyl)benzoyl peroxide (**13**) was used as the starting material for the *in situ* generation of the (3,5-di-*tert*-butyl)phenyl radical (**12**). The formation of the radical proceeded via the process of O–O homolysis, which was followed by the process of decarboxylation.²⁷ A mixture of **9** and **13** was heated to 120 °C in *o*-dichlorobenzene in the presence of (2,6-di-*tert*-butyl)pyridine (**14**; used as a base) until the characteristic blue color of **9** disappeared. The reaction conditions were selected from the results of the screening experiments (*vide infra*). The desired Ar₄N⁺ salt **15** was successfully formed in a low yield (0.1%), which was then isolated using the normal-phase ion-pair chromatography technique.²⁸ Under these conditions, 4 g of **9** could be converted to 5 mg of **15**. The byproducts formed during the reaction were triarylamine **11** (11%), solvent adduct **16** (4% based on **13**), and sterically congested triarylamines **17** (7%) and **18** (8%) possessing *ortho*-[(3,5-di-*tert*-butyl)benzoyl]oxy and *ortho*-(3,5-di-*tert*-butyl)phenyl groups, respectively. The structures of **17** and **18** were determined using the single-crystal X-ray diffraction technique (Supplementary Tables 2 and 3, respectively). The formation of **17** and **18** indicated that the extent of steric protection provided by the *meta-tert*-butyl groups in **9** was not sufficient to efficiently inhibit the occurrence of the *ortho*-substitution reactions at the Ph rings. Supplementary Table 4 shows the process of reaction condition screening for the intermolecular radical coupling reaction conducted on a small scale using **9** (80–100 mg). When the reaction was conducted in *o*-dichlorobenzene in the presence of **14** (entry 1), the yield of the desired ammonium salt **15** was 0.12% (determined by ¹H-NMR spectroscopic analysis). Although the same yield (0.12%, entry 2) of **15** was obtained when the reaction was carried out in the absence of **14**, it was difficult to purify the product under these conditions as various byproducts were also formed during the process. The use of other solvents in combination with **14** afforded lower (entries 3–10) or undetectable (entries 11–14) yields of **15**, and a complex mixture of compounds which could not be purified or analyzed (entries 16–21). Thus, the reaction conditions presented in entry 1 were used to synthesize **15** from **9** (4 g). We also attempted the intermolecular radical coupling reaction involving **13** and tris[(3,5-di-*tert*-butyl)phenyl]ammoniumyl BF₄[–] (**19**; devoid of the *p*-bromo groups). The latter was prepared following the one-electron oxidation of **10**. However, the desired product tetrakis[(3,5-di-*tert*-butyl)phenyl]ammonium BF₄[–] (**20**) could not be isolated as the reaction yielded a complex mixture. Therefore, the removal of all the bromo groups in **15** was carried out following the process of bromine–lithium exchange using ^{*n*}BuLi at –78 °C. The resulting product was protonated with (2,6-di-*tert*-butyl)pyridinium BF₄[–] salt (**21**), affording **20** in 90% yield. Since we selected diacyl peroxide **13** as the precursor of aryl radical **12** to introduce the (3,5-di-*tert*-butyl)phenyl

group in **9**, the ammonium nitrogen of **20** was connected to four identical aryl groups. The counter anion of **20** was exchanged to prepare the corresponding $\text{B}(\text{C}_6\text{F}_5)_4^-$ salt (**22**), the structure of which was confirmed using the single-crystal X-ray diffraction technique (Supplementary Table 5). The final step toward the formation of Ph_4N^+ involved the dealkylation of the *tert*-butyl groups present on the aromatic rings of **20**. All the eight *tert*-butyl groups could be successfully removed when **20** was heated at 150 °C over a period of 14 h in a solvent amount of trifluoromethanesulfonic acid (TfOH).²⁹ The reaction afforded $\text{Ph}_4\text{N}^+ \text{BF}_4^-$ (**23**) in 59% yield. This result indicates the high stability of Ph_4N^+ under extremely harsh acidic conditions. Following the process of counter anion exchange, the BF_4^- salt (**23**) was converted to the $\text{B}(\text{C}_6\text{F}_5)_4^-$ salt (**24**; yield: 81%; white solid). The purity of the counter anion was confirmed using the ^{19}F -NMR spectroscopy technique.

^1H - and ^{13}C -NMR spectra. The ^1H -NMR signals corresponding to **24** (spectra recorded in $(\text{CD}_3)_2\text{CO}$) appeared at approximately 7.89, 7.69, and 7.65 ppm. The signal corresponded to the *ortho*, *meta*, and *para*-protons present in the Ph ring, respectively. The ^{13}C -NMR signals corresponding to **24** (spectra recorded in $(\text{CD}_3)_2\text{CO}$) appeared at 149.7 (*ipso*), in the range of 131.4–131.2 (*para* and *meta*), and at 126.8 (*ortho*) ppm. The signals were assigned to the corresponding carbon atoms using the HMQC technique. The ^1H and ^{13}C -NMR signals corresponding to **24** appeared downfield compared to the signals corresponding to **8** (Figs. 5a,b). The downfield shift can be attributed to the strong inductive effect exerted by the ammonium nitrogen in **24** and the loss of the resonance effect of the lone pair of electrons on nitrogen present in **8** following *N*-quaternization. The signals corresponding to the *meta* and *para* protons present in **24** (at ~ 7.69 and ~ 7.65 ppm, respectively) appeared at up-field compared to the signals corresponding to $\text{Ph}_4\text{P}^+ \text{B}(\text{C}_6\text{F}_5)_4^-$ ³⁰ (**25**; ~7.88 and ~ 8.02 ppm for *meta* and *para* protons, respectively). The up-field shift may be attributed to the strong anisotropic effects observed in Ph_4N^+ . The generation of the strong anisotropic effects can be attributed to the fact that Ph_4N^+ is smaller than Ph_4P^+ . Similarly, we observed that the signals corresponding to the *meta* and *para* protons in Ph_4C ($(\text{CD}_3)_2\text{CO}$; at ~ 7.29 and ~ 7.21 ppm, respectively) appeared up-field compared to the signals corresponding to Ph_4Si (*meta* and *para* protons appear at ~ 7.44 and ~ 7.48 ppm, respectively; Supplementary Fig. 1).³¹

Single-crystal X-ray structure analysis. The single-crystal X-ray diffraction technique was used to analyze the structure of **24**. Analysis of the results proved the quaternary ammonium structure of **24** (Fig. 5c, top view). The counter anion $\text{B}(\text{C}_6\text{F}_5)_4^-$ was omitted for clarity (Supplementary Table 6). The Ph_4N^+ structure exhibited S_4 -like symmetry and not D_{2d} -like symmetry. The result agreed well with the theoretically predicted result.³² The N–C(sp^2) bond length in **24** (present between the Ph_4N^+ nitrogen unit and the sp^2 carbon atom) in the Ph group was 1.529 ± 0.003 Å (Fig. 5c, side view). This bond is longer than the N–C(sp^2) bonds in $(\text{CH}_3)_3\text{PhN}^+$, $(\text{CH}_3)_2\text{Ph}_2\text{N}^+$, $(\text{CH}_3)\text{Ph}_3\text{N}^+$, and *N,N*-diphenylcarbazolium, which were 1.50,³³ 1.51,²¹ 1.52,²¹ and 1.51–1.52¹⁶ Å, respectively (data from Cambridge Crystallographic Data Center (CCDC) deposition numbers of 291166, 1433867, 1433868, and 1890475, respectively). The long N–

C(sp²) bond in Ph₄N⁺ indicates the presence of an unusually hindered environment around the ammonium nitrogen atom. The lengths of the bonds formed between the central atom and the sp² carbons in Ph₄C, Ph₄B[−], Ph₄P⁺, Ph₄Si, and Ph₄Al[−] were 1.56,³⁴ 1.64–1.66,³⁵ 1.79,³⁶ 1.88,³⁷ and 2.00–2.03³⁸ Å, respectively. Thus, Ph₄N⁺ is characterized by the most sterically congested environment among these Ph₄Z^{0±1}, reflecting the difficulty faced during synthesis. The shortest distance between the *ortho*-hydrogen in the Ph unit and the *ipso* carbon in the adjacent Ph group in Ph₄N⁺ was 2.46 Å (Fig. 5c, side view). The Van der Waals radii for hydrogen (1.00 Å) and carbon (1.77 Å) indicate that steric repulsion is generated.³⁹ The corresponding H–C distances in Ph₄C, Ph₄B[−], and Ph₄P⁺ were 2.54,³⁴ 2.59,³⁵ and 2.76³⁶ Å, respectively, indicating that the extent of steric repulsion observed in these cases was lower than that observed in Ph₄N⁺. The N–C(sp²) bond length in **22** was in the range of 1.53–1.54 Å and the H–C distance was 2.48 Å. These values are slightly higher than the corresponding values recorded for **24**. This suggested the generation of steric and electronic effects in the presence of the *meta-tert*-butyl groups in **22** present in the ammonium structure.

Conclusion

We have synthesized Ph₄N⁺ salts which are structurally simple non-bridged Ar₄N⁺ salts. The ¹H- and ¹³C-NMR spectra of the Ph₄N⁺ salts have been presented. The single-crystal X-ray structure analysis revealed the long N–C bond present in this organic cation. The Ph₄N⁺ salts described herein are essential benchmarks for non-bridged Ar₄N⁺ salts. The intramolecular radical coupling reaction (between a triarylammoniumyl and an aryl radical) reported herein can be conducted for the synthesis of various non-bridged Ar₄N⁺ salts that are otherwise difficult to synthesize. Further studies need to be conducted to achieve higher product yields.

Declarations

Data availability

CCDC 2117248, 2117243, 2117249, and 2117251 contain the supplementary crystallographic data for compounds **17**, **18**, **22**, and **24**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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Author contributions

M. Kunishima supervised the project; H. Fujita, O. Sasamoto, M. Kitamura, and M. Kunishima designed the synthetic strategy; H. Fujita wrote the original draft with contributions from O. Sasamoto; H. Fujita and M. Kunishima reviewed and edited the paper; O. Sasamoto performed experiments with contributions from S. Kobayashi; H. Fujita, O. Sasamoto, M. Kitamura, and M. Kunishima analyzed the obtained data.

Competing interests

The authors declare no competing interests.

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Additional Information

Supplementary Information is not available with this version.

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Figures

	13	14	15	Group
2	<p>Tetraphenylborate Ph_4B^- (1948)</p>	<p>Tetraphenylmethane Ph_4C (1897)</p>	<p>Tetraphenylammonium Ph_4N^+ <i>Unknown</i></p>	
3	<p>Tetraphenylaluminate Ph_4Al^- (1950)</p>	<p>Tetraphenylsilane Ph_4Si (1885)</p>	<p>Tetraphenylphosphonium Ph_4P^+ (1928)</p>	
Period				

Figure 1

Structures of Ph_4 -substituted elements belonging to the groups 13–15, $\text{Ph}_4\text{Z}^{0\pm 1}$. The number in the parentheses indicates the year of synthesis (reported in the literature).

Figure 2

Ar₄N⁺ salts reported in the literature. Counter anions are depicted in the general form X⁻. **a**, Pentatritiated Ph₄N⁺ salts (**1**) reported without proper structural data. **b**, Synthesis of (*N,N*-diphenyl)carbazolium salts (**2**) from precursor **3** following the process of intramolecular *N*-arylation. The bridge moiety indicated in blue must be removed to obtain the Ph₄N⁺ salts. **c**, Other bridged Ar₄N⁺ salts such as (*N,N*-diphenyl)carbazolium salts (**4**) bearing various substituents Y on the aryl groups, spirobicarbazolium salts (**5**), sulfide-bridged Ar₄N⁺ salts (**6**), and amide-bridged Ar₄N⁺ salts (**7**) prepared following the intramolecular *N*-arylation strategy. The bridge moieties are indicated in blue.

Figure 3

Synthetic strategy followed for the construction of a non-bridged Ar_4N^+ structure. **a**, Direct N -phenylation of **8** with a Ph^+ cation is difficult as the N atom is a weak nucleophile. **b**, Intermolecular radical coupling reaction between an aryl radical and the triarylammonium salt **9** bearing bulky protecting groups that exert steric hindrance and block the reactions at the Ph groups.

Figure 5

Structural characterization of Ph_4N^+ . **a**, Comparison of the ^1H -NMR spectral profiles (600 MHz, $(\text{CD}_3)_2\text{CO}$) recorded for **24**, **8**, and **25**. The number of protons is presented in the parentheses. **b**, Comparison of the ^{13}C -NMR spectral profiles (150 MHz, $(\text{CD}_3)_2\text{CO}$) recorded for **24** and **8**. **c**, Single-crystal X-ray structure of **24**. All ellipsoids are contoured at the 50% probability level. The counter anion was omitted for clarity.