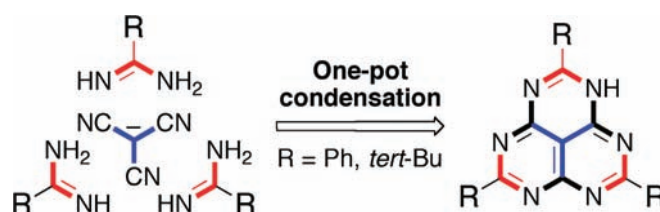


Hexaazaphenalenene Derivatives: One-Pot
Synthesis, Hydrogen-Bonded Chiral
Helix, and Fluorescence PropertiesShuichi Suzuki,^{†,‡} Koza Fukui,[‡] Akira Fuyuhiro,[†] Kazunobu Sato,[‡] Takeji Takui,[‡]
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ABSTRACT



Symmetric hexaazaphenalenenes (R = phenyl and *tert*-butyl) have been synthesized by one-pot condensations of corresponding amidine hydrochlorides with tricyanomethanide. The hexaazaphenalenenes are linked with each other by a N–H...N hydrogen-bonding interaction in the crystalline states. Interestingly, a planar and achiral *tert*-butylated derivative was crystallized in a chiral space group with assembly of one-handed helical hydrogen-bonded chains. Hexaazaphenalenyl anions were isolated as air- and water-stable tetraethyl ammonium salts.

Recently, phenalenyl **1**^{1,2} has attracted great attention as a basic molecular system for creating functional materials with high conductivity,³ two photon absorption,⁴ ambipolar field-

effect transistor (FET) properties,⁵ as well as electrode-active properties in the secondary battery.⁶ Furthermore, incorporation of nitrogen atoms into the phenalenyl skeleton affords an azaphenalenyl system and has a substantial effect on its electronic structure, providing new spin-delocalized radicals,^{7–9} metal complex ligands,¹⁰ and hydrogen-bonded (H-bonded) electron-donor molecules.¹¹

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The phenalenyl radical derivatives form unique dimer structures, π - or σ -dimers, in the crystalline states and even in a solution state.^{1e,12} Thus, the azaphenalenyl radicals give an intriguing opportunity to discuss bonding interactions in the aggregate states from both experimental and theoretical sides.^{2,12} Hexaazaphenalenyl (HAP) **2** is a highly symmetric heterocycle with a six-nitrogen incorporation in all α -sites of the phenalenyl system, which possesses a unique directionality of the lone-pair electrons at six nitrogen sites, realizing the radially extended mode in multiple H-bonds and metal-coordination bonds (Figure 1).¹⁰ Furthermore,

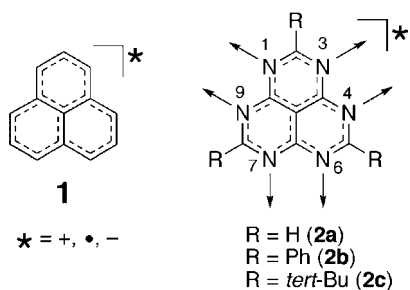


Figure 1. Structures of phenalenyl derivatives **1** and **2**. The arrows show radially extended mode of coordination and H-bonding interactions.

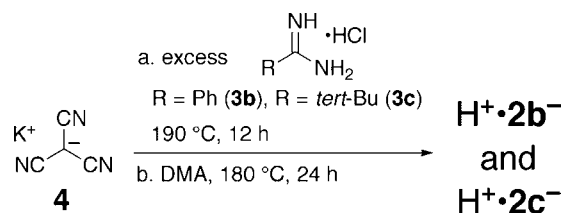
quantum chemical calculation indicates that large positive spin densities of HAP radical **2**[•] reside on the α -sites, being similar to that of the parent phenalenyl radicals.² Thus, from the viewpoint of difference in bond energy between C–C and N–N, the HAP radical **2**[•] is of great interest in evaluating intermolecular bonding natures.

We succeeded in the synthesis of HAP anion **2a**⁻ according to Tomlin's method with some modifications and isolated it as crystals for the first time.^{10,13} It turned out that π - π stacking and radially extended hydrogen/coordination bonds were constructed by the HAP anions in the crystal of potassium salts and copper complex of **2a**⁻.¹⁰ The experimental and theoretical results encouraged us to design and synthesize new HAP derivatives with substituents and functional groups for the creation of diverse assembled structures and developments of exotic electronic properties intrinsic to the phenalenyl system.² Here, we have reported one-pot syntheses of symmetric HAP, $H^+\cdot 2b^-$, and $H^+\cdot 2c^-$, from commercially available compounds. We consider that

the flexible and easily accessible synthetic method opens a new chance to execute the creation of functional materials using HAP derivatives. Crystal structures and fluorescence properties of the newly synthesized HAP systems are also reported.

Tomlin reported the synthesis of triphenyl hexaazaphenalenene $H^+\cdot 2b^-$ by a condensation with benzamide and 4,6-diamino-5-cyano-2-phenylpyrimidine.¹³ It is known that the pyrimidine derivative is prepared from benzamidine hydrochloride (**3b**) with tricyanomethanide **4**.^{14,15} The amidine **3b** is considered as a synthetic equivalent of benzamide. Thus, we have conceived a one-pot synthetic method by using **3b** and succeeded in the synthesis of $H^+\cdot 2b^-$ via the following method: heating a mixture of **3b** and **4** at 190 °C and then additional heating in *N,N*-dimethylacetamide (DMA) at 180 °C (Scheme 1). Unfortunately, the isolated yield was quite

Scheme 1. One-Pot Synthetic Procedures of $H^+\cdot 2b^-$ and $H^+\cdot 2c^-$



low (4% based on **4**) probably because of the poor solubilities in common solvents under the isolation procedure. Therefore, we next tried to synthesize a *tert*-butyl derivative $H^+\cdot 2c^-$ that might have a high solubility. By the optimized condensation condition between **3c** with **4**, we have succeeded in the one-pot synthesis of $H^+\cdot 2c^-$ in 25% yield (Scheme 1).^{16,17} The obtained $H^+\cdot 2c^-$ is soluble in common organic solvents such as dichloromethane and ethyl acetate. In ¹H NMR, a broad signal was observed at 13.1 ppm in dimethylsulfoxide-*d*₆ (DMSO-*d*₆) and 9.3 ppm in chloroform-*d* (CDCl₃).¹⁶ We assumed that the signal was assigned to the NH proton of $H^+\cdot 2c^-$. Fortunately, single crystals of $H^+\cdot 2b^-$ and $H^+\cdot 2c^-$ suitable for X-ray crystal structure analysis were obtained by vapor diffusion methods with water and DMSO.

In the crystal of $H^+\cdot 2b^-$, the HAP skeleton possesses a planar structure, similar to the parent HAP anion $H^+\cdot 2a^-$ (Figure 2a).^{10,18} The two substituted phenyl groups

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(16) Selected compound data of $H^+\cdot 2c^-$: colorless solid; ¹H NMR (300 MHz, DMSO-*d*₆) δ 13.09 (bs, 1H), 1.41 (s, 27H); ¹H NMR (300 MHz, CDCl₃) δ 9.31 (bs, 1H), 1.52 (s, 9H), 1.50 (s, 18H); HRMS (EI) C₁₉H₂₈N₆ (M⁺) calcd 340.2374, found 340.2393. Anal. Calcd for C₁₉H₂₈N₆: C, 67.03; H, 8.29; N, 24.68. Found: C, 66.83; H, 8.17; N, 24.57.

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(18) Crystallographic data for $H^+\cdot 2b^-$: space group *P2₁/a* (No. 14), *a* = 9.588(4), *b* = 18.682(9), *c* = 11.326(7) Å; β = 108.987(19)°; *V* = 1918.4(16) Å³; *T* = 200 K, *R*₁ = 0.0377, *R_w* = 0.1090, GOF = 1.067.

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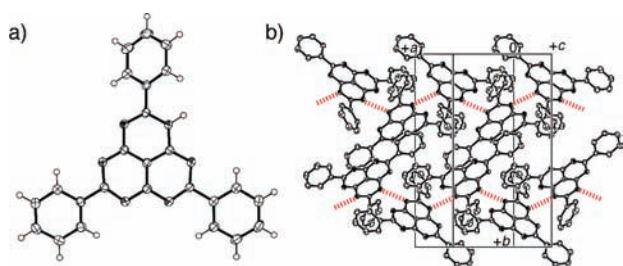


Figure 2. ORTEP presentations of for $\text{H}^+\cdot 2\text{b}^-$ (50% ellipsoid probability). (a) Molecular structure. (b) Packing diagram. Hydrogen atoms are omitted for clarity. The red dashed lines denote H-bonding interactions between 1,3-positions of the HAP skeleton.

are nearly coplanar to the HAP skeleton (phenyl-HAP angles, 5.2° and 8.4°), and the other is twisted (31.6°). A HAP molecule $\text{H}^+\cdot 2\text{b}^-$ is linked to the neighboring HAP molecules with nearly perpendicular arrangements by H-bonding interaction between 1,3-positions ($\text{N}\cdots\text{N}$ distance, 2.86 \AA) (Figure 2b). In addition, the H-bonding chain structures are assembled by π - π interactions between phenyl groups and HAP moiety (ca. 3.2 – 3.5 \AA).

Crystal structure of $\text{H}^+\cdot 2\text{c}^-$ shows that the HAP skeleton also possesses a planar structure, and the molecule has C_2 symmetry due to disordering in one of the *tert*-butyl groups and amino proton (Figure 3a).¹⁹ In addition, $\text{H}^+\cdot 2\text{c}^-$ is linked

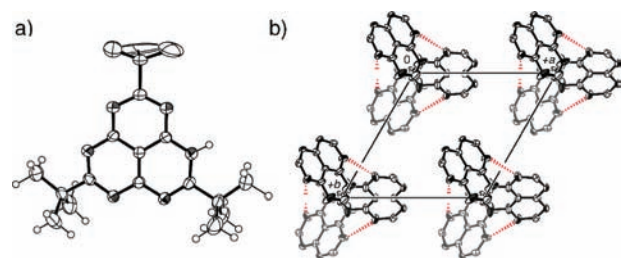


Figure 3. ORTEP presentations for $\text{H}^+\cdot 2\text{c}^-$ (50% ellipsoid probability). (a) Molecular structure. One of the *tert*-butyl groups is disordered. Disordered methyl groups, H-atoms, and amino protons are omitted for clarity. (b) Perspective view along the *c* axis packing diagram. *tert*-Butyl groups and H-atoms are omitted for clarity. The red dashed lines denote H-bonding interactions with one-handed helicities between 1,6-positions of the HAP skeleton. The dark and the light colored molecular frameworks are located in the upper and lower of the H-bonding chains.

to the neighboring molecules with nearly perpendicular arrangements by H-bonding interaction between 1,6-positions ($\text{N}\cdots\text{N}$ distance 3.09 \AA). Interestingly, the H-bonding chain structures of $\text{H}^+\cdot 2\text{c}^-$ form a one-handed helix along the *c*

(19) Crystallographic data for $\text{H}^+\cdot 2\text{c}^-$: space group $P3_121$ (No. 152), $a = 10.4770(16)$, $c = 15.328(3) \text{ \AA}$; $V = 1457.1(4) \text{ \AA}^3$; $T = 200 \text{ K}$, $R = 0.0671$, $R_w = 0.2081$, GOF = 1.126.

axis.²⁰ CD spectra of two kinds of the solid-state (KBr pellets) samples originating in two pieces of single crystals picked up show significant Cotton effects with a mirror image of each other (Figure 4).²¹ To our knowledge, this is rare

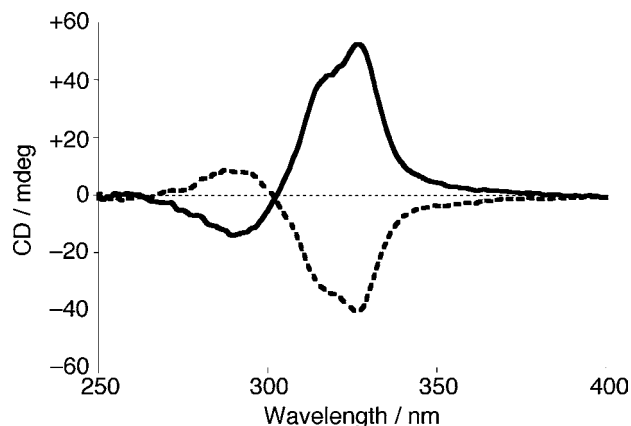


Figure 4. Solid-state CD spectra (KBr pellets) for two crystalline samples of $\text{H}^+\cdot 2\text{c}^-$. The solid and the dashed lines denote different single crystals picked up from the same batch.

event for the construction of H-bonded chiral helix composed of achiral rigid and π -conjugated planar molecules.²²

We also obtained the anion species 2b^- and 2c^- by treatment with sodium hydroxide and tetraethylammonium chloride. The ammonium salts $\text{Et}_4\text{N}^+\cdot 2\text{b}^-$ and $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$ are stable under air and water condition, similar to $\text{K}^+\cdot 2\text{a}^-$.^{10,23} The triphenyl derivative $\text{Et}_4\text{N}^+\cdot 2\text{b}^-$ is slightly soluble to common organic solvents, whereas the *tert*-butyl derivative $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$ is very soluble. In ^1H NMR of $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$, a signal assigned to *tert*-butyl protons was observed at 1.35 ppm in $\text{DMSO}-d_6$ and 1.47 ppm at CDCl_3 , which show magnetic field shifts slightly higher than those of $\text{H}^+\cdot 2\text{c}^-$ (1.41 ppm in $\text{DMSO}-d_6$, 1.52 and 1.50 ppm in CDCl_3).^{16,23} X-ray crystal structure analysis of $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$ showed that the structure of

(20) Unfortunately, the absolute configuration could not be identified because the refinement of flack parameter was not possible in the X-ray crystal structure analysis.

(21) A single crystal (ca. 0.01 mg) was picked up, ground with KBr (15 mg), and pressed for preparing a pellet, and the CD spectrum was measured. Then, another single crystal that was similar in size to the first one was picked up, and the CD spectrum was measured in the same manner. In the case using many crystals of $\text{H}^+\cdot 2\text{c}^-$ for the CD measurement, the Cotton effect was not observed, which indicates that formation of an almost 1:1 mixture of the right- and left-handed H-bonded helices and chirality enrichment did not occur under the crystallization process.

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(23) Selected compound data of $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$: ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 3.20 (q, $J = 7.2 \text{ Hz}$, 8H), 1.35 (s, 27H), 1.16 (tt, $J_{\text{H-H}} = 7.2 \text{ Hz}$ and $J_{\text{N-H}} = 1.8 \text{ Hz}$, 12H); ^1H NMR (300 MHz, CDCl_3) δ 2.92 (q, $J = 7.3 \text{ Hz}$, 8H), 1.47 (s, 27H), 1.15 (m, $J_{\text{H-H}} = 7.3 \text{ Hz}$ and $J_{\text{N-H}} = 1.9 \text{ Hz}$, 12H). Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{N}_6\cdot\text{C}_8\text{H}_{20}\text{N}^+(\text{CH}_2\text{Cl}_2)_{0.9}$: C, 61.36; H, 9.01; N, 17.95. Found: C, 61.28; H, 8.99; N, 17.99.

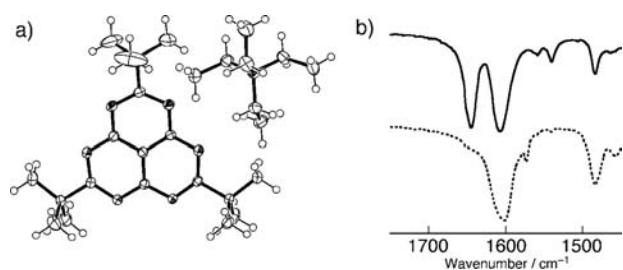


Figure 5. (a) ORTEP presentations of molecular structure for $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$ (50% ellipsoid probability). CH_2Cl_2 existing as crystal solvent is omitted for clarity. (b) IR spectra (KBr pellets) for $\text{H}^+\cdot 2\text{c}^-$ (solid line) and $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$ (dashed line).

2c^- possessed a high planarity (Figure 5a).²⁴ Additionally, bond equalization was observed in carbon–nitrogen bonds (1.33–1.36 Å) on the HAP skeleton. These results are experimental evidence of charge delocalization on the whole HAP skeleton.

In the IR spectra, C=N stretching vibrations were observed at 1592 cm^{-1} for $\text{Et}_4\text{N}^+\cdot 2\text{b}^-$ and 1602 cm^{-1} for $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$. Those were similar to $\text{K}^+\cdot 2\text{a}^-$ (1599 cm^{-1}).¹⁰ In contrast, two peaks were observed in the IR spectra of the hexaazaphenalene species, 1638 and 1596 cm^{-1} for $\text{H}^+\cdot 2\text{b}^-$, 1644 and 1607 cm^{-1} for $\text{H}^+\cdot 2\text{c}^-$ (Figure 5b, and see Supporting Information). These observations were consistent with the result of bond equalization proved by the X-ray crystal structure analysis of $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$. In UV spectra of $\text{H}^+\cdot 2\text{c}^-$ and $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$, no absorption bands were observed in the wavelength region above 350 nm (Figure 6). In the fluorescent spectra, the fluorescence of $\text{H}^+\cdot 2\text{c}^-$ was observed at 350 nm, whereas that of $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$ was quite weak (Figure 6).

A cyclic voltammogram (CV) of $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$ gave an irreversible oxidation wave at around +1.1 V vs Fc/Fc^+ , being assigned to the redox potential between 2c^- and $2\text{c}^{\cdot -}$ (see Supporting Information). These observations were consistent with the result of parent derivative 2a^- .¹⁰ Furthermore, the CV measurement of $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$ gave a quasi-reversible reduction wave at around -2.0 V (see Supporting Information), being assigned to the redox potential between 2c^- and 2c^{2-} (or more reduced state). The reduction wave

(24) Crystallographic data for $\text{Et}_4\text{N}^+\cdot 2\text{c}^- \cdot \text{CH}_2\text{Cl}_2$: monoclinic, space group $P2_1/c$ (No. 14), $a = 12.412(7)$, $b = 19.626(11)$, $c = 13.146(8)$ Å; $\beta = 106.484(6)^\circ$; $V = 3070.7(30)$ Å³; $T = 200\text{ K}$, $R = 0.0852$, $R_w = 0.2245$, $\text{GOF} = 1.068$.

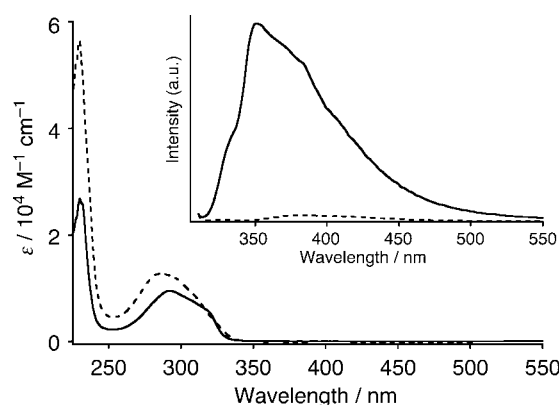


Figure 6. UV–vis and fluorescence (inset: $\lambda_{\text{ex}} = 300\text{ nm}$) spectra of $\text{H}^+\cdot 2\text{c}^-$ (line) and $\text{Et}_4\text{N}^+\cdot 2\text{c}^-$ (dashed line). The fluorescence intensities of these compounds were compared at the same absorbance of the excitation wavelength.

was not observed in usual conditions of CV measurements for the corresponding hydrocarbon phenalenyl system, which indicated a substantial decrease in the calculated LUMO energy of the HAP anion system.¹⁰

In summary, we have succeeded in the one-pot syntheses of symmetric HAP derivative, $\text{H}^+\cdot 2\text{b}^-$ and $\text{H}^+\cdot 2\text{c}^-$, by the condensations of the corresponding amidine hydrochloride with tricyanomethanide. Syntheses of other HAP derivatives and neutral radicals are underway. We believe that the present synthetic method of HAP derivatives is very useful for further development of HAP chemistry.

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Supporting Information Available: Detailed synthetic procedure, IR spectra, UV and fluorescence spectra, and cyclic voltammogram. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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