

Allyl, Amidinium and Cyclopropenyl Cations from the Reactions of Primary and Secondary Amines with Pentachlorocyclopropane

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The action of secondary amines on $c\text{-C}_3\text{HCl}_5$ is a simple new route to aminocyclopropenyl ions, whereas primary amines cause ring opening to an allyl cation, e.g. $[(\text{Bu}^t\text{HN})_2\text{CCHC}(\text{NHBu}^t)_2]^+$ identified crystallographically, which is reversibly protonated at the central carbon to become a *bis*(amidinium) dication.

Cyclopropenyl cations $[\text{C}_3\text{X}_3]^+$ can bear various substituents.¹ The existing route to aminocyclopropenyl ions ($\text{X} = \text{NR}_2$)² requires the prior conversion of pentachlorocyclopropane to tetrachlorocyclopropene using aqueous KOH in which the yield is low and side reactions cause hydrolysis to α,β -dichloroacrylic acid. The direct preparation of **1** or **2** in Scheme 1, where the secondary amine alone provides the strong base, is a much better method. The products are identical with those we have obtained from $c\text{-C}_3\text{Cl}_4$.

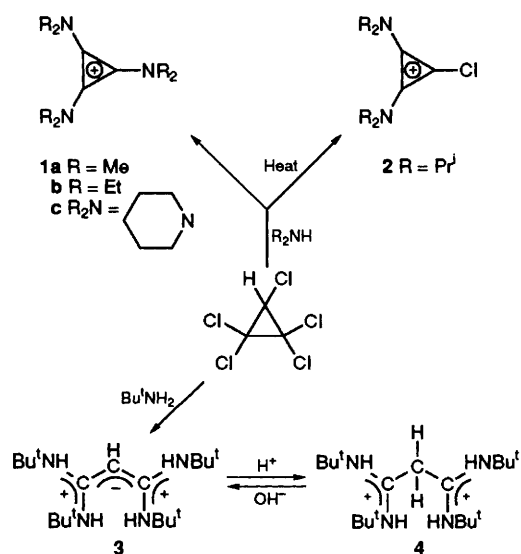
The crystal structure of **1c**·ClO₄³ shows piperidine rings in the chair conformation attached to a planar C₃N₃ core within which the C–C and C–N distances are in harmony with previous measurements of **1a**.⁴ Parallel investigations of **2**·Cl, which is the end product (even when excess Prⁱ₂NH is employed and the mixture is refluxed) explore a cyclopropenyl ion in which the structural properties respond to the different substituents. NMR and vibrational spectra are diagnostic; e.g. **2** gives ¹³C signals at δ 93.2 and 131.8 from the carbons bearing Cl and N atoms, respectively, whereas $[\text{C}_3(\text{NR}_2)_3]^+$ ions, **1a–c**, give a signal close to δ 118.⁵ X-Ray analysis³ of **2** finds a C–C bond of 1.39 Å between the carbons bearing the amino groups, and two shorter ring bonds of 1.29 Å. The C–Cl single bond of 1.75 Å is in marked contrast to the contracted C–Cl bonds of 1.64 Å in $[\text{C}_3\text{Cl}_3]^+$.⁶

Short exocyclic C–N bonds of 1.30 Å in **2**, implying partial double bond character, are matched by NMR spectra which demonstrate inequivalent Prⁱ groups of the Prⁱ₂N substituents. The ¹H spectrum at 400 MHz and 298 K in D₂O consists of an overlapping pair of Me doublets with centres 2.7 Hz apart and two CH septets separated by 32.4 Hz. Coalescence occurs at 322 and 350 K, and furnishes $\Delta G^\ddagger = 74.3$ and 73.8 ± 0.7 kJ mol⁻¹, respectively, with ΔS^\ddagger ca. zero. These values are typical of C–N bonds with restricted rotation.⁷

Primary amines act on $c\text{-C}_3\text{HCl}_5$ by a different course where replacement of chlorine is accompanied by ring opening, so that the C₃ unit becomes the nucleus of an allyl

cation with amino substituents.[†] Thus, reaction of Bu^tNH₂ with $c\text{-C}_3\text{HCl}_5$ is rapid at ambient temperature in chloroform to yield **3**·Cl.[‡] Treatment with AgNO₃ gave crystals of **3**·NO₃ suitable for X-ray study.[§] Fig. 1 shows the presence of four –NHBu^t groups. The central carbons, of which C(2) carries a hydrogen atom, each have trigonal coordination, and the N–C–N planes are inclined at just 28.2° to one another. These facts, plus the uniformity in the C–C and C–N bond lengths, suggest electron delocalisation over all seven atoms of the N₂CCCN₂ framework which should contribute significantly to its stability. Interestingly, the kindred species $[(\text{Me}_2\text{N})_2\text{CCHC}(\text{NMe}_2)_2]^+$ is the minor product (yield 9%) of alkaline hydrolysis of the tris(dimethylamino)cyclopropenyl ion **1a**, alongside bis(dimethylamino)cyclopropenone (65%).⁹

Seeking other salts, we added HCl to an aqueous solution of **3** as a prelude to introducing a metal chloride complex anion. The acidification caused an unexpected change in NMR to give two inequivalent sets of *tert*-butyl signals. After adding GaCl₃ in 6 mol dm⁻³ HCl the solution deposited colourless crystals of $[\text{4}][\text{GaCl}_4]_2$.[‡] Only slight changes in the IR or Raman spectra accompany the protonation which has occurred, and **3** is regenerated when the acidic solution is neutralised. X-Ray crystallography established the structure of **4** in which the extra H⁺ is attached to C(2) converting this previously unsaturated atom into a methylene group.[§] In consequence the C–C–C bond angle (127.1° in **3**) is now 112.4° and close to the tetrahedral value. The C–C bonds have extended from 1.40 in **3** to 1.51 Å in **4**, becoming single bonds and destroying the allyl character. Meanwhile the pairs of C–N bonds contract from 1.36 (average) to 1.32 Å to become amidinium systems. The N–C–N planes are now inclined at an angle of 82.0°, which argues decisively against their being encompassed by overall π -bonding.



Scheme 1 Reagents and conditions: CHCl₃ for **1–3**; 6 mol dm⁻³ HCl for **4**

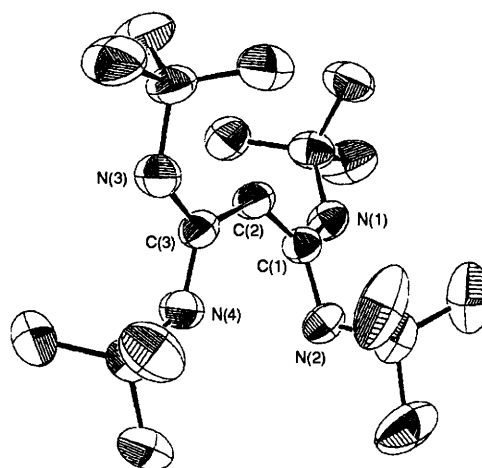


Fig. 1 The 1,1,3,3-tetrakis(*tert*-butylamino)allyl cation, $[(\text{Bu}^t\text{HN})_2\text{CCHC}(\text{NHBu}^t)_2]^+$ **3**, with 50% thermal ellipsoids. Selected bond distances (Å) and angles (°): C(2)–C(1,3) 1.375(4), 1.416(4), C(1)–N(1,2) 1.340(4), 1.409(4); C(3)–N(3,4) 1.345(4), 1.336(4); C(1)–C(2)–C(3) 127.1(3); C(2)–C(1)–N(1,2) 124.2(3), 120.5(3); N(1)–C(1)–N(2) 115.3(3); C(2)–C(3)–N(3,4) 120.4(3), 121.5(3); N(3)–C(3)–N(4) 118.0(3). Hydrogen-bonded contacts to NO₃⁻ ion: N(1)⋯O(1) 2.94; N(2)⋯O(3) 3.15 Å.

The C–N bonds of **4** are similar in length to those of **2** and again produce a barrier to rotation. In the ^1H NMR spectrum of acidified D_2O solution of **4**, at 400 MHz and 298 K, the Me hydrogen signals of the distinct Bu^iN^- environments (where the geometry about the C–N bond is *cis* or *trans* to the central CH_2 group) are separated by 18.2 Hz but these coalesce at 345 K, giving a value of ΔG^\ddagger , $74.3 \pm 0.6 \text{ kJ mol}^{-1}$, near that of **2**.

We return to the aminocyclopropenyl system to stress its stability; not only is the C_3 nucleus resistant to prolonged exposure to hot water, it is also capable of oxidation to a radical dication.¹⁰ Treatment of **1b** as the chloride in CH_2Cl_2 with SbCl_5 affords dark-red crystals of $[\text{C}_3(\text{NET}_2)_3](\text{SbCl}_6)_2$. Confirmation that the ring remains intact is provided by the FT Raman spectrum which has a peak at 1555 cm^{-1} matching the IR-active C–C band at 1550 cm^{-1} . A strong peak at 1906 cm^{-1} is assignable to the ring-breathing mode, being the counterpart of that of **1b** at 1963 cm^{-1} . Oxidation removes an electron from the HOMO of a_2'' symmetry¹¹ and the decrease of 57 cm^{-1} in the symmetric C–C stretch reflects the consequent bond weakening.

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Footnotes

† The reaction of pyridines with $c\text{-C}_3\text{Cl}_4$ is of interest since it also causes ring-opening and displacement of Cl substituents: K. C. Waterman and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, 1984, **106**, 3874.

‡ Compound **3-Cl**: *tert*-butylamine (3.35 g, 46 mmol) was added dropwise to a stirred solution of pentachlorocyclopropane (1.23 g, 5.7 mmol) in CHCl_3 (40 cm^3) at 20°C . After 1 h the mixture was filtered to remove precipitated *tert*-butylammonium chloride and concentrated under vacuum to an oil which formed a cream-coloured microcrystalline solid on adding Et_2O (1.0 g, 48%); mp $157\text{--}159^\circ\text{C}$; MS: m/z 325 (M^+); ^1H NMR (200 MHz, CDCl_3 , 25°C): δ 1.43 (36H, s, CH_3), 4.29 (1H, s, CH), 6.82 (4H, s, NH); ^{13}C (50.3 MHz, CDCl_3 , 25°C): δ 30.0 (Me), 53.7 (CMe_3), 73.7 (CCHC), 160.7 (CCHC); IR: ν/cm^{-1} 1560 (vs, $\text{C}=\text{N}_{\text{sym}}$), 1610, 1626 (vs, $\text{C}=\text{N}_{\text{asym}}$).

Compound **4** $[\text{GaCl}_4]_2$: a solution containing GaCl_3 (2 equiv.) in 6 mol dm^{-3} HCl was added to an aqueous solution of **3-Cl** which then deposited colourless crystals identified by X-ray analysis and spectroscopically; mp (decomp) $212\text{--}222^\circ\text{C}$; IR: ν/cm^{-1} 1559 (m, $\text{C}=\text{N}_{\text{sym}}$),

1632 (vs, $\text{C}=\text{N}_{\text{asym}}$). NMR of **4** in 6 mol dm^{-3} DCl; ^1H (200 MHz, 25°C): δ 1.58 (18H, s, Me), 1.61 (18H, s, Me); ^{13}C NMR (50.3 MHz, 25°C): δ 30.1 (Me), 32.0 (Me), 35.0 (CCH₂C), 58.6 (CMe_3), 60.9 (CMe_3), 160.0 (CCH₂C).

§ *Crystal data* (Enraf-Nonius CAD4 diffractometer): for compound **3-NO₃** $\text{C}_{19}\text{H}_{41}\text{N}_5\text{O}_3$, $M = 387.6$, monoclinic, space group, $P2_1/c$, $a = 12.195(3)$, $b = 17.717(3)$, $c = 12.388(2) \text{ \AA}$, $\beta = 114.57(2)^\circ$, $U = 2434 \text{ \AA}^3$, $T = 291 \text{ K}$, $F(000) = 856$; $Z = 4$, $D_c = 1.06 \text{ g cm}^{-3}$, Mo-K α , $\lambda = 0.71069 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 0.078 \text{ mm}^{-1}$, specimen $0.31 \times 0.29 \times 0.21 \text{ mm}$, 4281 unique reflections, 2120 with $F > 4\sigma(F)$ used in refinement, $2\theta_{\text{max}} = 50^\circ$.

Compound **4** $[\text{GaCl}_4]_2$, $\text{C}_{19}\text{H}_{42}\text{Cl}_8\text{Ga}_2\text{N}_4$, $M = 749.6$, monoclinic, space group $P2_1/c$, $a = 11.370(4)$, $b = 21.303(3)$, $c = 14.755(2) \text{ \AA}$, $\beta = 95.05(2)^\circ$, $U = 3560 \text{ \AA}^3$, $T = 293 \text{ K}$, $F(000) = 1528$; $Z = 4$, $D_c = 1.40 \text{ g cm}^{-3}$, Mo-K α , $\lambda = 0.71069 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 2.21 \text{ mm}^{-1}$, specimen $0.40 \times 0.37 \times 0.26 \text{ mm}$, 6892 unique reflections, 2456 with $F > 4\sigma(F)$ used in the refinement, $2\theta_{\text{max}} = 52^\circ$.

Structures were solved by direct methods using SHELXS-86 and refined by full-matrix least-squares analysis on F^2 using SHELXL-92. In **3-NO₃** the hydrogen atoms were located and refined with individual isotropic temperature factors; the final residuals were $R_1 = 0.059$, $wR_2 = 0.196$. In **4** $[\text{GaCl}_4]_2$, the $[\text{GaCl}_4]^-$ ions were disordered, limiting the accuracy of the structure, and the hydrogen atoms were not located; the final residuals were $R_1 = 0.100$, $wR_2 = 0.372$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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