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Structural and spectroscopic investigations of non-planar tris(dialkylamino)cyclopropenium cations

James R. Butchard[a], Owen J. Curnow[a]*, Robert J. Pipal[a], Ward T. Robinson[a] and Rong Shang[a]

The mixed triaminocyclopropenium cation bis(diisopropylamino)dimethylaminocyclopropenium was prepared from bis(diisopropylamino)chlorocyclopropenium by reaction with dimethylamine. It was isolated as the perchlorate salt and found to have a distorted structure in the solid state. Tris(diisopropylamino)cyclopropenium was prepared by reaction of pentachlorocyclopropane with diisopropylamine in a refluxing dichloroethane solution for 2 days. The solid state structure was found by X-ray crystallography to have two planar amino groups and one pyramidal amino group, however, the ^{1}H-NMR and infrared solution spectra show equivalent isopropyl groups in solution. The compounds were also characterised by Raman and infrared spectroscopy. Additionally, a new polymorph of $[C_3(NMe_2)_3]ClO_4$ is described as well as the X-ray structure of bis(diisopropylamino)cyclopropenone. Copyright © 2007 John Wiley & Sons, Ltd.

Keywords: cyclopropenium; amine; infrared spectroscopy; Raman spectroscopy; X-ray

INTRODUCTION

The cyclopropenium ion, $[C_3H_3]^+$, is the classic example of a Hückel 2π-electron aromatic ring system. Many investigations have been carried out on derivatives $[C_3X_3]^+$, and a large variety of substituents have been prepared (e.g. X = alkyl, aryl, SiR_3, NR_2, OR, F, Cl, Br, I, SR, SeMe, TeMe).[1,2] Despite the apparent ring strain, many of the cations are very stable due to the inherent aromaticity; some amino derivatives, for example, are stable to hydrolysis at 100 °C. Although most studies on such systems have been carried out for theoretical interest, synthetic chemistry utilising cyclopropenium cations has been developing recently in the areas of organic and organometallic chemistry.[1] Bertrand and coworkers[3] have recently isolated the first cyclopropenylidenes via deprotonation of the diaminocyclopropenium $[C_3(N^iPr_2)_2H]^+$.

Secondary aminocyclopropenium cations are generally synthesised by reaction of tetrachlorocyclopropene or pentachlorocyclopropane with a secondary amine.[4–6] An excess of amine is used as a base to remove the HCl, as a dialkylammonium chloride salt, produced during the reaction. These aminocyclopropenium cations exhibit planar geometries with the trigonal planar nitrogen atoms and its substituents coplanar with the C_3^+ ring to maximise π donation from the nitrogen atoms to the ring.[7–9] The unusual stability of these cationic compounds is attributed to this π donation and the reduced positive charge on the carbon atoms.[4] Indeed, these cations are sufficiently electron-rich as to be 'donor' species: Weiss *et al.*[10] have taken advantage of this property to prepare compounds with isolated anions as a result of the ion-pair strain. Barriers to rotation about the exocyclic C—N bonds have also been measured and found to decrease as the number of π-donor substituents is increased.[8,11]

Presented here are structural and spectroscopic investigations of tris(dialkylamino)cyclopropenium cations, the C_{2v}-symmetric bis(diisopropylamino)dimethylaminocyclopropenium and the sterically bulky tris(diisopropylamino)cyclopropenium, which both show significant deviations from a planar geometry. The synthesis of the tris(diisopropylamino)cyclopropenium salt had been attempted by others without success.[4,5,12] Gompper and Schönafinger[6] reported the preparation of the perchlorate salt of both of these cations as red oils. Some of our work has been communicated.[13]

RESULTS AND DISCUSSION

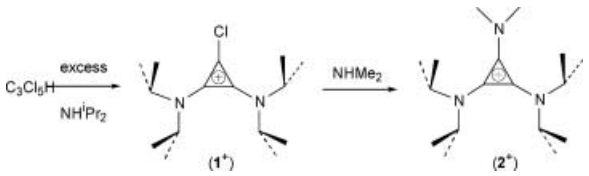
Synthesis and NMR spectra

Yoshida and Tawara[12] have previously reported the synthesis and characterisation of the bis(diisopropylamino)chlorocyclopropenium salt, $[C_3(NiPr_2)_2Cl][ClO_4]$ (**1**.ClO_4), from tetrachlorocyclopropene as well as the diethylamino analogue, but were unable to prepare a triaminocyclopropenium cation from this. We have found, however, that use of less bulky dimethylamine allows the synthesis of the mixed triamine system $[C_3(NiPr_2)_2(NMe_2)][ClO_4]$ (**2**.ClO_4) in 54% yield as colourless crystals. Gompper and

* *Department of Chemistry, Rutherford Building, University of Canterbury, Private Bag 4800, Christchurch, New Zealand.*
E-mail: owen.curnow@canterbury.ac.nz

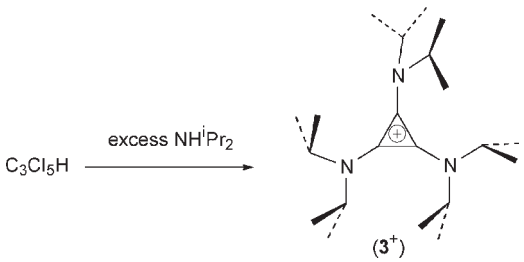
a *J. R. Butchard, O. J. Curnow, R. J. Pipal, W. T. Robinson, R. Shang*
Department of Chemistry, Rutherford Building, University of Canterbury, Christchurch, New Zealand

Schönafinger[6] reported the preparation of this compound in 78% yield as a red oil.



As expected for a C_{2v} cyclopropenium system, the ^{13}C-NMR spectrum of $\mathbf{2}^+$ exhibits two C_3 ring-carbon resonances (119.6 and 116.9 ppm – the latter has twice the intensity of the other and can therefore be assigned to the carbon atoms with the diisopropylamine groups attached to them) and one resonance (42.3 ppm) for the dimethylamino substituents.[8] At ambient temperature, the isopropyl groups are equivalent and only one resonance appears for the tertiary carbons (51.2 ppm) along with one for the methyl carbons (21.8 ppm). This is consistent with rapid rotation about the exocyclic C—N bonds. Krebs and Breckwoldt[11] have reported barriers to exocyclic C—N bond rotation of $\Delta G^{\ddagger} = 95$–105 kJ mol^{-1} for mono-amino-substituted cyclopropeniums $[C_3X_2NR_2]^+$ (where X = Me or Ph and R = Me or aryl) and Clark *et al.*[8] reported a barrier of $\Delta G^{\ddagger} = 75$ kJ mol^{-1} for the diamino-substituted cation $[C_3(N^iPr_2)_2Cl]^+$. An even lower barrier for the triamino cation $\mathbf{2}^+$ is expected due to a further reduction in π donation from each competing amino substituent. Increased steric interactions between the groups may also play a part in determining the barrier. The ^{1}H-NMR spectrum of $\mathbf{2}^+$ is also consistent with rapid rotation about the exocyclic C—N bonds: Only one set of resonances is observed for the isopropyl groups (3.85 ppm for the tertiary H atoms and 1.35 ppm for the Me groups) along with one resonance (3.22 ppm) for the dimethylamino substituent. Unfortunately, low temperature (−55 °C) NMR spectroscopy was unable to freeze out this rotation and, although some line broadening of the tertiary carbons occurred in the ^{13}C-NMR spectra, no decoalesence of any signal was observed.

The tris(diisopropylamino)cyclopropenium cation, $[C_3(N^iPr_2)_3]^+$ ($\mathbf{3}^+$), was initially isolated as an unexpected side-product from the synthesis of $\mathbf{2}.ClO_4$. It was then prepared in low yield (8%) by refluxing C_3Cl_5H with excess diisopropylamine in dichloroethane for 2 days. Gompper and Schönafinger[6] reported the preparation of the perchlorate salt by reaction in an autoclave at 150 °C to give a 75% yield of a red oil. The chloride salt was found to crystallise as a trihydrate from wet $CHCl_3$/diethylether.[13]



NMR spectroscopy of $\mathbf{3}^+$ in solution suggests D_{3h} symmetry: the cation displays a single ring-carbon resonance at 119.45 ppm that is characteristic of $[C_3(NR_2)_3]^+$ cations, and both ^{1}H- and ^{13}C-NMR spectroscopy show only one isopropyl environment down to −40 °C. However, the X-ray structure (see discussion below) shows one amino group to be non-planar with an sp^3 hybridised N atom and the associated isopropyl groups out of the C_3N_3 plane. This would make the isopropyl groups on the other amino substituents inequivalent. Clearly, $\mathbf{3}^+$ exhibits a low barrier to C—N bond rotation for the same reasons as $\mathbf{2}^+$, although the steric contribution is probably greater in $\mathbf{3}^+$.

Cations $\mathbf{2}^+$ and $\mathbf{3}^+$ were also characterised by ES-MS. Both gave the expected strong parent ion peak (280 and 336 *m/e* for $\mathbf{2}^+$ and $\mathbf{3}^+$, respectively) in CH_3CN/H_2O mixed solvent. For $\mathbf{3}^+$, however, there was also a significant peak due to the protonated cyclopropenone hydrolysis product $[C_3(N^iPr_2)_2OH]^+$ at 253 *m/e*. This sensitivity is no doubt a consequence of the steric crowding and the non-planar amino group.

X-ray structure determinations

The crystal structure of $\mathbf{2}^+$ was determined as a perchlorate salt. There is one independent molecule in the unit cell. Figure 1 contains an ORTEP of the molecule with the adopted numbering scheme and Fig. 2 shows a side-on perspective. Table 1 gives the crystal data and structure refinement parameters for all X-ray structures and Table 2 gives selected bond distances and angles for $\mathbf{2}.ClO_4$. Somewhat surprisingly, a few crystals of $[C_3(NMe_2)_3][ClO_4]$ ($\mathbf{4}.ClO_4$) were also isolated from the product mixture. The space group for these crystals ($P2_{1/n}$) is different from that reported earlier for the same salt (*P*nma).[7] The metrical details found for $\mathbf{4}^+$ are not significantly different with both structures having an umbrella-like shape with the amino groups bent towards the perchlorate anions in the crystal lattice. Table 3 gives selected bond distances and angles for $\mathbf{4}.ClO_4$, Fig. 3 contains an ORTEP of $\mathbf{4}^+$ with the adopted numbering scheme and Fig. 4 shows a side-on perspective.

As with other crystallographically characterised aminocyclopropenium cations, $\mathbf{2}^+$ is essentially planar with trigonal planar N atoms so as to maximise π donation into the C_3 ring. The isopropyl groups in $\mathbf{2}^+$ display the same conformational arrangement about the ring as $\mathbf{1}^+$:[8] two isopropyl groups are oriented towards the less bulky chloro or dimethylamino

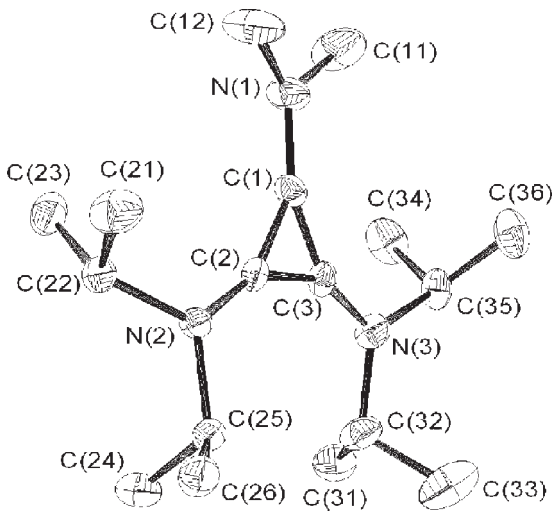


Figure 1. ORTEP of $\mathbf{2}^+$ with the atomic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level and the hydrogen atoms have been omitted for clarity

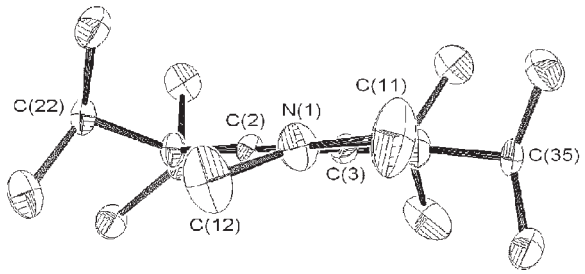


Figure 2. Side-on perspective of $\mathbf{2}^+$. Thermal ellipsoids are drawn at the 40% probability level and the hydrogen atoms have been omitted for clarity

substituent and the other two are oriented towards these isopropyl groups and away from each other. Within experimental error, there is no significant variation in the cyclic C—C and exocyclic C—N bond distances (averages of 1.381 and 1.334 Å, respectively) which are essentially the same as those found in $\mathbf{4}^+$ and the trispiperidinyl analogue $[C_3(NC_5H_{10})_3]+$ ($\mathbf{5}^+$)[8] (1.373 and 1.330 Å, respectively, for $\mathbf{4}^+$ and 1.381 and 1.333 Å, respectively, for $\mathbf{5}^+$). On the other hand, the N—Me bond lengths in $\mathbf{2}^+$ appear to be slightly shorter than those in $\mathbf{4}^+$ (1.438(6) *vs.* 1.457(8) Å) while the N—iPr distances are slightly longer than these at 1.483(6) Å.

Whereas cation $\mathbf{1}^+$ exhibits planarity of not only the C_3N_3 core but also of the nitrogen atom substituents, in cation $\mathbf{2}^+$, the substituents on the N atoms do not all lie in the C_3N_3 plane (refer to Fig. 2), even though the nitrogen atoms are very close to trigonal planar (sum of angles = 358.2°, 358.5° and 359.9° for N(1)—N(3), respectively). The substituents on N(1) and N(2) show the most deviation with one substituent being bent to one side of the ring and the other to the other side. Effectively, this is exhibiting a partial rotation about the exocyclic C—N bond. Thus, at N(2), the dihedral angle C22—N2—C2—C1 = −23.7° and C25—N2—C2—C3 = −9.4° while at N(1) the corresponding dihedral angles are C(11)—N(1)—C(1)—C(3) = −4.7° and C(12)—N(1)—C(1)—C(2) = −20.9°. The distortions at N(3), on the other hand, are comparatively small; the corresponding dihedral angles are C(32)—N(3)—C(3)—C(2) = −6.6° and C(35)—N(3)—C(3)—C(1) = −6.2°. For $\mathbf{4}^+$, these dihedral angles range from 4.2° to

Table 1. Crystal data and structure refinement for $[C_3(NMe_2)_3]ClO_4$ (**2**.ClO_4), $[C_3(N^iPr_2)_2(NMe_2)]ClO_4$ (**4**.ClO_4) and $(^iPr_2N)_2C_3O$ (**6**)

Compound	**2**.ClO_4	**4**.ClO_4	**6**
Empirical formula	$C_{17}H_{34}ClN_3O_4$	$C_9H_{18}ClN_3O_4$	$C_{15}H_{28}N_2O$
Formula weight	379.92	267.71	252.39
Temperature (K)	293(2)	293(2)	99(2)
Wavelength (Å)	0.71073	1.54180	0.71073
Crystal system, space group	Monoclinic, *P*2(1)/*c*	Monoclinic, *P*2(1)/*n*	Monoclinic, *P*2(1)
a (Å)	10.033(4)	8.187(2)	14.0595(6)
b (Å)	10.472(3)	13.087(4)	7.8470(3)
c (Å)	20.151(7)	12.673(4)	14.0898(6)
α (°)	90	90	90
β (°)	102.46(3)	105.56(2)	97.448(2)
γ (°)	90	90	90
Volume (Å^3)	2067.3(12)	1307.2(7)	1541.34(11)
Z, calculated density (mg/m^3)	4, 1.221	4, 1.360	4, 1.088
Absorption coefficient (mm^{-1})	0.210	2.692	0.068
F(000)	824	568	560
Crystal size (mm)	0.85 × 0.26 × 0.18	0.22 × 0.06 × 0.03	0.85 × 0.40 × 0.30
θ range for data collection (°)	2.07–22.51	4.96–60.23	1.46–34.54
Limiting indices	$-13 \le h \le 1$	$-9 \le h \le 8$	$-21 \le h \le 20$
	$-1 \le k \le 11$	$0 \le k \le 14$	$-11 \le k \le 10$
	$-20 \le l \le 21$	$0 \le l \le 14$	$-21 \le l \le 21$
Reflections collected/unique	3275/2713 [Rint = 0.0316]	2043/1949 [Rint = 0.0520]	29361/10022 [$r_{int.}$ = 0.0336]
Completeness to θmax	99.9%	99.6%	99.9%
Absorption correction	Psi-scan	Psi-scan	Semi-empirical
Data/restraints/parameters	2713/1/237	1949/0/160	10022/1/342
Goodness-of-fit on F^2	0.894	1.044	1.071
Final *R* indices [I > 2σ(I)]			
R_1	0.0564	0.0503	0.0375
wR_2	0.1347	0.1379	0.0937
R indices (all data)			
R_1	0.0944	0.0862	0.0429
wR_2	0.1466	0.1612	0.1029
Largest diff. peak (e Å^{-3})	0.592	0.415	0.311
Largest diff. hole (e Å^{-3})	−0.355	−0.347	−0.202

Table 2. Selected bond lengths (Å) and angles(°) for $[C_3(N^iPr_2)_2(NMe_2)]ClO_4$ (**2**.ClO_4)

C(1)–C(2)	1.378(5)	N(1)–C(1)	1.339(5)
C(1)–C(3)	1.377(6)	N(2)–C(2)	1.333(5)
C(2)–C(3)	1.387(5)	N(3)–C(3)	1.330(5)
N(1)–C(11)	1.439(5)	N(1)–C(12)	1.436(6)
N(2)–C(22)	1.484(5)	N(2)–C(25)	1.477(5)
N(3)–C(32)	1.485(5)	N(3)–C(35)	1.486(5)
C(2)–C(1)–C(3)	60.5(3)	C(1)–C(3)–C(2)	59.8(3)
C(1)–C(2)–C(3)	59.7(3)	N(2)–C(2)–C(3)	148.9(4)
N(1)–C(1)–C(2)	147.7(4)	N(3)–C(3)–C(1)	152.3(4)
N(1)–C(1)–C(3)	151.8(4)	N(3)–C(3)–C(2)	147.9(4)
N(2)–C(2)–C(1)	151.4(4)	C(1)–N(1)–C(11)	121.4(4)
C(2)–N(2)–C(22)	121.8(3)	C(1)–N(1)–C(12)	122.1(3)
C(2)–N(2)–C(25)	118.8(3)	C(11)–N(1)–C(12)	114.7(4)
C(22)–N(2)–C(25)	117.9(3)	C(3)–N(3)–C(32)	120.5(3)
C(32)–N(3)–C(35)	118.5(3)	C(3)–N(3)–C(35)	120.9(4)

Table 3. Selected bond lengths (Å) and angles (°) for $[C_3(NMe_2)_3]ClO_4$ (**4**.ClO_4)

C(1)–C(2)	1.373(5)	N(1)–C(1)	1.330(4)
C(1)–C(3)	1.376(5)	N(2)–C(2)	1.329(4)
C(2)–C(3)	1.370(5)	N(3)–C(3)	1.332(4)
N(1)–C(4)	1.450(5)	N(1)–C(5)	1.458(5)
N(2)–C(6)	1.463(5)	N(2)–C(7)	1.454(5)
N(3)–C(8)	1.452(5)	N(3)–C(9)	1.448(5)
C(2)–C(1)–C(3)	59.8(2)	C(1)–C(3)–C(2)	60.0(2)
C(1)–C(2)–C(3)	60.2(3)	N(2)–C(2)–C(3)	149.6(3)
N(1)–C(1)–C(2)	150.4(3)	N(3)–C(3)–C(1)	149.7(4)
N(1)–C(1)–C(3)	149.8(3)	N(3)–C(3)–C(2)	150.2(4)
N(2)–C(2)–C(1)	150.2(3)	C(1)–N(1)–C(4)	118.7(3)
C(2)–N(2)–C(6)	119.2(3)	C(1)–N(1)–C(5)	119.1(3)
C(2)–N(2)–C(7)	120.0(3)	C(4)–N(1)–C(5)	118.4(3)
C(6)–N(2)–C(7)	117.8(3)	C(3)–N(3)–C(8)	118.7(3)
C(8)–N(3)–C(9)	117.6(3)	C(3)–N(3)–C(9)	119.6(3)

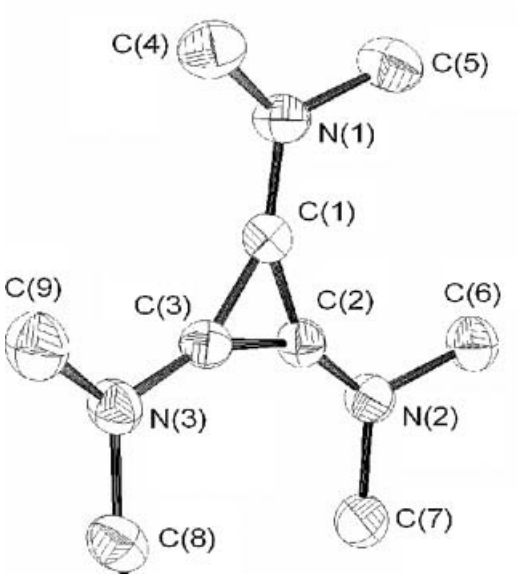


Figure 3. ORTEP of $\mathbf{4}^+$ with the atomic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level and the hydrogen atoms have been omitted for clarity

12.6°. The C_3N_3 core of $\mathbf{2}^+$ is close to being planar, with only minor distortions of the nitrogen atoms from the plane of the C_3 ring (the angle between the exocyclic C–N vectors and the C_3 plane are 3.2°, 2.4° and 1.0° for N(1), N(2) and N(3), respectively). In contrast, cations $\mathbf{4}^+$ and $\mathbf{5}^+$ show significant deviations of the N atoms from the C_3 plane in which the substituents are all on the same side and the N atoms adopt distorted trigonal planar geometries (average sum of angles = 356° and 352° for $\mathbf{4}^+$ and $\mathbf{5}^+$, respectively). In the case of $\mathbf{5}^+$, the substituents are bent to the opposite side of the ring from which the N atoms are bent, whereas in $\mathbf{4}^+$ the substituents are bent to the same side, thus giving an umbrella-like structure.

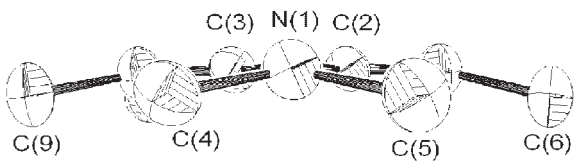


Figure 4. Side-on perspective of $\mathbf{4}^+$. Thermal ellipsoids are drawn at the 40% probability level and the hydrogen atoms have been omitted for clarity

Table 4. Selected bond lengths (Å) and angles (°) for $[C_3(N^iPr_2)_3]Cl \cdot 3H_2O$ (**3**.Cl · $3H_2O$)

C(1)–C(2)	1.3861(8)	N(1)–C(1)	1.3219(7)
C(1)–C(3)	1.4316(9)	N(2)–C(2)	1.3928(8)
C(2)–C(3)	1.3881(8)	N(3)–C(3)	1.3260(8)
N(1)–C(11)	1.4856(8)	N(1)–C(14)	1.4938(8)
N(2)–C(22)	1.4940(8)	N(2)–C(21)	1.5115(9)
N(3)–C(31)	1.4932(8)	N(3)–C(34)	1.4928(8)
C(2)–C(1)–C(3)	59.00(4)	C(1)–C(3)–C(2)	58.87(4)
C(1)–C(2)–C(3)	62.13(4)	N(2)–C(2)–C(3)	151.11(6)
N(1)–C(1)–C(2)	149.58(6)	N(3)–C(3)–C(1)	154.12(6)
N(1)–C(1)–C(3)	151.37(6)	N(3)–C(3)–C(2)	146.97(6)
N(2)–C(2)–C(1)	146.69(6)	C(1)–N(1)–C(11)	121.78(5)
C(2)–N(2)–C(22)	113.83(5)	C(1)–N(1)–C(14)	119.90(5)
C(2)–N(2)–C(21)	109.57(5)	C(11)–N(1)–C(14)	118.33(5)
C(22)–N(2)–C(21)	118.99(5)	C(3)–N(3)–C(31)	116.91(5)
C(31)–N(3)–C(34)	118.75(5)	C(3)–N(3)–C(34)	124.22(5)

The solid state structure of **3**.Cl · $3H_2O$ was determined to investigate the effect of the anticipated steric interactions between the isopropyl groups. The experimental details and results have been communicated.[13] It was found to crystallise with one independent molecule in the unit cell. Table 4 gives selected bond distances and angles, Fig. 5 illustrates the cation with the atomic labelling scheme and Fig. 6 shows a side-on perspective of $\mathbf{3}^+$. The chloride is particularly interesting in its own right; it forms a discrete dichloride hexahydrate cluster, $[Cl_2(H_2O)_6]^{2-}$, with chlorides in opposite corners of a Cl_2O_6 cube. The structure of this interesting inorganic cluster has been discussed elsewhere.[13]

Like other cyclopropenium cations, the C_3N_3 unit in $\mathbf{3}^+$ is essentially planar. However, unlike other aminocyclopropenium cations, only two of the amino groups, N(1) and N(3), are trigonal planar (the sum of angles are 360.0° and 359.9° for N(1) and N(3), respectively) while the third, N(2), is closer to sp^3 hybridisation than sp^2 hybridisation (the sum of angles is 342.4° with two bond angles less than 114°). This has a dramatic effect on the C_3 ring distances since N(2) is not able to π donate into the ring: the bond opposite N(2), C(1)—C(3), at 1.4316(9) Å, is significantly longer than the other C—C ring bonds (average of 1.387 Å) which are similar to those found in $\mathbf{2}^+$, $\mathbf{4}^+$ and $\mathbf{5}^+$ (1.373–1.381 Å). Similarly, in the structure of $\mathbf{1}^+$,[8] the C—C bond opposite the Cl atom is lengthened (to 1.427(5) Å), however, in this case the other cyclic C—C bonds are noticeably shortened (to an average of 1.331 Å). The effect on the exocyclic C—N bonds to N(1) and N(3) in $\mathbf{3}^+$ is minimal with an average distance of 1.324 Å as compared to 1.334 Å in $\mathbf{2}^+$. This contrasts with $\mathbf{1}^+$ in which the exocyclic C—N bonds are shortened to an average of 1.285 Å. As would be expected, the exocyclic C—N bond distance to N(2) in $\mathbf{3}^+$ is lengthened compared to the other two C—N bonds: 1.3928(8) *versus* 1.3219(7) and 1.3260(8) Å. However, it is still significantly shorter than the N—C distances to the sp^3 carbon atoms (1.485–1.512 Å). The non-planarity of N(2) and significant steric interactions result in its isopropyl groups lying out of the C_3N_3 plane: C(21)—N(2)—C(2)—C(1) = 79.8° and C(22)—N(2)—C(2)—C(3) = 39.7°. Steric interactions between the two planar amino groups are also apparent: one isopropyl group on N(3) is oriented towards N(1) with the result that the isopropyl groups on N(3) are pushed away from N(1): C(3)—N(3)—C(34) = 124.22(5)° and C(3)—N(3)—C(31) = 116.91(5)°. For comparison,

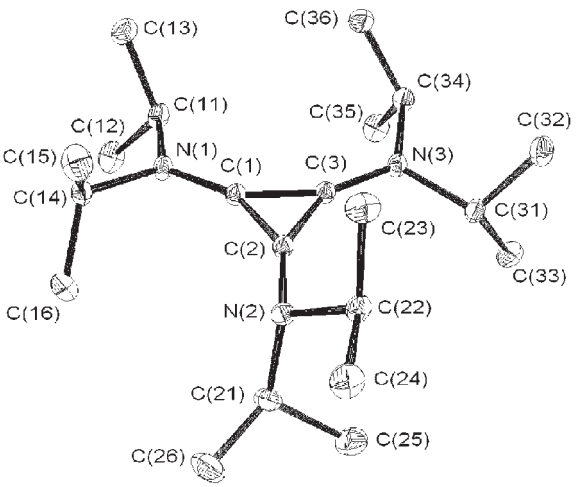


Figure 5. ORTEP of $\mathbf{3}^+$ with the atomic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level and the hydrogen atoms have been omitted for clarity

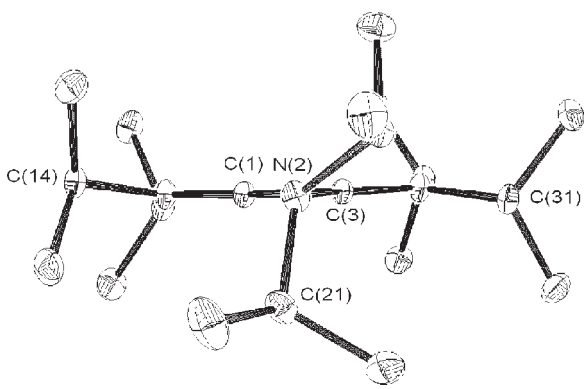


Figure 6. Side-on perspective of $\mathbf{3}^+$. Thermal ellipsoids are drawn at the 40% probability level and the hydrogen atoms have been omitted for clarity

C_3—N—R (R = Me or ^{i}Pr) angles for planar amino groups in $\mathbf{2}^+$, $\mathbf{3}^+$ and $\mathbf{4}^+$ all fall in the range 118–122°.

Cation $\mathbf{3}^+$ belongs to the crystallographically characterised series of compounds $[C_3(N^iPr_2)_2X]^+$, where X is an essentially σ-bonding only substituent such as Cl, H,[3] and Li,[3] as well as the cyclopropenylidene $[C_3(N^iPr_2)_2]$.[3] It seems that generally the C—C bond opposite X lengthens with the electronegativity of X (from 1.344(3) Å for the cyclopropenylidene to 1.389(5) Å for X = Li, 1.406(3) Å for X = H and 1.427(5) Å for X = Cl), the other ring bonds shorten slightly (average distances of 1.405, 1.409, 1.359 and 1.331 Å, respectively) and the C—C—C angle at the unique ring C atom increases (57.2(2)°, 59.1(3)°, 62.3(2)° and 64.9(2)°, respectively). Cation $\mathbf{3}^+$ does not fit particularly well with this sequence since the bond opposite the sp^3 N atom at 1.4316(9) Å is consistent with an electronegative group, the other two bonds (average 1.387 Å) are more consistent with an electropositive group and the C—C—C bond angle of 62.13(4)° is close to that found for X = H.

During the syntheses of $\mathbf{2}^+$ and $\mathbf{3}^+$, the hydrolysis product bis(diisopropylamino)cyclopropenone, $(^iPr_2N)_2C_3{=}O$ (**6**), was isolated by extraction of the crude product with diethylether. Its NMR and infrared spectra are consistent with that given in the literature.[14] An X-ray crystallographic analysis was carried out since we know of no previously reported structure of a diaminocyclopropenone and since the compound also fits into the series of compounds $[(^iPr_2N)_2C_3X]^+$ with $X = O^-$. Table 5 gives selected bond distances and angles; Fig. 7 illustrates the molecule with the atomic labelling scheme.

The solid state conformation is similar to that of $\mathbf{1}^+$ and $\mathbf{2}^+$ with the isopropyl groups oriented towards the less bulky substituent, the oxygen atom. Significant structural differences arise from the increased π-donor ability of the O^- group compared to the dimethylamino and chloro groups. Although the C—C bond (average of 1.387 Å) opposite the O atom is the same as the corresponding bond in $\mathbf{2}^+$ (1.387(5) Å), the other ring C—C bonds are noticeably longer (average of 1.4181 Å). Remarkably, the ring structural parameters are very similar to that of the Li derivative: C—C bond distances of 1.387 Å for **6** *versus* 1.389(5) Å for the unique C—C bond and 1.4181 Å for **6** *versus* 1.409 Å for the other C—C bonds. Even the C—C—C bond angle at the unique C atom is similar: 58.6° for **6** *versus* 59.1(3)°. In diferrocenylcyclopropenone[15] and diphenylcyclopropenone,[16] the unique ring C—C distances are slightly shorter than **6** (1.358(3) and 1.349(6) Å, respectively) whereas the other ring C—C distances (1.411 and 1.417 Å, respectively) and unique ring C—C—C bond angle (57.54(15)° and 56.9(4)°, respectively) are essentially the same as **6**. The C=O distance in **6** (average of 1.232 Å) is only slightly longer than in diferrocenylcyclopropenone and diphenylcyclopropenone (1.215(3) and 1.225(6) Å), but is close to that in the $SnMe_2Cl_2$-coordinated diisopropylcyclopropenone[17] (1.229(6) Å).

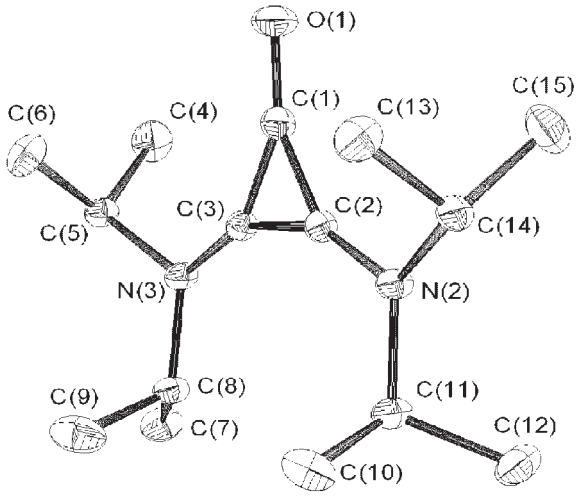


Figure 7. ORTEP of one independent molecule of **6** with the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and the hydrogen atoms have been omitted for clarity

Infrared and Raman spectroscopy

Infrared and Raman spectra of $\mathbf{2}^+$ and $\mathbf{3}^+$ were collected, along with spectra for the cyclopropenone **6** (Table 6), both in the solution and the solid state to investigate the effects of asymmetry on the properties of the cyclopropenium cations. The D_{3h}-symmetric triaminocyclopropenium cations have an a_1' band in the Raman spectra at 1950–1985 cm^{-1} which is not observed in the infrared spectra.[8,18] This has been assigned to the symmetric ring-stretching vibration. The asymmetric vibration (e') is found as a strong absorption at 1500–1560 cm^{-1} in the infrared spectra.[8,18] Upon reducing the symmetry to C_{2v} for the cyclopropenium $\mathbf{1}^+$, a medium intensity IR band is found at 1922 cm^{-1} due to the a_1 ring mode along with a strong Raman

Table 5. Selected bond lengths (Å) and angles (°) for $(^iPr_2N)_2C_3O$ (**6**) (second value is for the primed atoms)

C(1)–C(2)	1.4212(18), 1.4119(18)	O(1)–C(1)	1.2300(17), 1.2336(17)
C(1)–C(3)	1.4192(17), 1.4201(18)	N(2)–C(2)	1.3463(15), 1.3482(16)
C(2)–C(3)	1.3895(15), 1.3850(17)	N(3)–C(3)	1.3530(15), 1.3422(16)
N(2)–C(11)	1.4686(16), 1.4715(16)	N(2)–C(14)	1.4845(15), 1.4754(16)
N(3)–C(5)	1.4810(15), 1.4711(17)	N(3)–C(8)	1.4697(15), 1.4745(16)
C(2)–C(1)–C(3)	58.58(8), 58.56(9)	N(2)–C(2)–C(1)	148.39(11), 149.43(12)
C(1)–C(2)–C(3)	60.64(8), 61.02(9)	N(2)–C(2)–C(3)	150.97(12), 149.51(12)
C(1)–C(3)–C(2)	60.79(8), 60.43(9)	N(3)–C(3)–C(1)	148.09(11), 148.86(12)
O(1)–C(1)–C(2)	150.73(12), 150.74(13)	N(3)–C(3)–C(2)	151.12(11), 150.71(13)
O(1)–C(1)–C(3)	150.67(12), 150.71(13)	C(3)–N(3)–C(5)	115.33(10), 117.06(11)
C(2)–N(2)–C(11)	120.71(10), 119.18(11)	C(3)–N(3)–C(8)	120.13(10), 122.23(11)
C(2)–N(2)–C(14)	116.03(10), 116.85(10)	C(5)–N(3)–C(8)	120.25(10), 120.62(11)
C(11)–N(2)–C(14)	120.38(9), 120.99(10)		

Table 6. Infrared and Raman spectra of $[C_3(N^iPr_2)_2NMe_2][ClO_4]$ (**2**.ClO_4), $[C_3(N^iPr_2)_3]Cl$ (**3**.$Cl \cdot 3H_2O$) and $C_3(N^iPr_2)_2O$ (**6**)

Assignment	Infrared (KBr) **2**.ClO_4	Infrared ($CDCl_3$) **2**.ClO_4	Raman (crystal) **2**.ClO_4	Infrared (ATR) **3**.$Cl \cdot 3H_2O$	Infrared ($CDCl_3$) **3**.$Cl \cdot 3H_2O$	Raman (crystal) **3**.$Cl \cdot 3H_2O$	Infrared (KBr) **6**	Infrared ($CHCl_3$) **6**	Raman (crystal) **6**
$\nu(CH_3)_a$	2980(ms)	2982(m)	2980(w)	2976(m)	2980(m)	2982(s)	2977(ms)	2976(ms)	2982(s)
$\nu'(CH_3)_a/\nu(CH)$	2940(m)	2941(mw)	2949(m)	2939(mw)	2939(mw)	2945(s)	2935(m)	2935(mw)	2940(m)
$\nu(CH_3)_s$	2880(m)	2879(w)	2879(w)	2876(mw)	2880(w)	2874(m)	2874(m)	2875(w)	2872(w)
$\nu_1 a_1'$			1943(s)	1900(w)		1899(m)	1901(m)	1907(w)	1903(m,br)
							1865(mw)		1870(w)
$\nu_4 e'$		1531(s)	1531(w)	1529(s)	1510(sh)		1578(ms)	1565(s)	1583(ms,br)
$\nu_4 e'$	1514(s)	1504(s)	1516(w)				1555(ms)	1550?(m,sh)	
							1510(m)		
	1475(ms)			1481(ms)	1487(vs)	1482(s)	1472(ms)	1472(m)	
$\delta(CH_3)_a$	1450(ms)	1456(ms)	1469(s)	1454(ms)	1456(ms)	1467(m)	1460(ms)	1460(m)	1461(ms)
	1423(ms)	1420(ms)	1425(m)				1427(s)	1437(ms)	1444(ms)
	1390(w)	1392(mw)					1386(ms)	1392(mw)	1388(vw)
$\delta(CH_3)_s$	1375(ms)	1375(ms)		1371(ms)	1375(m)		1368(ms)	1371(m)	
$\delta'(CH_3)_s$	1341(ms)	1352(ms)		1360(ms)	1348(m)		1352(ms)	1360(w)	1365(w)
a″(CH) or γ(CH)				1315(m)	1315(w)	1317(w)	1304(s)	1312(s)	1317(w)
	1257(m)	1250(w)	1268(s)					1261(m)	
	1208(m)	1207(m)	1202(w)	1205(m)	1209(m)		1221(ms)	1221(ms)	1225(vw)
	1183(ms)	1186(ms)		1196(m)	1186(w)		1195(ms)	1194(m)	1197(w,br)
	1165(ms)			1155(s)	1151(mw)		1160(ms)	1161(m)	1172(w)
	1135(ms)				1113(mw)	1123(w)	1130(m)	1128(m)	1127(w)
	1093(vs)	1097(vs)	1053(s)			1055(s)			1065(m)
							1030(s)	1030(m)	
									1013(ms)
			1002(m)			983(m)			999(m)
			985(s)				961(mw)		963(s)
			910(mw)						945(w)
	879(m)		890(mw)			872(s)			870(s)
	739(w)			743(ms,br)					775(vw)
	623(s)		626(w)	610(s,br)					618(s)
			609(s)				560(m)		582(mw)
			534(mw)						534(mw)
			497(mw)				501(mw)		481(m)
			468(w)						407(w)
			424(w)						330(w)
			305(s)						204(m)

band at 1490 cm^{-1} and a strong IR band at 1590 cm^{-1} belonging to the a_1 and b_2 asymmetric ring-stretching vibrations.[8] Cation $\mathbf{2}^+$, which might be expected to exhibit C_{2v} symmetry, appears to exhibit D_{3h} symmetry in its vibrational spectroscopic properties: the symmetric a_1' stretch is observed in the Raman spectrum only, at 1943 cm^{-1} while the e' band is observed at 1514 cm^{-1} in the solid state IR but is split in the solution IR (1531 and 1504 cm^{-1}) and Raman solid state (1531 and 1516 cm^{-1}) spectra. Cation $\mathbf{3}^+$, on the other hand, appears to exhibit C_{2v} symmetry in the solid state, as evidenced by a weak a_1' band in the IR spectrum at 1900 cm^{-1} (1899 cm^{-1} in the Raman solid state spectrum) but approximate D_{3h} symmetry in solution, as this band is not observed in the solution IR spectrum. The e' band appears to be split into a strong band at 1529 cm^{-1} and a medium strong band at 1481 cm^{-1} in the solid state IR spectrum and as a shoulder at 1510 cm^{-1} and strong band at 1487 cm^{-1} in the solution IR spectrum. The Raman spectrum shows a single strong band at 1482 cm^{-1}. The observed symmetries in the solid state spectra are consistent with the solid state structures: the C_{2v}-symmetric $\mathbf{2}^+$ cation has approximately equal ring C—C and C—N bond distances, giving local D_{3h} symmetry, whereas the $\mathbf{3}^+$ cation is locked into a conformation in which the distances of the C_3N_3 unit are consistent with local C_{2v} symmetry (one long C—C and C—N bond and two short C—C and C—N bonds). The local D_{3h} symmetry of $\mathbf{2}^+$ is retained in solution, but it is particularly interesting that $\mathbf{3}^+$ appears to exhibit D_{3h} symmetry, rather than C_{2v}, in the solution spectra. This would be consistent with a rapid rotation about the exocyclic C—N bonds.

Wilcox and Breslow[19] reported two infrared bands in CCl_4 solution for the cyclopropenones $(Me_2N)_2C_2C{=}O$ and $(Et_2N)_2C_2C{=}O$: a high-energy symmetric ring stretch at 1885 and 1900 cm^{-1}, respectively, and a low-energy stretch at 1615 and 1600 cm^{-1}, respectively. Yoshida *et al.*[14], however, reported three IR bands for the isopropyl analogue **6** (1902, 1857 and 1578 cm^{-1}), however, they did not report the relative intensities or the medium in which the spectrum was recorded. We found that the IR spectrum of **6** in $CDCl_3$ gave only two bands: a weak band at 1907 cm^{-1} and a strong band at 1565 cm^{-1}. This result is consistent with the results of Wilcox and Breslow: an increase in energy with mass for the high-energy band and a decrease in energy with mass for the low-energy band. When run in KBr, however, we found three resonances, similar to that reported by Yoshida and coworkers: a medium intensity band at 1901 cm^{-1}, a weak band at 1865 cm^{-1} and a strong band at 1578 cm^{-1}. The Raman spectrum of a powdered sample, similarly, exhibits three bands: 1903 (m), 1870 (w) and 1583 (ms) cm^{-1}. It may be that crystal packing is lowering the symmetry in the solid state and allowing the band at *ca* 1865 cm^{-1} to be observed in the infrared spectrum.

CONCLUSIONS

In this paper we have reported the structures of three tris(dialkylamino)cyclopropenium cations as determined by X-ray crystallography and found that two have highly distorted non-planar structures resulting from steric interactions between isopropyl groups. The solution NMR and IR spectra are consistent with a rapid rotation of the amino groups about the exocyclic C—N bonds. The importance of running infrared spectra in different matrices (solution and solid state) is illustrated by the differing spectra obtained as a result of the different local symmetries.

EXPERIMENTAL

General

All procedures before addition of water were carried out under an N_2 atmosphere using standard Schlenk techniques. All NMR spectra were recorded on a Varian 300 spectrophotometer, IR spectra were recorded on a Shimadzu 8001 FTIR and Raman spectra were collected using a Jobin Yvon U1000 system coupled to a Spectral Physics 2016 argon ion laser tuned to the green line of 514.5 nm or red line at 633 nm at a power of 20–50 mW. Dichloroethane and dichloromethane were distilled from CaH_2. Tris(diisopropylamino)cyclopropenium chloride trihydrate (**3**.Cl · $3H_2O$) was prepared and characterised as given in Ref. [13]. All other chemicals were used as supplied. Pentachlorocyclopropane was purchased from Aldrich. Microanalysis results were obtained from Campbell Microanalytical Services, Dunedin, New Zealand.

*Bis(diisopropylamino)dimethylaminocyclopropenium perchlorate (**2**.ClO_4)*

Diisopropylamine (2.01 g, 0.0199 mol) was added dropwise with stirring to a solution of pentachlorocyclopropane (3.07 g, 0.0143 mol) in CH_2Cl_2 (50 ml). After stirring overnight, a white precipitate formed with a yellow solution. Additional $^iPr_2NH$ (10.68 g, 0.1056 mol) was added dropwise and the solution was stirred overnight, heated to reflux for 3.5 h, cooled and the precipitate filtered off. The solution was then cooled to 0 °C and Me_2NH (6.64 g, 0.147 mol) added dropwise. The solution was allowed to reach ambient temperature and was stirred for 3 days. A precipitate formed and the solution was heated to reflux for 3.5 h. The solution was cooled and filtered and the solvent removed *in vacuo* to give a brown crystalline mass. Extraction with diethylether gave 0.077 g (1.7% yield) of colourless $(^iPr_2N)_2C_2C{=}O$ (**6**). $HClO_4$ (30 ml, 70%) and water (50 ml) were added to the crystalline mass and the organics were extracted with chloroform (3 × 30 ml). This was repeated three times. Colourless crystals were obtained by recrystallisation from a diethylether/dichloromethane 5:1 mixture to give 2.9 g (53% yield) of product.

^{1}H-NMR ($CDCl_3$): δ 3.85 (septet, $^3J = 6.8$ Hz, 2H, $CH(CH_3)_2$), 3.22 (s, 3H CH_3), 1.35 (d, $^3J = 6.8$ Hz, 12H, $CH(CH_3)_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 119.6 (s, C_3), 116.9 (s, 2 × C_3), 51.2 (s, $CH(CH_3)_2$), 42.3 (s, CH_3), 21.8 (s, $CH(CH_3)_2$) ppm. ES-MS (CH_3CN/H_2O, 20 V cone voltage): 280 *m/e*. Elemental analysis, calculated for $C_{17}H_{34}ClN_3O_4$: C, 53.74; H, 9.02; N, 11.06. Found C, 53.60; H, 9.03; N, 10.89. Infrared and Raman spectra are given in Table 6.

X-ray structure determinations

For **2**.ClO_4, a crystal was attached to a thin glass fibre and mounted on a Siemens P4 SMART diffractometer with a Siemens CCD area detector. The program SADABS[20] was utilised for the scaling of diffraction data, the application of a decay correction and empirical absorption correction based on redundant

reflections. Data processing was undertaken with SAINT[20] and the structure was solved by direct methods.[21]

X-ray crystallographic data for **4**.ClO_4 were collected from a single crystal sample which was mounted on a glass fibre. Data were collected using a Rigaku AFC6R diffractometer equipped with a 12 kW rotating anode generator and a point detector. Eighteen high angle reflections were used to determine the unit cell. The structure was solved from the Patterson map.[22]

X-ray crystallographic data for **6** were collected from a single crystal sample which was mounted on a glass fibre. Data were collected using a Bruker-Nonius diffractometer equipped with an APEX-II CCD area detector and the associated software. Processing was carried out by use of the program SAINT[23] which applied Lorentz and polarisation corrections to three-dimensionally integrated diffraction spots. The program SADABS[23] was utilised for the scaling of diffraction data, the application of a decay correction and empirical absorption corrections based on redundant reflections. The structure was solved by direct methods.[22]

All structures were refined by least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added as riding contributors, at calculated positions with isotropic thermal parameters based on the attached carbon atom. Crystal data and structure refinement parameters are given in Table 1.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers: 649181 (**2**.ClO_4), 649182 (**4**.ClO_4) and 649183 (**6**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web: http://www.ccdc.cam.ac.uk

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