Crystal structure of *tert*-butyl-*N*-phenyl-carbonitrilium tetrachloridoaluminate
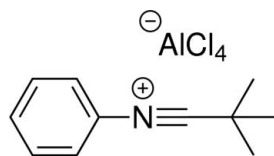
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In the title compound, $(C_{11}H_{14}N)[AlCl_4]$, the nitrilium (systematic name: 2,2-dimethyl-*N*-phenylpropanenitrilium) ion adopts a slightly distorted linear configuration [C—N≡C = 178.87 (16) and N≡C—C = 179.13 (17)°]. In the crystal, while there are no intermolecular hydrogen bonds, pairs of nitrilium ions are linked through π–π interactions [inter–centroid distance = 3.8091 (13) Å].

1. Chemical context

Nitrilium salts are highly electrophilic species that can be generated from imidoyl chlorides by abstracting its chloride using a Lewis acid, $SbCl_5$ having been most widely applied (Meerwein, Laasch, Mersch & Nentwig, 1956; Klages & Grill, 1955; Kanemasa, 2004). Recently, we have shown that tri-methylsilyl triflate (TMSOTf) can also be used as a Lewis acid, generating nitrilium triflates, which are excellent imine synthons in the preparation of 1,3-iminophosphane ligands (van Dijk *et al.*, 2014). Interestingly, nitrilium tetrachlorido-aluminates, which can be synthesised using the much cheaper $AlCl_3$, have found little application (Meerwein, Laasch, Mersch & Spille, 1956; Al-Talib *et al.* 1992). Therefore, we also focused on these species of which the title compound is illustrative.
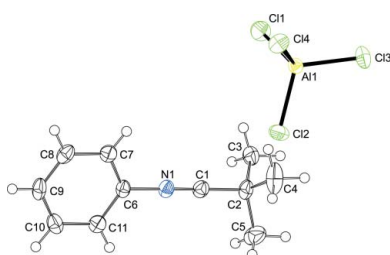

2. Structural commentary

The asymmetric unit of the crystal (Fig. 1) contains one nitrilium cation and one tetrachloridoaluminate anion, which are ion-separated. The nitrilium cation adopts a slightly distorted linear configuration [C—N≡C = 178.87 (16) and N≡C–C = 179.13 (17)°] and features an N≡C bond length of 1.1353 (19) Å, which is in the range of previously reported nitrilium ions (see *Database survey*). The tetrachlorido-aluminate anion has an approximately tetrahedral geometry and is in the range of those reported previously (Bezombes *et al.*, 2004).

3. Supramolecular features

In the unit cell, pairs of inversion-related nitrilium cations are linked through π–π interactions with an inter-centroid

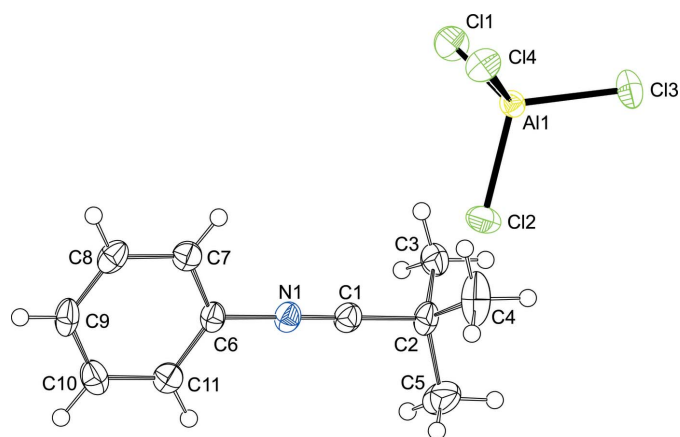OPEN ACCESS

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Figure 1
Molecular structure of *tert*-butyl-*N*-phenylcarbonitrilium tetrachlorido-aluminate with displacement ellipsoids drawn at the 50% probability level.

distance of 3.8091 (13) Å. There is a plane-to-plane shift of the phenyl rings of 1.563 (3) Å. The nitrilium cations and tetra-chloridoaluminate anions are arranged in alternating planes parallel to (011).

4. Database survey

A search in the Cambridge Structural Database (Version 5.35, last update May 2014; Groom & Allen, 2014) showed five structures of nitrilium salts (Gjøystdal & Rømming, 1977; MacLaughlin *et al.*, 1983; Casey *et al.*, 1988; Bykhovskaya *et al.*, 1993, Okazaki *et al.*, 2013), and two structures of nitrilium ylides (Janulis *et al.*, 1984; Doherty *et al.*, 1999)). The title compound is very closely related to *N*-(2,6-dimethylphenyl)-acetonitrilium tetrafluoridoborate (Gjøystdal & Rømming, 1977), which has an N≡C bond length of 1.131 Å, and (*N*-phenyl)(*tert*-butyl)carbonitrilium trifluoromethanesulfonate [van Dijk *et al.*, 2014; N≡C bond length of 1.125 (3) Å], both of which feature similar bond lengths and angles for the nitrilium group.

5. Synthesis and crystallization

This experiment was performed under an atmosphere of dry nitrogen using standard Schlenk-line and glovebox techniques. NMR spectra were recorded at 300 K on a Bruker Advance 500 and referenced internally to residual solvent resonance of CD_2Cl_2, ^1H at δ 5.32, $^{13}C\{^1H\}$ at δ 53.84. The melting point was measured in a sealed capillary on a Stuart Scientific SMP3 melting point apparatus and is uncorrected. The IR spectrum was recorded on a Shimadzu FTIR–8400S spectrophotometer. Solvents were distilled from the appropriate drying agents CaH_2 (DCM), NaK/benzophenone (diethyl ether), and P_2O_5 (CD_2Cl_2), and kept under an inert atmosphere of dry nitrogen.

The title compound was obtained as follows: to a suspension of $AlCl_3$ (3.00 g, 22.4 mmol) in DCM (10 ml) cooled to 195 K, an equimolar amount of *N*-phenylpivalimidoyl chloride

Crystal data	
Chemical formula	$(C_{11}H_{14}N)[AlCl_4]$
M_r	329.03
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	153
a, b, c (Å)	6.4531 (6), 13.6967 (13), 17.9352 (17)
β (°)	93.636 (1)
V (Å^3)	1582.0 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.78
Crystal size (mm)	$0.16 \times 0.05 \times 0.03$
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2007)
T_{min}, T_{max}	0.885, 0.977
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16388, 4063, 3294
R_{int}	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.675
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.081, 1.03
No. of reflections	4063
No. of parameters	210
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.35, −0.26

Computer programs: *APEX2* and *SAINT-Plus* (Bruker, 2007), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009), *WinGX* (Farrugia, 2012) and *OLEX2* (Dolomanov *et al.*, 2009).

(4.38 g, 22.4 mmol) in DCM (25 ml) was added dropwise, after which the reaction mixture was warmed to room temperature and stirred for 16 h. All volatiles were removed *in vacuo*, after which the product was redissolved in DCM (60 ml), layered with diethyl ether (90 ml) and cooled to 193 K for 48 h. The analytically pure product was isolated as a grey crystalline solid (6.23 g, 18.9 mmol, 85%). Recrystallization from DCM at 278 K yielded crystals suitable for X-ray crystallography. The crystals were coated with paratone oil and mounted on a glass fibre in the cooled nitrogen stream of the diffractometer. M.p. 411 K. ^1H NMR (500.2 MHz, CD_2Cl_2): δ 7.89 [*d*, ^3J(H,H) = 7.6 Hz, 2H; *o*-Ph*H*], 7.80 [*t*, ^3J(H,H) = 7.6 Hz, 1H; *p*-Ph*H*], 7.66 [*t*, ^3J(H,H) = 7.6 Hz, 2H; *m*-Ph*H*], 1.84 [*s*, 9H; C(C*H*$_3$)$_3$]. $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): δ 135.1 (*s*; *p*-Ph*C*), 131.0 (*s*; *m*-Ph*C*), 128.7 (*s*; *o*-Ph*C*), 121.1 [*t*, ^1J(C,N) = 42.7 Hz; N≡*C*], 120.7 [*t*, ^1J(C,N) = 14.2 Hz; *ipso*-Ph*C*], 31.7 [*s*; *C*(CH$_3$)$_3$], 27.3 [*s*; C(*C*H$_3$)$_3$]. IR: 3065 (*w*), 2990 (*w*), 1692 (*w*), 1611 (*w*), 1588 (*w*), 1483 (*w*), 1474 (*m*), 1456 (*m*), 1445 (*w*), 1373 (*w*), 1296 (*w*), 1238 (*w*), 1198 (*w*), 1186 (*w*), 1161 (*w*), 1028 (*w*), 1005 (*w*), 939 (*w*), 928 (*w*), 876 (*w*), 845 (*w*), 781 (*w*), 758 (*s*), 692 (*w*), 677 (*m*), 669 (*w*), 652 (*w*).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

References

Al-Talib, M., Jochims, J. C., Hamed, A., Wang, Q. & Ismail, A. E.-H. (1992). *Synthesis*, pp. 697–701.

Bezombes, J.-P., Borisenko, K. B., Hitchcock, P. B., Lappert, M. F., Nycz, J. E., Rankin, D. W. H. & Robertson, H. E. (2004). *Dalton Trans.* pp. 1980–1988.

Bruker (2007). *APEX2*, *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bykhovskaya, O. V., Aladzheva, I. M., Petrovskii, P. V., Antipin, M. Y., Struchkov, Y. T., Mastryukova, T. A. & Kabachnik, M. I. (1993). *Mendeleev Commun.* **3**, 200–202.

Casey, C. P., Crocker, M., Niccolai, G. P., Fagan, P. J. & Konings, M. S. (1988). *J. Am. Chem. Soc.* **110**, 6070–6076.

Dijk, T. van, Burck, S., Rong, M. K., Rosenthal, A. J., Nieger, M., Slootweg, J. C. & Lammertsma, K. (2014). *Angew. Chem. Int. Ed.* **53**, 9068–9071.

Doherty, S., Hogarth, G., Waugh, M., Scanlan, T. H., Clegg, W. & Elsegood, M. R. J. (1999). *Organometallics*, **18**, 3178–3186.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Gjøystdal, A. K. & Rømming, C. (1977). *Acta Chem. Scand. Ser. B*, **31**, 56–62.

Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.

Janulis, E. P., Wilson, S. R. & Arduengo, A. J. (1984). *Tetrahedron Lett.* **25**, 405–408.

Kanemasa, S. (2004). In *Science of Synthesis*, Vol. 19, edited by S.-I. Murahashi, pp. 53–63. Stuttgart: Thieme Verlag.

Klages, F. & Grill, W. (1955). *Justus Liebigs Ann. Chem.* **594**, 21–32.

MacLaughlin, S. A., Johnson, J. P., Taylor, N. J., Carty, A. J. & Sappa, E. (1983). *Organometallics*, **2**, 352–355.

Meerwein, H., Laasch, P., Mersch, R. & Nentwig, J. (1956). *Chem. Ber.* **89**, 224–238.

Meerwein, H., Laasch, P., Mersch, R. & Spille, J. (1956). *Chem. Ber.* **89**, 209–224.

Okazaki, M., Taniwaki, W., Miyagi, K., Takano, M., Kaneko, S. & Ozawa, F. (2013). *Organometallics*, **32**, 1951–1957.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Crystal structure of *tert*-butyl-*N*-phenylcarbonitrilium tetrachloridoaluminate

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Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2* (Bruker, 2007); data reduction: *SAINT-Plus* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and OLEX2 (Dolomanov *et al.*, 2009).

2,2-Dimethyl-*N*-phenylpropanenitrilium tetrachloridoaluminate

Crystal data

$(C_{11}H_{14}N)[AlCl_4]$	$F(000) = 672$
$M_r = 329.03$	$D_x = 1.381$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 411 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.4531$ (6) Å	Cell parameters from 5175 reflections
$b = 13.6967$ (13) Å	$\theta = 2.3$–28.5°
$c = 17.9352$ (17) Å	$\mu = 0.78$ mm^{-1}
$\beta = 93.636$ (1)°	$T = 153$ K
$V = 1582.0$ (3) Å^3	Needle, colorless
$Z = 4$	$0.16 \times 0.05 \times 0.03$ mm

Data collection

Bruker APEXII diffractometer	16388 measured reflections
Radiation source: rotating anode	4063 independent reflections
Graphite monochromator	3294 reflections with $I > 2\sigma(I)$
Detector resolution: 80 pixels mm^{-1}	$R_{int} = 0.035$
ω and Phi scans	$\theta_{max} = 28.7°$, $\theta_{min} = 1.9°$
Absorption correction: multi-scan ($SADABS$; Bruker, 2007)	$h = -8 \rightarrow 8$
	$k = -18 \rightarrow 18$
$T_{min} = 0.885$, $T_{max} = 0.977$	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.030$	
$wR(F^2) = 0.081$	All H-atom parameters refined
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.1953P]$
4063 reflections	where $P = (F_o^2 + 2F_c^2)/3$
210 parameters	$(\Delta/\sigma)_{max} = 0.001$
0 restraints	$\Delta\rho_{max} = 0.35$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Experimental. Corrections were done with the *SADABS* program, utilizing the none merged raw data obtained from the integration process. Integration and final cell refinement were done with *SAINT*.
SADABS reports ratio of Tmin/Tmax = 0.797049

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Al1	0.96022 (7)	0.22733 (3)	0.35138 (2)	0.02252 (11)
C1	0.5146 (2)	0.96503 (11)	0.27377 (8)	0.0280 (3)
C2	0.5280 (3)	0.91716 (11)	0.34748 (8)	0.0301 (3)
C3	0.6685 (3)	0.82750 (13)	0.34364 (10)	0.0333 (3)
C4	0.6215 (5)	0.99100 (15)	0.40414 (11)	0.0544 (6)
C5	0.3056 (3)	0.88817 (17)	0.36455 (14)	0.0492 (5)
C6	0.4893 (2)	1.04868 (10)	0.14690 (8)	0.0246 (3)
C7	0.6619 (3)	1.09623 (11)	0.12260 (9)	0.0287 (3)
C8	0.6442 (3)	1.13970 (11)	0.05267 (9)	0.0321 (3)
C9	0.4587 (3)	1.13540 (11)	0.00948 (9)	0.0329 (4)
C10	0.2892 (3)	1.08788 (12)	0.03538 (9)	0.0337 (4)
C11	0.3023 (3)	1.04317 (11)	0.10465 (9)	0.0290 (3)
Cl1	1.07491 (7)	0.12249 (3)	0.27615 (2)	0.03826 (11)
Cl2	0.63285 (6)	0.24128 (3)	0.33003 (2)	0.03784 (11)
Cl3	1.03104 (7)	0.17986 (3)	0.46328 (2)	0.03810 (11)
Cl4	1.09572 (6)	0.36715 (3)	0.33438 (2)	0.03407 (11)
N1	0.5044 (2)	1.00304 (9)	0.21740 (7)	0.0270 (3)
H5	0.678 (3)	0.7947 (13)	0.3913 (11)	0.032 (4)*
H6	0.803 (3)	0.8453 (14)	0.3297 (11)	0.042 (5)*
H12	0.449 (3)	1.1638 (13)	−0.0347 (10)	0.031 (4)*
H14	0.781 (3)	1.0977 (13)	0.1524 (10)	0.037 (5)*
H10	0.189 (3)	1.0117 (13)	0.1246 (10)	0.033 (5)*
H4	0.615 (3)	0.7821 (17)	0.3065 (13)	0.059 (6)*
H13	0.760 (3)	1.1708 (14)	0.0343 (10)	0.037 (5)*
H3	0.311 (3)	0.8571 (16)	0.4147 (13)	0.059 (6)*
H8	0.635 (4)	0.9609 (17)	0.4530 (14)	0.067 (7)*
H11	0.165 (3)	1.0868 (15)	0.0039 (12)	0.054 (6)*
H7	0.539 (3)	1.0444 (18)	0.4074 (12)	0.055 (6)*
H1	0.229 (4)	0.9457 (17)	0.3674 (13)	0.061 (7)*
H2	0.243 (4)	0.8431 (19)	0.3264 (15)	0.074 (8)*
H9	0.763 (4)	1.0135 (19)	0.3925 (15)	0.080 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Al1	0.0237 (2)	0.0221 (2)	0.0215 (2)	0.00139 (16)	−0.00057 (16)	−0.00156 (15)
C1	0.0313 (8)	0.0270 (7)	0.0263 (8)	0.0037 (6)	0.0048 (6)	0.0011 (6)
C2	0.0392 (9)	0.0296 (8)	0.0220 (7)	0.0008 (6)	0.0055 (6)	0.0068 (6)
C3	0.0368 (9)	0.0350 (8)	0.0279 (8)	0.0042 (7)	0.0003 (7)	0.0072 (7)
C4	0.100 (2)	0.0342 (10)	0.0280 (10)	−0.0045 (11)	−0.0013 (10)	0.0001 (8)
C5	0.0420 (11)	0.0531 (12)	0.0542 (13)	0.0093 (9)	0.0179 (9)	0.0245 (10)
C6	0.0331 (8)	0.0202 (6)	0.0208 (7)	0.0057 (5)	0.0036 (6)	0.0021 (5)
C7	0.0307 (8)	0.0265 (7)	0.0291 (8)	0.0033 (6)	0.0034 (6)	0.0006 (6)
C8	0.0401 (9)	0.0251 (7)	0.0323 (8)	0.0022 (6)	0.0132 (7)	0.0041 (6)
C9	0.0524 (10)	0.0266 (8)	0.0201 (7)	0.0119 (7)	0.0052 (7)	0.0043 (6)
C10	0.0408 (9)	0.0320 (8)	0.0273 (8)	0.0093 (7)	−0.0054 (7)	−0.0009 (6)
C11	0.0319 (8)	0.0253 (7)	0.0300 (8)	0.0026 (6)	0.0040 (6)	0.0008 (6)
Cl1	0.0421 (2)	0.0355 (2)	0.0370 (2)	0.00888 (16)	0.00073 (17)	−0.01397 (16)
Cl2	0.02347 (19)	0.0465 (2)	0.0431 (2)	0.00328 (15)	−0.00125 (16)	0.00606 (17)
Cl3	0.0468 (2)	0.0410 (2)	0.02528 (19)	−0.00252 (17)	−0.00698 (16)	0.00525 (16)
Cl4	0.0377 (2)	0.02523 (18)	0.0400 (2)	−0.00444 (15)	0.00856 (17)	−0.00103 (15)
N1	0.0331 (7)	0.0245 (6)	0.0238 (6)	0.0057 (5)	0.0047 (5)	0.0024 (5)

Geometric parameters (Å, º)

Al1—Cl3	2.1315 (6)	C2—C5	1.539 (3)
Al1—Cl2	2.1316 (6)	C6—C7	1.384 (2)
Al1—Cl1	2.1347 (6)	C6—C11	1.386 (2)
Al1—Cl4	2.1351 (6)	C6—N1	1.4084 (18)
C1—N1	1.1353 (19)	C7—C8	1.386 (2)
C1—C2	1.473 (2)	C8—C9	1.385 (2)
C2—C4	1.530 (3)	C9—C10	1.378 (3)
C2—C3	1.531 (2)	C10—C11	1.383 (2)
Cl3—Al1—Cl2	110.32 (2)	C4—C2—C5	111.84 (18)
Cl3—Al1—Cl1	109.13 (3)	C3—C2—C5	111.39 (15)
Cl2—Al1—Cl1	109.04 (2)	C7—C6—C11	122.93 (14)
Cl3—Al1—Cl4	110.05 (2)	C7—C6—N1	118.70 (14)
Cl2—Al1—Cl4	107.71 (2)	C11—C6—N1	118.36 (13)
Cl1—Al1—Cl4	110.58 (3)	C6—C7—C8	117.71 (15)
N1—C1—C2	179.13 (17)	C9—C8—C7	120.42 (16)
C1—C2—C4	107.46 (14)	C10—C9—C8	120.51 (15)
C1—C2—C3	108.54 (13)	C9—C10—C11	120.48 (16)
C4—C2—C3	110.50 (17)	C10—C11—C6	117.95 (15)
C1—C2—C5	106.91 (15)	C1—N1—C6	178.87 (16)