Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N-Chloromethyl-4-(dimethylamino)-*N*,*N*-dimethylanilinium chloride

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.115
Data-to-parameter ratio = 26.7

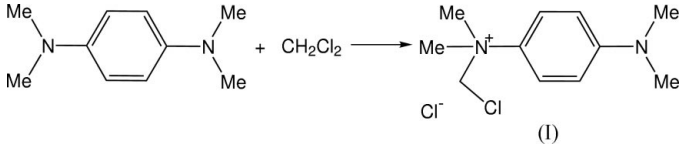
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 14 December 2004
Accepted 20 December 2004
Online 8 January 2005

In the cation of the title compound $C_{11}H_{18}ClN_2^+\cdot Cl^-$, the quaternary N atom has a distorted tetrahedral geometry, and the other N a nearly planar-trigonal (owing to conjugation with the benzene ring) bonding geometry.

Comment

The title compound, (I), was obtained as an accidental by-product while co-crystallizing *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine (TMPD) and octafluoronaphthalene (OFN) from CH_2Cl_2 (Collings *et al.*, 2004). The asymmetric unit comprises one chloride anion and one $Me_2(ClCH_2)N^+$–C_6H_4–NMe_2 cation. This cation has been structurally studied earlier as its tetraphenylborate salt dichloromethane solvate (II) by Winter (2001), and the non-chlorinated analogue trimethyl{4-(dimethylamino)phenyl}ammonium cation as its ozonide salt (III) by Assenmacher & Jansen (1995). Unfortunately, the precision of both structure determinations was limited (*R* = 0.09), in (III) owing to disorder of the ozonide anion and to chemical instability (the compound explodes at 303 K), and in (II) probably because of some unrecognized disorder, as indicated by the discrepant N^+—CH_3 bond lengths of 1.50 (1) and 1.62 (1) Å.



(I)

The atom N2 has nearly planar geometry, the sum of the bond angles being 358.1°. The C10/N2/C11 plane forms an angle of 11.9 (1)° with the benzene ring plane, so that the *pπ* orbitals of N2 and C4 are nearly coplanar. This and the N2—C4 bond distance of 1.371 (2) Å are indicative of strong

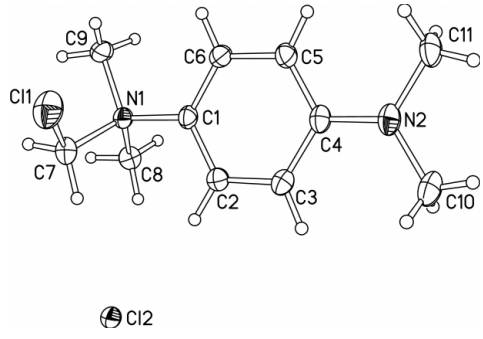


Figure 1
The cation and anion in the structure of (I). Atomic displacement ellipsoids are drawn at the 50% probability level.

π-conjugation. The quaternary atom N1 has a distorted tetrahedral environment. The chloride anion is surrounded by eight H atoms of four different cations at Cl···H distances of 2.46 (2) to 2.60 (2) Å (calculated for the idealized C—H bond lengths of 1.08 Å).

Experimental

Slow evaporation at room temperature of a dichloromethane solution of equimolar amounts of TMPD and OFN yielded mainly co-crystals of TMPD and OFN (1:1) and a few smaller crystals of different habit, which were identified by the present study as (I).

Crystal data

$C_{11}H_{18}ClN_2^+\cdot Cl^-$
M_r = 249.17
Monoclinic, $P2_1/c$
a = 15.121 (3) Å
b = 7.234 (1) Å
c = 12.773 (2) Å
β = 114.95 (1)°
V = 1266.8 (4) Å^3
Z = 4
D_x = 1.306 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 977 reflections
θ = 10.2–26.9°
μ = 0.48 mm^{-1}
T = 120 (2) K
Parallelepiped, colourless
0.22 × 0.15 × 0.10 mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
ω scans
Absorption correction: by integration (*XPREP* in *SHELXTL*; Bruker, 2001*b*)
T_{min} = 0.923, T_{max} = 0.962
17336 measured reflections
3689 independent reflections
2994 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 30.0°
$h = -21 \rightarrow 21$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.115
S = 1.05
3689 reflections
138 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 0.4607P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}

Methyl groups bonded to N2 were refined as rigid bodies rotating around the N2—C bonds, and other H atoms were treated as riding on the corresponding C atoms in idealized positions. The C—H distances were fixed at 0.98 Å for methyl, 0.99 Å for methylene, 0.95 Å for benzene H atoms, with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for the rest.

Data collection: *SMART* (Bruker, 2001*a*); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001*a*); program(s) used to solve structure: *SHELXTL* (Bruker, 2001*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

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supporting information

Acta Cryst. (2005). E**61**, o201–o202 [https://doi.org/10.1107/S1600536804033860]

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Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
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Cell parameters from 977 reflections
$\theta = 10.2$–$26.9°$
$\mu = 0.48$ mm^{-1}
$T = 120$ K
Parallelepiped, colourless
0.22 × 0.15 × 0.10 mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 5.6 pixels mm^{-1}
ω scans
Absorption correction: integration (XPREP;SHELXTL), R(int) = 0.053 before correction
$T_{min} = 0.923$, $T_{max} = 0.962$
17336 measured reflections
3689 independent reflections
2994 reflections with $I > 2\sigma(I)$
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$h = -21 \rightarrow 21$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.115$
$S = 1.05$
3689 reflections
138 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 0.4607P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

Special details

Experimental. The data collection nominally covered full sphere of reciprocal space, by a combination of 4 sets of ω scans; each set at different φ and/or 2θ angles and each scan (30 sec exposure) covering 0.3° in ω. Crystal to detector distance 4.83 cm.

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.13260 (3)	0.94831 (6)	0.50991 (4)	0.03711 (13)
N1	0.14834 (9)	0.61049 (18)	0.42545 (11)	0.0191 (2)
N2	0.56069 (10)	0.6864 (2)	0.65487 (13)	0.0270 (3)
C1	0.25717 (10)	0.6300 (2)	0.48375 (13)	0.0196 (3)
C2	0.30675 (11)	0.5631 (2)	0.59580 (13)	0.0212 (3)
H2	0.2715	0.5060	0.6335	0.025*
C3	0.40730 (11)	0.5796 (2)	0.65257 (14)	0.0233 (3)
H3	0.4403	0.5332	0.7289	0.028*
C4	0.46152 (11)	0.6645 (2)	0.59844 (14)	0.0216 (3)
C5	0.40898 (11)	0.7286 (2)	0.48480 (14)	0.0237 (3)
H5	0.4433	0.7837	0.4454	0.028*
C6	0.30805 (11)	0.7133 (2)	0.42875 (14)	0.0233 (3)
H6	0.2741	0.7602	0.3527	0.028*
C7	0.10071 (11)	0.7136 (2)	0.49168 (14)	0.0232 (3)
H72	0.1205	0.6556	0.5685	0.028*
H73	0.0290	0.7026	0.4497	0.028*
C8	0.11909 (11)	0.4104 (2)	0.42498 (14)	0.0226 (3)
H81	0.0478	0.4009	0.3904	0.034*
H82	0.1455	0.3639	0.5044	0.034*
H83	0.1450	0.3368	0.3798	0.034*
C9	0.10507 (12)	0.6747 (3)	0.30206 (14)	0.0285 (4)
H91	0.0338	0.6671	0.2703	0.043*
H92	0.1287	0.5960	0.2568	0.043*
H93	0.1245	0.8030	0.2987	0.043*
C10	0.61542 (12)	0.5952 (3)	0.76493 (16)	0.0328 (4)
H101	0.6052	0.4614	0.7555	0.049*
H102	0.5930	0.6403	0.8219	0.049*
H103	0.6850	0.6226	0.7915	0.049*
C11	0.61399 (12)	0.7603 (3)	0.59259 (16)	0.0292 (4)
H111	0.6829	0.7744	0.6457	0.044*
H112	0.5869	0.8810	0.5599	0.044*
H113	0.6081	0.6754	0.5302	0.044*
Cl2	0.13930 (3)	0.37737 (6)	0.70918 (3)	0.02326 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0342 (2)	0.0226 (2)	0.0516 (3)	0.00034 (16)	0.0153 (2)	−0.00322 (18)

N1	0.0148 (5)	0.0219 (6)	0.0193 (6)	−0.0002 (5)	0.0059 (4)	0.0022 (5)
N2	0.0160 (6)	0.0309 (7)	0.0293 (7)	−0.0019 (5)	0.0046 (5)	−0.0022 (6)
C1	0.0136 (6)	0.0208 (7)	0.0223 (7)	0.0000 (5)	0.0055 (5)	0.0012 (5)
C2	0.0191 (7)	0.0227 (7)	0.0216 (7)	0.0000 (5)	0.0083 (6)	0.0011 (5)
C3	0.0187 (7)	0.0251 (8)	0.0220 (7)	0.0013 (6)	0.0048 (6)	0.0008 (6)
C4	0.0162 (6)	0.0192 (7)	0.0272 (7)	−0.0006 (5)	0.0070 (6)	−0.0023 (6)
C5	0.0174 (7)	0.0227 (7)	0.0306 (8)	−0.0004 (5)	0.0097 (6)	0.0046 (6)
C6	0.0187 (7)	0.0241 (7)	0.0248 (7)	0.0005 (6)	0.0071 (6)	0.0065 (6)
C7	0.0191 (7)	0.0220 (7)	0.0279 (8)	0.0005 (6)	0.0093 (6)	−0.0028 (6)
C8	0.0213 (7)	0.0213 (7)	0.0232 (7)	−0.0037 (5)	0.0076 (6)	−0.0041 (5)
C9	0.0180 (7)	0.0426 (10)	0.0208 (7)	0.0005 (7)	0.0043 (6)	0.0102 (7)
C10	0.0199 (8)	0.0352 (10)	0.0332 (9)	0.0005 (7)	0.0013 (7)	0.0002 (7)
C11	0.0167 (7)	0.0258 (8)	0.0415 (10)	−0.0033 (6)	0.0090 (7)	−0.0016 (7)
Cl2	0.01681 (17)	0.0308 (2)	0.02126 (18)	0.00192 (13)	0.00712 (13)	0.00527 (14)

Geometric parameters (Å, º)

Cl1—C7	1.7532 (17)	C5—H5	0.9500
N1—C1	1.4995 (19)	C6—H6	0.9500
N1—C9	1.5027 (19)	C7—H72	0.9900
N1—C8	1.513 (2)	C7—H73	0.9900
N1—C7	1.518 (2)	C8—H81	0.9800
N2—C4	1.372 (2)	C8—H82	0.9800
N2—C11	1.452 (2)	C8—H83	0.9800
N2—C10	1.454 (2)	C9—H91	0.9800
C1—C6	1.380 (2)	C9—H92	0.9800
C1—C2	1.392 (2)	C9—H93	0.9800
C2—C3	1.386 (2)	C10—H101	0.9800
C2—H2	0.9500	C10—H102	0.9800
C3—C4	1.416 (2)	C10—H103	0.9800
C3—H3	0.9500	C11—H111	0.9800
C4—C5	1.407 (2)	C11—H112	0.9800
C5—C6	1.390 (2)	C11—H113	0.9800
C1—N1—C9	113.14 (12)	Cl1—C7—H72	109.1
C1—N1—C8	110.47 (12)	N1—C7—H73	109.1
C9—N1—C8	107.13 (12)	Cl1—C7—H73	109.1
C1—N1—C7	110.87 (12)	H72—C7—H73	107.9
C9—N1—C7	109.47 (12)	N1—C8—H81	109.5
C8—N1—C7	105.42 (11)	N1—C8—H82	109.5
C4—N2—C11	119.40 (14)	H81—C8—H82	109.5
C4—N2—C10	120.39 (14)	N1—C8—H83	109.5
C11—N2—C10	118.40 (14)	H81—C8—H83	109.5
C6—C1—C2	120.06 (14)	H82—C8—H83	109.5
C6—C1—N1	121.26 (13)	N1—C9—H91	109.5
C2—C1—N1	118.68 (13)	N1—C9—H92	109.5
C3—C2—C1	120.26 (14)	H91—C9—H92	109.5
C3—C2—H2	119.9	N1—C9—H93	109.5

C1—C2—H2	119.9	H91—C9—H93	109.5
C2—C3—C4	121.00 (14)	H92—C9—H93	109.5
C2—C3—H3	119.5	N2—C10—H101	109.5
C4—C3—H3	119.5	N2—C10—H102	109.5
N2—C4—C5	121.36 (14)	H101—C10—H102	109.5
N2—C4—C3	121.55 (14)	N2—C10—H103	109.5
C5—C4—C3	117.08 (14)	H101—C10—H103	109.5
C6—C5—C4	121.64 (14)	H102—C10—H103	109.5
C6—C5—H5	119.2	N2—C11—H111	109.5
C4—C5—H5	119.2	N2—C11—H112	109.5
C1—C6—C5	119.95 (14)	H111—C11—H112	109.5
C1—C6—H6	120.0	N2—C11—H113	109.5
C5—C6—H6	120.0	H111—C11—H113	109.5
N1—C7—Cl1	112.42 (11)	H112—C11—H113	109.5
N1—C7—H72	109.1		

Cl1—C7—N1—C1	56.59 (14)	C5—C4—N2—C11	−6.2 (2)
C7—N1—C1—C2	61.05 (18)	C3—C4—N2—C10	10.5 (2)
C6—C1—N1—C9	4.9 (2)		