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Crystal structure of 4,5-diiodo-1,3-dimesityl-1*H*-1,2,3-triazol-3-ium chloride – chloroform (1/1), $C_{21}H_{23}Cl_4I_2N_3$

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Abstract

$C_{21}H_{23}Cl_4I_2N_3$, monoclinic, $P2_1/c$ (no. 14), $a = 26.110(2)$ Å, $b = 9.1149(8)$ Å, $c = 33.793(3)$ Å, $\beta = 134.138(3)^\circ$, $V = 5771.8(9)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0624$, $wR_{ref}(F^2) = 0.1525$, $T = 297.93$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

1,3-Dimesityl-1,2,3-triazol-3-ium tetrafluoroborate 0.45 g (1 mmol) and potassium *tert*-butoxide 0.25 g (2.2 mmol)

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.26 × 0.18 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.56 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	27.5°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	35,149, 13,155, 0.048
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 8313
$N(param)_{refined}$:	581
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

and iodine (510 mg, 2 mmol) were added in a Schlenk tube under dry nitrogen condition, then THF (25 mL) was added at -78 temperature. The mixture was stirred for 10 h. After evaporation of THF, dichloromethane (100 mL) was added and inorganic salts were removed by filtration. The dichloromethane solution and silver tetrafluoroborate 0.20 g (1 mmol) were added in Schlenk tube under nitrogen condition, and then stirred for 3 h under dark condition. Then AgI were removed by filtration, and dichloromethane was removed under reduced pressure. The obtained solid and potassium chloride (0.75 g, 10 mmol) were mixed in acetonitrile (30 mL), then the mixture was stirred for 24 h under air. The acetonitrile was removed under reduced pressure. Dichloromethane (50 mL) was added again and the inorganic salt was removed by filtration. Then the dichloromethane was removed by evaporation to give the final white product. Yield: 78%. Single crystal was obtained under ambient conditions via solvent evaporation in the solvents of chloroform. ¹H NMR (400 MHz, chloroform-*d*): δ (ppm) 7.05 (s, 4H), 2.39 (s, 6H), 1.98 (s, 12H); ¹³C NMR (100 MHz, chloroform-*d*): δ (ppm) 142.9, 134.2, 132.1, 130.1, 113.2, 21.4, 17.4.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with $d(C-H) = 0.98$ Å (methyl), $U_{iso}(H) = 1.5 U_{eq}(C)$, and 0.95 Å (aromatic),

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
I1	−0.10677 (3)	0.23754 (6)	0.00940 (2)	0.04987 (14)
I2	−0.10437 (3)	0.12601 (6)	0.12560 (2)	0.05325 (15)
N1	0.0493 (3)	0.2161 (7)	0.1202 (3)	0.0513 (16)
N2	0.0945 (3)	0.1901 (7)	0.1742 (3)	0.0562 (17)
N3	0.0514 (3)	0.1630 (7)	0.1812 (3)	0.0540 (16)
C1	−0.0203 (4)	0.2056 (9)	0.0940 (3)	0.0481 (18)
C2	−0.0191 (4)	0.1710 (8)	0.1338 (3)	0.0481 (18)
C23	0.0816 (4)	0.1359 (10)	0.2359 (3)	0.060 (2)
C24	0.0910 (5)	0.2526 (11)	0.2658 (3)	0.072 (3)
C25	0.1180 (6)	0.2229 (13)	0.3181 (4)	0.093 (4)
H	0.124197	0.299608	0.339295	0.112*
C26	0.1352 (6)	0.0842 (14)	0.3386 (4)	0.099 (4)
C27	0.1260 (6)	−0.0285 (12)	0.3070 (4)	0.091 (3)
HA	0.138873	−0.122986	0.321517	0.109*
C28	0.0986 (6)	−0.0076 (12)	0.2551 (4)	0.079 (3)
C29	0.0718 (7)	0.4055 (13)	0.2431 (5)	0.106 (4)
HB	0.091189	0.474305	0.272178	0.159*
HC	0.020855	0.415412	0.214874	0.159*
HD	0.091221	0.424768	0.227770	0.159*
C30	0.1656 (8)	0.0565 (16)	0.3963 (5)	0.132 (5)
HE	0.131718	0.088198	0.397633	0.198*
HF	0.209241	0.110249	0.422952	0.198*
HG	0.174732	−0.046427	0.404512	0.198*
C31	0.0861 (9)	−0.1335 (13)	0.2208 (5)	0.128 (5)
HH	0.105049	−0.109959	0.205322	0.192*
HI	0.035844	−0.151868	0.191573	0.192*
HJ	0.109557	−0.219505	0.243423	0.192*
C32	0.0768 (4)	0.2375 (9)	0.0953 (3)	0.0504 (19)
C33	0.0861 (5)	0.3793 (9)	0.0873 (4)	0.061 (2)
C34	0.1066 (4)	0.3954 (11)	0.0585 (4)	0.068 (2)
HK	0.112859	0.489211	0.051637	0.082*
C35	0.1175 (4)	0.2763 (11)	0.0402 (4)	0.063 (2)
C36	0.1091 (4)	0.1380 (10)	0.0509 (4)	0.061 (2)
HL	0.117870	0.057407	0.039461	0.073*
C37	0.0876 (4)	0.1151 (10)	0.0782 (3)	0.058 (2)
C38	0.0758 (6)	−0.0383 (10)	0.0874 (5)	0.084 (3)
HM	0.092471	−0.044291	0.123209	0.126*
HN	0.101600	−0.107022	0.085223	0.126*
HO	0.025805	−0.061105	0.059680	0.126*
C39	0.1407 (6)	0.2977 (15)	0.0101 (5)	0.097 (4)
HP	0.160441	0.394171	0.017624	0.146*
HQ	0.100186	0.286742	−0.028800	0.146*
HR	0.176094	0.225728	0.022507	0.146*
C40	0.0747 (6)	0.5116 (11)	0.1069 (5)	0.095 (4)
HS	0.024472	0.528613	0.083058	0.142*
HT	0.096397	0.595708	0.106465	0.142*
HU	0.095980	0.494948	0.143836	0.142*
I3	0.30748 (3)	−0.03062 (6)	0.11913 (2)	0.05192 (15)
I4	0.29824 (3)	0.09149 (6)	−0.00007 (2)	0.05574 (15)
N4	0.3930 (3)	0.2550 (7)	0.1555 (3)	0.0505 (16)
N5	0.4117 (3)	0.3637 (7)	0.1413 (3)	0.0550 (17)
N6	0.3836 (3)	0.3237 (7)	0.0916 (3)	0.0510 (16)
C3	0.3539 (4)	0.1498 (8)	0.1162 (3)	0.0483 (18)
C4	0.3480 (4)	0.1934 (8)	0.0745 (3)	0.0495 (18)
C5	0.3900 (4)	0.4222 (8)	0.0616 (3)	0.0503 (19)

Table 2: (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C6	0.3440 (4)	0.5404 (9)	0.0350 (3)	0.055 (2)
C7	0.3484 (5)	0.6293 (10)	0.0048 (4)	0.065 (2)
HV	0.318071	0.709776	−0.013451	0.078*
C8	0.3970 (5)	0.6022 (11)	0.0009 (4)	0.074 (3)
C9	0.4415 (5)	0.4837 (12)	0.0284 (4)	0.077 (3)
HW	0.474676	0.466643	0.026295	0.092*
C10	0.4395 (5)	0.3888 (11)	0.0589 (4)	0.065 (2)
C11	0.2898 (5)	0.5725 (11)	0.0379 (4)	0.068 (2)
HX	0.258103	0.490393	0.023599	0.103*
HY	0.262862	0.658263	0.016417	0.103*
HZ	0.314066	0.589240	0.075580	0.103*
C12	0.4005 (7)	0.7036 (16)	−0.0335 (6)	0.126 (5)
H1	0.384268	0.651329	−0.065172	0.188*
H2	0.448885	0.735025	−0.011467	0.188*
H3	0.370663	0.787608	−0.045215	0.188*
C13	0.4892 (5)	0.2587 (11)	0.0881 (4)	0.084 (3)
H4	0.506811	0.249238	0.124137	0.125*
H5	0.528559	0.272936	0.091501	0.125*
H6	0.463857	0.171168	0.067241	0.125*
C14	0.4174 (4)	0.2636 (8)	0.2094 (3)	0.0488 (18)
C15	0.4875 (4)	0.2241 (9)	0.2552 (3)	0.053 (2)
C16	0.5092 (5)	0.2353 (10)	0.3055 (3)	0.067 (2)
H7	0.555070	0.204441	0.336603	0.080*
C17	0.4666 (5)	0.2900 (11)	0.3121 (4)	0.069 (2)
C18	0.3970 (5)	0.3295 (10)	0.2651 (4)	0.066 (2)
H8	0.367300	0.365196	0.268969	0.079*
C19	0.3704 (4)	0.3172 (9)	0.2123 (3)	0.055 (2)
C20	0.2946 (5)	0.3611 (12)	0.1625 (4)	0.081 (3)
H9	0.294618	0.439346	0.143454	0.121*
H10	0.271626	0.393535	0.173941	0.121*
H11	0.269279	0.278430	0.138233	0.121*
C21	0.5346 (5)	0.1598 (12)	0.2494 (4)	0.082 (3)
H12	0.510672	0.078687	0.224117	0.122*
H13	0.578191	0.126143	0.284665	0.122*
H14	0.545160	0.233126	0.235524	0.122*
C22	0.4919 (6)	0.3099 (16)	0.3678 (4)	0.111 (4)
H15	0.488461	0.218158	0.379792	0.167*
H16	0.462647	0.381727	0.365064	0.167*
H17	0.540601	0.342379	0.393936	0.167*
Cl0A ^a	0.2821 (11)	0.402 (2)	0.3111 (6)	0.253 (8)
Cl0B ^b	0.2703 (13)	0.303 (3)	0.3067 (6)	0.191 (8)
Cl1A ^a	0.3029 (9)	0.1655 (12)	0.3692 (9)	0.252 (7)
Cl1B ^b	0.3449 (16)	0.201 (2)	0.4120 (11)	0.230 (10)
Cl2A ^a	0.4045 (5)	0.3832 (19)	0.4301 (6)	0.211 (7)
Cl2B ^b	0.3766 (12)	0.478 (2)	0.3873 (12)	0.184 (9)
C41	0.3168 (6)	0.3513 (13)	0.3731 (4)	0.139 (6)
H41 ^a	0.288797	0.398577	0.378892	0.166*
H41A ^b	0.283813	0.403133	0.372930	0.166*
Cl1	0.22608 (12)	−0.2741 (2)	0.11123 (9)	0.0695 (6)
Cl2	0.22992 (12)	0.5660 (3)	0.39428 (9)	0.0665 (6)
Cl3	0.2494 (4)	0.0230 (9)	0.2269 (3)	0.260 (3)
Cl4	0.3009 (5)	−0.2689 (10)	0.2677 (4)	0.296 (4)
Cl5	0.3847 (3)	−0.0546 (6)	0.2768 (2)	0.1739 (19)
C42	0.3002 (6)	−0.1222 (12)	0.2373 (5)	0.127 (5)
H18	0.281935	−0.152412	0.201542	0.153*

^aOccupancy: 0.616 (18), ^bOccupancy: 0.384 (18).

$U_{iso}(H) = 1.2U_{eq}(C)$. The disorder of chloroform was refined and RIGU, ISOR, and SADI were applied to restrain the atoms.

Comment

Weak intermolecular interactions play a very important role in the crystal engineering [5]. The most common weak interaction is hydrogen bonding. The halogen bonding interaction has been exploited as construction tool in crystal engineering, anion recognition, supramolecular chemistry, even tuning of biomolecular systems [6]. Competition between halogen and hydrogen bond was studied through polyiodide ion [7]. While both halogen bonding and hydrogen bonding influence the crystal structures [8].

In our previous study, 4,5-diiodo-1,3-dimesityl-1,2,3-triazolium salts are strong halogen bond donors which can form different conformations with different anions [9, 10]. All the crystals were obtained by evaporation of dichloromethane. The hydrogen atom in chloroform shows strong acidity which can be and has been applied to form cocrystals [11].

Single crystal structure analysis revealed that the title compound crystallized in the monoclinic space group $P2_1/c$ with $Z = 8$. The title crystal structure does not exist as a tetramer (saddle conformation) but a dimer induced by halogen bond and hydrogen bond. The distances of $I \cdots Cl$ are 2.957(2) ($I1 \cdots Cl1$), 2.954(3) ($I3 \cdots Cl1$), 2.903(4) ($I2 \cdots Cl2$), and 3.020(3) ($I4 \cdots Cl2$). The $C-I \cdots Cl$ angles are 177.5(3) ($C1-I1 \cdots Cl1$), 173.5(3) ($C31-I3 \cdots Cl1$), 175.9(3) ($C2-I2 \cdots Cl2$), and 177.8(3) ($C4-I4 \cdots Cl2$). The reduction ratio RXB [12], defined as the ratio of the actual distance over the sum of van der Waals radii, amounts to 0.77. The hydrogen atoms of chloroform molecule showed hydrogen bonding with the chloride anion. The distance of $Cl1 \cdots H18$ is 2.544 and distance of $Cl2 \cdots H41$ is 2.465. The $C-H \cdots Cl$ angles are 167.8 ($C41-H41 \cdots Cl2$) and 169.0 ($C42-H18 \cdots Cl1$). The anion chloride anion were showed strong halogen bond and hydrogen bond in the crystal structure. Both halogen bonding and hydrogen bonding are around the central chloride anion (see the Figure).

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