Crystal structure of 1-isopropyl-2,3,4,6-tetramethylpyridinium perchlorate, $C_{12}H_{20}ClNO_4$

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Abstract

$C_{12}H_{20}ClNO_4$, monoclinic, $P12_1/c1$ (No. 14), $a = 14.8626(5)$ Å, $b = 11.7049(8)$ Å, $c = 16.279(1)$ Å, $\beta = 90.329(4)^\circ$, $V = 2831.9$ Å³, $Z = 8$, $R_{gt}(F) = 0.069$, $wR_{ref}(F^2) = 0.151$, $T = 173$ K.

Source of material

The pyridinium salt was prepared by heating for 1 h in 2-propanol at reflux 2,3,4,6-tetramethylpyrylium perchlorate [1] and a two fold molar amount of 2-aminopropane. After cooling to room temperature, ethyl ether was added to complete the precipitation and the salt was filtered off and air dried. Recrystallization from 2-propanol gave colourless crystals, mp 417 K – 418 K.

Discussion

The non-bonded interactions between polyhedral alkyl substituents linked to planar frameworks leading to a conformational transmission through interlocking of the groups was defined as 'gear effect' [2] (with a later addendum of 'static' when ground states are involved [3]). A recent review gives a historical perspective on the development of this concept, based on experimental data as well as theoretical contributions gathered so far [4].

However, particularly challenging appeared to be the gearing of the smallest among alkyls, namely methyl groups. For to get experimental proof for methyl gearing, the isopropyl group has been used as internal monitor in conformational analysis of polymethylisopropyl-pyridinium salts and -benzenes. It appears from conformational analysis that, the more likely conformer is those in which the bulky face of isopropyl is turned towards the methyl in 2-position, the neighboring 2-Me and 3-Me being 'gear-clashed', so that 2-Me has a hydrogen atom in the plane, pointing towards the isopropyl [5].

The structure determination of the title compound has been undertaken in the purpose to establish the different substituents stereochemistry. This compound, composed of a pyridinium ring and perchlorate group present two twinned molecules [6–7] on asymmetric unit related by an extra symmetry center [7]. X-ray analysis shows that all substituents admit the plane of pyridinium ring as bisector plane, an hydrogen atom being eclipsed with the ring. The bulky face of isopropyl is turned towards the 2-Me. This latter having his hydrogen atom in plane pointed towards isopropyl and being clashed to 3-Me as excepted by conformational analysis. The different positions of these substituents show well the existence of intramolecular interactions at short distances $d(C7A-C8A) = 2.953$ Å, $d(C7A-C11A) = 2.855$ Å, $d(C8A-C9A) = 2.879$ Å, $d(C9A-C10A) = 2.966$ Å, $d(C7B-C8B) = 2.939$ Å, $d(C7B-C11B) = 2.861$ Å, $d(C8B-C9B) = 2.859$ Å, $d(C9B-C10B) = 2.970$ Å. We note also the existence of disorder at oxygen atoms level of one perchlorate group in proportion of occupancy 0.55/0.45.

Table 1. Data collection and handling.

Crystal:	colourless needle, size $0.12 \times 0.15 \times 0.3$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	2.76 cm ⁻¹
Diffractionmeter, scan mode:	KappaCCD, φ
$2\theta_{max}$:	52.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5167, 5157
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 4606
$N(param)_{refined}$:	367
Programs:	SHELXS-97 [8], SHELXL-97 [9], ORTEP-3 [10]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U _{iso}
H(7A)	4e		0.6404	0.7916	0.8227	0.070
H(8A1)	4e		0.6040	0.8818	1.0221	0.070
H(8A2)	4e		0.6639	0.8292	1.0949	0.070
H(8A3)	4e		0.5567	0.8166	1.0967	0.070
H(9A1)	4e		0.6466	0.6567	1.1759	0.070
H(9A2)	4e		0.6081	0.5291	1.1723	0.070
H(9A3)	4e		0.5410	0.6354	1.1635	0.070
H(10A)	4e		0.6211	0.3270	1.0191	0.070
H(10B)	4e		0.5686	0.3831	1.0946	0.070
H(10C)	4e		0.6762	0.3827	1.0937	0.070
H(11A)	4e		0.5961	0.6410	0.7702	0.070
H(11B)	4e		0.6505	0.5237	0.7792	0.070
H(11C)	4e		0.7029	0.6430	0.7834	0.070
H(12A)	4e		0.7026	0.9423	0.9437	0.070
H(12B)	4e		0.7362	0.9268	0.8511	0.070
H(12C)	4e		0.7644	0.8355	0.9198	0.070
H(13A)	4e		0.4969	0.8333	0.8591	0.070
H(13B)	4e		0.5503	0.9510	0.8485	0.070
H(13C)	4e		0.5299	0.9026	0.9384	0.070
H(7B)	4e		0.1188	−0.2979	0.3202	0.070
H(8B1)	4e		0.1218	−0.3864	0.5226	0.070
H(8B2)	4e		0.0941	−0.3203	0.6047	0.070
H(8B3)	4e		0.1979	−0.3315	0.5804	0.070

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(9B1)	4e		0.1871	−0.1711	0.6613	0.070
H(9B2)	4e		0.0869	−0.1235	0.6715	0.070
H(9B3)	4e		0.1694	−0.0363	0.6640	0.070
H(10D)	4e		0.1072	0.1667	0.5145	0.070
H(10E)	4e		0.1890	0.1245	0.5712	0.070
H(10F)	4e		0.0875	0.1072	0.6011	0.070
H(11D)	4e		0.1524	−0.1399	0.2675	0.070
H(11E)	4e		0.0875	−0.0315	0.2767	0.070
H(11F)	4e		0.0466	−0.1579	0.2798	0.070
H(12D)	4e		0.0253	−0.4034	0.4496	0.070
H(12E)	4e		0.0380	−0.4623	0.3618	0.070
H(12F)	4e		−0.0164	−0.3448	0.3691	0.070
H(13D)	4e		0.2570	−0.3356	0.3989	0.070
H(13E)	4e		0.2200	−0.4287	0.3351	0.070
H(13F)	4e		0.2027	−0.4445	0.4314	0.070
O(2B)	4e	0.45(2)	0.076(2)	0.308(1)	0.773(2)	0.034(4)
O(3B)	4e	0.45	0.2061(9)	0.261(1)	0.838(1)	0.12(1)
O(4B)	4e	0.45	0.074(1)	0.201(2)	0.887(1)	0.29(3)
O(2B)	4e	0.55	0.0472(5)	0.2773(9)	0.8213(9)	0.081(5)
O(3B)	4e	0.55	0.192(1)	0.293(1)	0.789(2)	0.16(1)
O(4B)	4e	0.55	0.152(2)	0.181(1)	0.8972(8)	0.17(1)
H(5A)	4e		0.1029	0.0572	0.4011	0.070
H(5B)	4e		0.6324	0.4324	0.8997	0.070

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
N(1A)	4e	0.6273(2)	0.7074(2)	0.9307(2)	0.033(2)	0.030(1)	0.036(1)	−0.001(1)	0.002(2)	0.003(1)
C(2A)	4e	0.6165(3)	0.7082(3)	1.0151(2)	0.027(2)	0.031(2)	0.042(2)	−0.002(1)	−0.002(2)	−0.001(1)
C(3A)	4e	0.6139(3)	0.6055(3)	1.0585(2)	0.029(2)	0.035(2)	0.037(2)	−0.000(1)	0.000(2)	0.001(1)
C(4A)	4e	0.6215(3)	0.5019(3)	1.0162(2)	0.027(2)	0.032(2)	0.042(2)	−0.000(2)	−0.004(2)	0.005(1)
C(5A)	4e	0.6315(3)	0.5048(2)	0.9315(2)	0.034(2)	0.032(2)	0.034(2)	−0.001(2)	−0.000(2)	0.002(1)
C(6A)	4e	0.6340(3)	0.6066(3)	0.8886(2)	0.029(2)	0.035(2)	0.038(2)	−0.002(2)	0.001(2)	0.000(1)
C(7A)	4e	0.6327(4)	0.8170(3)	0.8809(2)	0.078(3)	0.028(2)	0.047(2)	−0.005(2)	0.003(2)	0.010(1)
C(8A)	4e	0.6097(3)	0.8185(3)	1.0612(2)	0.057(3)	0.037(2)	0.048(2)	−0.000(2)	0.000(2)	−0.004(2)
C(9A)	4e	0.6013(3)	0.6068(3)	1.1507(2)	0.066(3)	0.042(2)	0.037(2)	0.002(2)	0.000(2)	0.001(2)
C(10A)	4e	0.6219(4)	0.3889(3)	1.0597(2)	0.055(2)	0.032(2)	0.048(2)	0.002(2)	0.004(2)	0.010(2)
C(11A)	4e	0.6470(3)	0.6033(3)	0.7975(2)	0.054(3)	0.047(2)	0.038(2)	0.000(2)	0.002(2)	0.006(2)
C(12A)	4e	0.7164(4)	0.8866(4)	0.9006(5)	0.072(4)	0.046(3)	0.142(6)	−0.019(2)	0.017(4)	0.034(3)
C(13A)	4e	0.5447(4)	0.8817(4)	0.8818(4)	0.084(4)	0.046(3)	0.094(4)	−0.005(2)	−0.040(3)	0.028(3)
Cl(1A)	4e	0.62819(8)	0.20228(6)	0.79867(6)	0.0422(5)	0.0357(4)	0.0519(5)	−0.0014(4)	−0.0027(5)	−0.0090(4)
O(1A)	4e	0.6285(3)	0.2098(3)	0.8853(2)	0.102(3)	0.097(2)	0.046(2)	−0.006(3)	−0.005(2)	−0.022(2)
O(2A)	4e	0.6342(4)	0.3124(3)	0.7668(3)	0.194(5)	0.050(2)	0.104(3)	−0.046(3)	−0.023(4)	0.012(2)
O(3A)	4e	0.5482(2)	0.1512(3)	0.7715(2)	0.051(2)	0.108(3)	0.091(3)	−0.023(2)	−0.002(2)	−0.037(2)
O(4A)	4e	0.7008(3)	0.1344(4)	0.7718(3)	0.078(3)	0.132(3)	0.091(3)	0.053(2)	−0.008(2)	−0.037(3)
N(1B)	4e	0.1214(2)	−0.2128(2)	0.4279(2)	0.034(2)	0.032(1)	0.035(1)	−0.002(1)	0.001(2)	−0.006(1)
C(2B)	4e	0.1303(3)	−0.2128(2)	0.5117(2)	0.030(2)	0.031(2)	0.036(2)	−0.003(2)	−0.002(2)	−0.002(1)
C(3B)	4e	0.1341(3)	−0.1089(3)	0.5549(2)	0.029(2)	0.034(2)	0.037(2)	−0.002(2)	−0.001(2)	−0.004(1)
C(4B)	4e	0.1246(3)	−0.0065(3)	0.5123(2)	0.027(2)	0.034(2)	0.042(2)	−0.001(2)	−0.004(2)	−0.003(1)
C(5B)	4e	0.1144(3)	−0.0116(3)	0.4280(2)	0.039(2)	0.031(2)	0.044(2)	−0.002(2)	−0.005(2)	0.010(1)
C(6B)	4e	0.1120(3)	−0.1128(3)	0.3856(2)	0.033(2)	0.039(2)	0.040(2)	−0.007(2)	−0.004(2)	0.004(1)
C(7B)	4e	0.1208(4)	−0.3231(3)	0.3789(2)	0.064(3)	0.035(2)	0.048(2)	0.001(2)	−0.004(2)	−0.014(2)
C(8B)	4e	0.1366(3)	−0.3222(3)	0.5589(2)	0.059(3)	0.033(2)	0.048(2)	−0.002(2)	−0.002(2)	0.003(2)
C(9B)	4e	0.1453(3)	−0.1101(3)	0.6456(2)	0.056(3)	0.045(2)	0.039(2)	−0.004(2)	−0.008(2)	−0.003(2)
C(10B)	4e	0.1273(3)	0.1078(3)	0.5533(2)	0.046(2)	0.034(2)	0.057(2)	−0.002(2)	−0.002(2)	−0.006(2)
C(11B)	4e	0.0985(3)	−0.1103(4)	0.2946(3)	0.060(3)	0.067(3)	0.041(2)	−0.008(2)	−0.008(2)	0.008(2)
C(12B)	4e	0.0343(4)	−0.3892(4)	0.3909(4)	0.058(3)	0.053(3)	0.110(5)	−0.005(2)	−0.022(3)	−0.032(3)
C(13B)	4e	0.2077(3)	−0.3887(4)	0.3868(4)	0.058(3)	0.047(3)	0.109(5)	0.001(2)	0.020(3)	−0.034(3)
Cl(1B)	4e	0.12658(9)	0.21922(7)	0.81858(7)	0.0462(6)	0.0376(4)	0.0718(7)	0.0015(5)	−0.0035(6)	−0.0216(4)
O(1B)	4e	0.1265(3)	0.1208(2)	0.7688(2)	0.088(2)	0.052(2)	0.072(2)	0.007(2)	−0.005(2)	−0.030(1)

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