Polish J. Chem., **76**, 129–135 (2002) **COMMUNICATION**

An Empirical Estimation of the Interactions $H^{\delta+}...Cl^{-}$. The Crystal and Molecular Structure of the 1-Methyl-2-tert-butylamino-4-isopropyl-5(4H)-imidazolone hydrochloride

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Out of over 2×10^5 entries of CSD [1] more than 1000 are hydrochlorides. Undoubtedly, the interactions between the counterions in such a system are of crucial importance. Except the application of the principle of structural correlation [2], or more detailed theory-based papers, in most crystallographic reports the interactions between constituents of the crystal are discussed in terms of the so-called short contacts between the atoms [3], which are closer or not much longer than the sum of the van der Waals radii [4].

The aim of this communication is to present an empirical way, which enables estimation of the energy of interaction between chloride anion and the partly positive charged H-atoms of the nearest neighborhood. The idea is based on an extension of the model based on Pauling's bond number concept [5], used for estimation of the energy of interactions between H...O and H...N [6,7] as well as for covalent interactions, in CC bonds [8]. For illustration of this model, extended for $H...Cl^{-}$ interactions, we have chosen the crystal and molecular structure of 1-methyl-2-tert-butylamino-4-isopropyl-5(4H)-imidazolone hydrochloride. This compound was obtained in the course of our continued studies on reactions of unsymmetrically substituted dialkycarbodiimides with various amino acid derivatives [9,10]. The structure of products could explain the influence of alkyl group on the course of reactions.

Synthesis of 1-methyl-2-tert-butylamino-4-isopropyl-5(4H)-imidazolone hydrochloride was carried out as follows: to HCl, Val-Merrifield resin (4.1 g, 2 mmol) in CH_2Cl_2 (50 ml) N-tert-butyl-N′-methylcarbodiimide (0.67 g, 6 mmol) was added and the mixture was shaken for 24 h. After removal of the solvent, the product was treated with diisopropylethylamine (0.5 ml, 3 mmol) in CH_2Cl_2 (25 ml) for 1 h. The resin was filtered off and washed with CH_2Cl_2 (3×25 ml). The combined filtrates were evaporated and the resulting solid was dissolved in ethyl acetate (250 ml) and washed with water (10 ml). The solvent was evaporated and the resulting material treated with anhydrous 4 N HCl in dioxane (20 ml). After evaporation of dioxane, the product was crystallized from ethanol; m.p. 228–233°C. Anal. Calcd. for $C_{11}H_{22}N_3OCl$: C, 53.32:

H, 8.95; N, 16.96: Cl, 14.32. Found C, 53.28; H, 9.02; N, 16.97; Cl 14.85. ^{1}H-NMR (200 MHz, $CDCl_3$), δ 5.50 (1H, broad s, $(CH_3)_3$-C-$\underline{NH}$-), 4.01 (1h, d, Val $C^{\alpha}\underline{H}$), 3.08 (3H, s, $\underline{CH_3}$-N=), 2.27 (1H, m, Val $(CH_3)_2$-$\underline{CH}$-), 1.51 (9H, s, $(CH_3)_3$-C-NH), 1.01–0.84 (6H, dd, Val $(CH_3)_2$-CH-). The X-ray measurement was done on a KM-4 KUMA diffractometer with graphite monochromated MoKα radiation. The data were collected at room temperature using the ω-2θ scan technique. The intensity of control reflections varied by less than 3%, and the linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarization effects, but no absorption correction was applied. The structure was solved by direct methods [11] and refined by the procedure of [12]. The refinement was based on F^2 for all reflections except those with very negative F^2. The weighted R factor, wR, and all goodness-of-fit S values are based on F^2. The non-hydrogen atoms were refined anisotropically, whereas the H-atoms were placed in the calculated positions, and their thermal parameters were refined isotropically. The atomic scattering factors were taken from the International Tables [13]. The details of X-ray measurements, structural computations and crystal data for the title compound are given in Table 1, whereas the ORTEP scheme and labelling of atoms are given in Fig. 1. Table 2 presents the observed bond lengths, bond angles and selected torsion angles. Crystallographic data for the structure has been deposited at the Cambridge Crystallographic Data Centre (with deposition number CCDC152204).

Table 1. Crystal data and structure refinement for 1-methyl-2-tert-butylamino-4-isopropyl-5(4H)-imidazolone hydrochloride.

Empirical formula	$C_{11}H_{22}N_3OCl$
Formula weight	247.77
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	*P*2(1)/*c*
Unit cell dimensions	a = 10.990(2) Å
	b = 9.452(2) Å
	c = 14.602(3) Å
	β = 110.23(3)°
Volume	1423.2(5) $Å^3$
Z	4
Calculated density	1.156 Mg/m^3
Absorption coefficient	2.267 mm^{-1}
F(000)	536
Crystal size	0.3×0.26×0.24 mm

Table 1 (continuation)

Theta range for data collection	4.29 to 79.27°
Index ranges	–12 <= h <= 12, –11 <= k <= 11, –17 <= l <= 6
Reflections collected/unique	5418/2832 [R(int) = 0.1039]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2822/0/174
Goodness-of-fit on F^2	0.984
Final R indices [$I > 2$ sigma(I)]	R1 = 0.0677, wR2 = 0.1722
R indices (all data)	R1 = 0.1554, wR2 = 0.2507
Extinction coefficient	0.0065(14)
Largest diff. peak and hole	0.196 and –0.217 e.A^{-3}

Table 2. Bond lengths [Å], angles and selected torsion angles [°] for 1-methyl-2-tert-butylamino-4-isopropyl-5(4H)-imidazolone hydrochloride.

C(1)–O(1)	1.208(6)
C(1)–N(2)	1.393(6)
C(1)–C(2)	1.507(7)
C(2)–N(1)	1.448(6)
C(2)–C(5)	1.527(7)
N(1)–C(3)	1.329(6)
C(3)–N(3)	1.318(5)
C(3)–N(2)	1.373(5)
N(2)–C(4)	1.467(6)
C(5)–C(6)	1.489(8)
C(5)–C(7)	1.492(8)
N(3)–C(8)	1.492(5)
C(8)–C(9)	1.505(7)
C(8)–C(10)	1.525(6)
C(8)–C(11)	1.535(6)
O(1)–C(1)–N(2)	123.0(5)
O(1)–C(1)–C(2)	129.1(5)
N(2)–C(1)–C(2)	107.8(4)
N(1)–C(2)–C(1)	100.7(4)
N(1)–C(2)–C(5)	112.7(4)
C(1)–C(2)–C(5)	116.3(4)

Table 2 (continuation)

C(3)–N(1)–C(2)	112.8(4)
N(3)–C(3)–N(1)	129.8(4)
N(3)–C(3)–N(2)	120.9(4)
N(1)–C(3)–N(2)	109.3(4)
C(3)–N(2)–C(1)	109.3(4)
C(3)–N(2)–C(4)	125.7(4)
C(1)–N(2)–C(4)	124.6(4)
C(6)–C(5)–C(7)	115.4(8)
C(6)–C(5)–C(2)	112.4(6)
C(7)–C(5)–C(2)	110.5(5)
C(3)–N(3)–C(8)	126.3(3)
N(3)–C(8)–C(9)	110.1(4)
N(3)–C(8)–C(10)	111.3(4)
C(9)–C(8)–C(10)	110.8(4)
N(3)–C(8)–C(11)	104.8(3)
C(9)–C(8)–C(11)	110.4(4)
C(10)–C(8)–C(11)	109.3(4)
O(1)–C(1)–C(2)–N(1)	173.5(5)
N(2)–C(1)–C(2)–N(1)	–3.1(5)
O(1)–C(1)–C(2)–C(5)	51.9(8)
N(2)–C(1)–C(2)–C(5)	–125.1(4)
C(1)–C(2)–N(1)–C(3)	3.5(5)
C(5)–C(2)–N(1)–C(3)	128.1(5)
C(2)–N(1)–C(3)–N(3)	178.8(4)
C(2)–N(1)–C(3)–N(2)	–2.7(5)
N(3)–C(3)–N(2)–C(1)	179.1(4)
N(1)–C(3)–N(2)–C(1)	0.4(5)
N(3)–C(3)–N(2)–C(4)	5.4(7)
N(1)–C(3)–N(2)–C(4)	–173.2(4)
O(1)–C(1)–N(2)–C(3)	–175.4(5)
C(2)–C(1)–N(2)–C(3)	1.8(5)
O(1)–C(1)–N(2)–C(4)	–1.6(8)
C(2)–C(1)–N(2)–C(4)	175.6(5)
N(1)–C(3)–N(3)–C(8)	1.7(7)
N(2)–C(3)–N(3)–C(8)	–176.7(4)

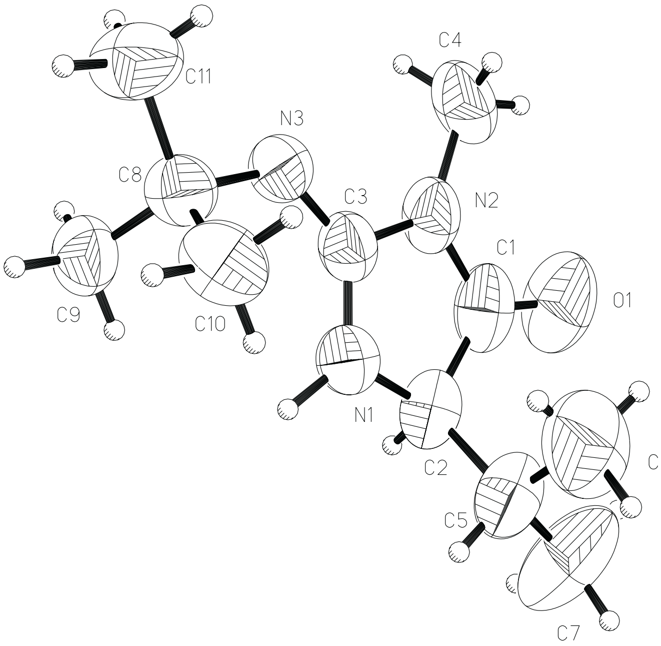

Figure 1. The molecular structure of 1-methyl-2-tert-butylamino-4-isopropyl-5(4H)-imidazolone hydrochloride. Thermal ellipsoids are drawn at the 50% probability level.

Pauling defined a fractional bond number [5], n, in terms of a difference between an interatomic distance d(n) and a standard "single bond" length d(1), in which n = 1 and an empirical constant c:

$$d(n) - d(1) = -c\ln(n)$$

Application of the Johnston and Parr empirical formula [14] relating the bond number, n, and bond energy E(n) leads to the empirical formula relating bond length, d(n) (or interatomic distance) and the energy of interactions of atoms involved:

$$E(n) = E(1)\exp\{\alpha[d(1) - d(n)]\}$$

for which α may be obtained by taking all other parameters from experiment. This has already been done successfully for $H^{(\delta+)}\ldots{}^{(\delta-)}O$ [6] and for $H^{(\delta+)}\ldots{}^{(\delta-)}N$ [7] interactions. Applying for $Cl^{-}\ldots H^{+}$- interactions d(1) = 1.274 Å [15] and E(1) = 431.79 kJ/mole [16] from HCl and d(0.5) = 1.61 Å [17] and E(0.5) = 92.47 kJ/mole [18] from

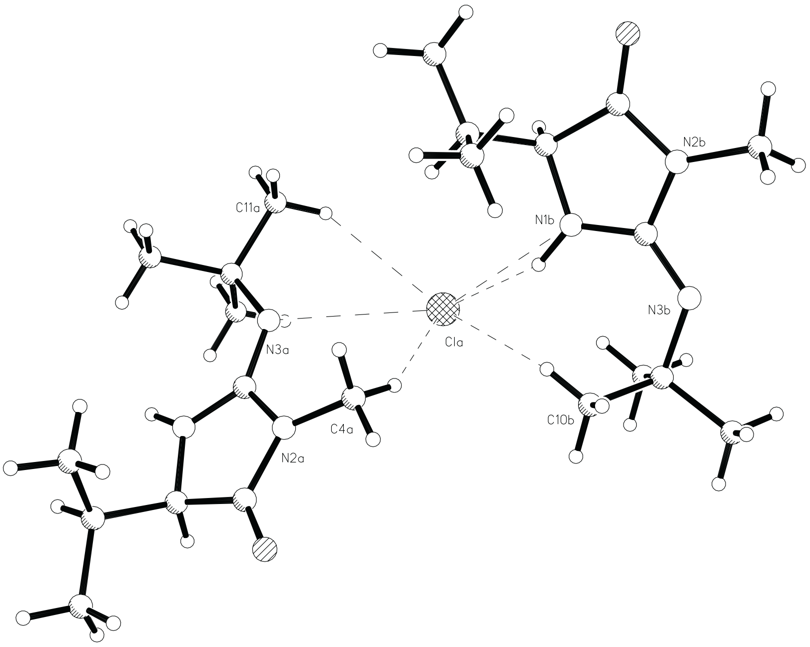

Figure 2. The intermolecular interactions in the title compound.

$[Cl\ldots H\ldots Cl]^-$ species one obtains $\alpha = 4.586$. Thus, the effective but approximate formula estimating $H^{(\delta+)}\ldots Cl^-$ interactions is

$$E(n) = 431.79\exp\{4.586[1.274 - d(n)]\} \tag{1}$$

where E(n) and d(n) are the energy and the interatomic distance of a given $H^{(\delta+)}\ldots Cl^{(\delta-)}$ pair. Summing up all contributions around a given Cl anion, one obtains its total but approximate energy of interactions of the H-bond type. Application of (1) to the crystal and molecular structure of 1-methyl-2-tert-butylamino-4-isopropyl-5(4H)-imidazolone hydrochloride shows that only one of the so-called close H...Cl contacts, Cl...H(N1b) (Fig. 2) represents a substantial energy, 5.82 kJ/mole, all others are much weaker, between 0.56 kJ/mole for Cl...H(C4a) to as low as 0.04 for Cl...H(C10b). It may be concluded, that practically only the first mentioned interaction plays a significant role in the construction of the crystal structure of 1-methyl-2-tert-butylamino-4-isopropyl-5(4H)-imidazolone hydrochloride.

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