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The X-ray crystal and molecular structure of 3,5-di-*tert*-butylpyrazole hydrochloride at 200 K

Cristina Fernández-Castaño[a], Concepción Foces-Foces[a], Nadine Jagerovic[b], José Elguero[b,*]

[a]*Instituto de Química Física 'Rocasolano', C.S.I.C., Serrano, 119, E-28006 Madrid, Spain*
[b]*Instituto de Química Médica, C.S.I.C., Juan de la Cierva, 3, E-28006 Madrid, Spain*

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Abstract

The title compound 1*H*,2*H*-3,5-di-*tert*-butylpyrazolium chloride (**2**) was prepared by reacting 1*H*-3,5-di-*tert*-butylpyrazole (**1**) with hydrochloric acid in methanol. The molecules of **2** are arranged in the crystal in dimers bridged by the chlorine ion through strong and quite linear hydrogen bonds. Several surveys were performed via the Cambridge Structural Database searching for $N^+(sp^2) - H \cdots Cl^-$ interactions and for pseudo-rings in which two chlorine ions were hydrogen bonded by two water molecules, both hydrogen atoms of each molecule being involved in the contacts.

1. Introduction

We are engaged in a systematic study of N*H*-pyrazoles by crystallography with special emphasis on hydrogen bonds [1–5]. Due to some anomalies in the corresponding CPMAS-NMR spectra, anomalies that could be due to the presence of the conjugated acids, we have decided to explore the domain of the pyrazolium salts resulting from protonation of neutral pyrazoles by mineral acids ($pzH + XH \rightleftharpoons pzH_2^+, X^-$). We began by studying the reaction between hydrochloric acid and 1*H*-3,5-di-*tert*-butylpyrazole (**1**) [6].

The structural information about N*H*-pyrazoles can be summarized as follows: they crystallize in four kinds of hydrogen-bonded networks: cyclic dimers, cyclic trimers, cyclic tetramers and open-chain catamers [3,4]. Compound **1** crystallizes forming dimers [5,6], and one of the *tert*-butyl groups, that at position 5, is disordered into two positions which differ by the conformation of the *tert*-butyl group: one of the three methyl groups eclipsing H_4 and one of the three methyl groups eclipsing the N*H*.

2. Experimental

Melting points were determined with a Reichert-Jung Thermovar and are uncorrected. IR spectra were recorded on a Perkin-Elmer 681. The NMR (^{1}H, ^{13}C, ^{15}N) spectra were obtained with the same spectrometers and experimental conditions described in other publications [7,8].

2.1. Synthesis and spectroscopic data

*1*H-*3,5-di*-tert-*Butylpyrazole* (*1*)

To 5 ml (2.4 mmol) of 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane) dissolved in

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* Corresponding author.

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Table 1
Crystal analysis parameters at 200 K

Crystal data			
Chemical formula	$C_{11}H_{21}N_2Cl$	Crystal system	Orthorhombic
Mr	216.75	Space group	*Pbca*
a (Å)	11.7643(4)	α (deg)	90
b (Å)	19.4375(10)	β (deg)	90
c (Å)	11.6143(4)	γ (deg)	90
Z	8	Dx (g cm^{-3})	1.08
V ($Å^3$)	2655.8(2)	Radiation	Cu Kα
Wavelength (Å)	1.5418	No. of reflections for lattice parameters:	82
θ range for lattice parameters (deg)	2–45		
Absorption coefficient (cm^{-1})	23.19	Temperature (K)	200
Crystal colour	Colourless	Crystal description	Plate-like
Crystal size (mm)	0.33 × 0.33 × 0.13		
Data collection			
Diffractometer type	Philips PW1100, four circle. Graphite oriented monochromator.		
Measurement time	1 min/reflection	Detector apertures (deg)	1 × 1
Collection method	$\omega/2\theta$ scans	θ_{max} (deg)	65
No. of standard reflections (interval)	2 (90 min). No variation	Scan width (deg)	1.5
No. of independent reflections	2264	No. of observed reflections, $I > 2\sigma(I)$	1898
Refinement			
Treatment of hydrogen atoms	See experimental part	Refinement: least-squares on F_0. Full matrix	
R	0.043	No. of parameters refined	211
wR	0.053	Degrees of freedom	1687
$(\Delta\rho)_{max}(e\ Å^{-3})$	0.29	Ratio of freedom	9.0
⟨Shift/error⟩	0.01	Max. thermal value ($Å^2$)	$U11[C(10)] = 0.075(2)$
Weighting scheme: empirical so as to give no trends in $\langle\omega\Delta^2F\rangle$ vs. $\langle\lvert F_{obs}\rvert\rangle$ and $\langle\sin\theta/\lambda\rangle$.			

ethanol (30 ml) were added 2 ml (4 mmol) of hydrazine hydrate and three drops of concentrated hydrochloric acid (35%, $d = 1.18$). The reaction mixture was heated to reflux for 10 h. After evaporation of the solvent, the residue was dissolved in dichloromethane. The solution was washed with water, dried over Na_2SO_4 and evaporated to yield 4.21 g (97%) of **1**. m.p. 195°C (193°C [9]). IR (nujol mull): 3230 (br), 1570, 1486, 1460, 1362, 1288, 1251, 1208, 1198, 1130, 1007, 992 and 808 cm^{-1}.

*1*H,*2*H-*3,5-di*-tert-*Butylpyrazolium chloride (2)*

Concentrated hydrochloric acid (35%, $d = 1.18$, 5 ml) was added to a solution of 4.21 g (2.34 mmol) of **1** in methanol (50 ml). Rotatory evaporation of the solution, used to remove methanol and the excess of hydrochloric acid, gave a white solid residue. Crystals of compound **2** were obtained by slow evaporation of a concentrated solution of this residue in methanol to which was added a drop of concentrated hydrochloric acid. IR (KBr): 3140, 3040, 2980, 2880, 2800–2500, 1594, 1518, 1482, 1467, 1375, 1370, 1341, 1276, 1253, 1204, 990. 832 and 776 cm^{-1}.

2.2. X-Ray structure determination

Details of data collection and processing are presented in Table 1. The crystal was cooled to 200 K utilizing an Oxford Cryostream device and the stated temperature was measured continuously during data collection. Empirical absorption correction was applied [10]. The structure was solved by Patterson. The non-hydrogen atoms were refined anisotropically and the hydrogen ones, obtained from difference Fourier synthesis, were included and refined as isotropic. Most of the calculations were performed using the XTAL system [11] on a VAX6410 computer. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography, Vol. 4 [12] and the weighting schemes were established using

Table 2
Final atomic coordinates and $U_{eq} = (1/3)\Sigma[U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j \cdot \cos(a_i, a_j)]$ (Å^2)

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Cl(1)	0.57679(5)	0.10767(3)	0.47922(5)	0.0328(2)	C(7)	0.2948(2)	−0.0683(1)	0.8463(2)	0.035(1)
N(1)	0.4079(2)	0.0021(1)	0.7086(2)	0.028(1)	C(8)	0.4035(2)	0.2192(1)	0.6861(2)	0.040(1)
N(2)	0.4454(2)	0.0674(1)	0.6944(2)	0.028(1)	C(9)	0.5729(3)	0.1872(2)	0.8050(3)	0.052(1)
C(3)	0.4122(2)	0.1057(1)	0.7840(2)	0.027(1)	C(10)	0.3849(3)	0.2112(1)	0.9005(2)	0.050(1)
C(4)	0.3516(2)	0.0631(1)	0.8573(2)	0.031(1)	C(11)	0.2502(3)	−0.0592(2)	0.9691(3)	0.051(1)
C(5)	0.3497(2)	−0.0022(1)	0.8076(2)	0.028(1)	C(12)	0.1958(3)	−0.0843(2)	0.7644(3)	0.056(1)
C(6)	0.4434(2)	0.1808(1)	0.7940(2)	0.032(1)	C(13)	0.3822(3)	−0.1265(1)	0.8438(3)	0.049(1)

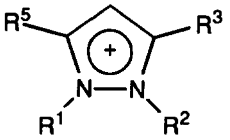
the PESOS program [13]. The final atomic coordinates for the non-hydrogen atoms are listed in Table 2.

3. Results and discussion

Compound **2** was prepared by dissolving the neutral pyrazole **1** in a mixture of concentrated hydrochloric acid and methanol; slow evaporation of methanol solution affords beautiful white crystals. The NMR spectroscopy data of this compound (^{1}H and ^{13}C) are in agreement with the proposed structure: δ (^{1}H, [^{2}H$_6$]-DMSO), 1.332 (Bu^t), 6.434 (H$_4$); δ (^{1}H, [^{2}H$_4$]-methanol) 1.422 (Bu^t), 6.589 (H$_4$); δ (^{13}C, [^{2}H$_6$]-DMSO), 29.71 (CH$_3$ of Bu^t), 31.68 (C of Bu^t), 100.65 (C$_4$), 157.28 (C$_3$ + C$_5$); δ (^{13}C, [^{2}H$_4$]-methanol), 29.90 (CH$_3$ of Bu^t), 32.87 (C of Bu^t), 102.76 (C$_4$), 160.17 (C$_3$ + C$_5$).

In ^{15}N NMR, compound **2** shows a single, narrow peak at −196.1 ppm with regard to external nitromethane or at +159.4 ppm with regard to ^{15}NH$_4$Cl(sat)/D$_2$O. We have used this last reference when comparing solution and solid-state ^{15}N chemical shifts of pyrazoles [14]. It appears that the signals of neutral pyrazole **1**, which appear in THF at 170 K at 176 ppm (NH) and 266 ppm (−N=) [14], are both shifted to 159.4 ppm ($\Delta\delta = -61.6$ ppm), a behaviour already reported for the solution in the case of pyrazole itself ($\Delta\delta = -62.2$ ppm) [15].

The molecular structure of **2** and the corresponding atom labelling scheme are shown in Fig. 1. The cation displays a pseudo-binary axis passing through the C(4) atom and the midpoint of the N–N bond (Table 3). The bond lengths and angles are in good agreement with the values reported for pyrazolium cations **3** when they are symmetrically substituted (R^1 = R^2, R^3 = R^5) (CSD [16] refcodes: JAMFEI, JIZKOS [17,18]). However, the N–N distance is longer in 1,2-bis(methoxycarbonylamino)-3,5-dimethylpyrazolium bromide (**3**, R^1 = NH–CO$_2$CH$_3$, R^3 = CH$_3$) (CSD refcode: MXCPZB10 [19]) probably due to mutual steric crowding of the N-substituents.



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The *tert*-butyl groups are in a staggered conformation with respect to the nitrogen atoms giving rise to some angular distortion at C(3) and C(5) (C(4)–C(3)–C(6) > N(2)–C(3)–C(6) and C(4)–C(5)–C(7) > N(1)–C(5)–C(7)) analogously to the neutral compound **1** where disorder of the *tert*-butyl groups was observed [5].

The chlorine anion is involved in two strong hydrogen bonds (Table 3) linking two centrosymmetrically related pyrazolium cations being responsible for the formation of dimers, Fig. 1. The N···Cl$^-$···N angle is 99.4(1)°. These dimers pack so as to give hydrophobic layers along the *a* axis with C–H···C interactions between the methyl groups of only one *tert*-butyl group; only one contact close to 4.0 Å is observed between both groups. The crystal can be described as formed by alternating hydrophilic and hydrophobic layers perpendicular to the *b* axis, Fig. 1. The structure is similar to that of the neutral compound (**1**) [5] which crystallizes in the same space group with similar cell dimensions (11.478, 21.100, 9.980 Å). However, the $N(1)\cdots N(2)$ distance between both pyrazoles of the dimer is elongated from 2.900(5) to 5.168(3) Å due to the presence of the chlorine anion in the bridge.

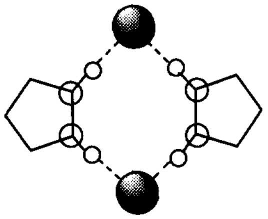
Organic crystal structures with $R < 0.075$ and presenting neither error nor disorder were retrieved from the Cambridge Structural Database (CSD) (October 1994 version [16]) in order to analyze contacts related to those of the present structure. Pathaneni and Desiraju [20] recently reported a CSD-based study of $Cl^{-}\cdots HOH\cdots Cl^{-}$ hydrogen bonds and conclude that hydrogen-bond linearity is the major factor determining their structure.

(i) Contacts of the $N^{+}(sp^{2})-H\cdots Cl^{-}$ type. Only charged nitrogen atoms were retained.

(ii) Structures where at least the chlorine ion is involved in $N^{+}(sp^{2})-H\cdots Cl^{-}\cdots H-N$ contacts. Hydrates and structures where the chlorine ion is involved in several interactions with the nitrogen atoms of a macrocycle were excluded. With regard to the nature of the second donor, 16 out of 59 data correspond to protonated nitrogen atoms. No significant differences were observed with respect to the mean value of the whole set reported in Table 4.

(iii) Hydrates where two water molecules are bridging two chlorine ions through both hydrogen atoms of the water molecules (**4**), in a similar way to that exhibited by the present compound (**2**).

Only contacts displaying $H\cdots Cl$ distances less than 3.0 Å were considered.



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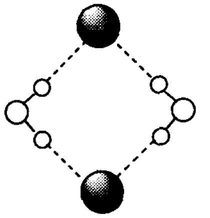

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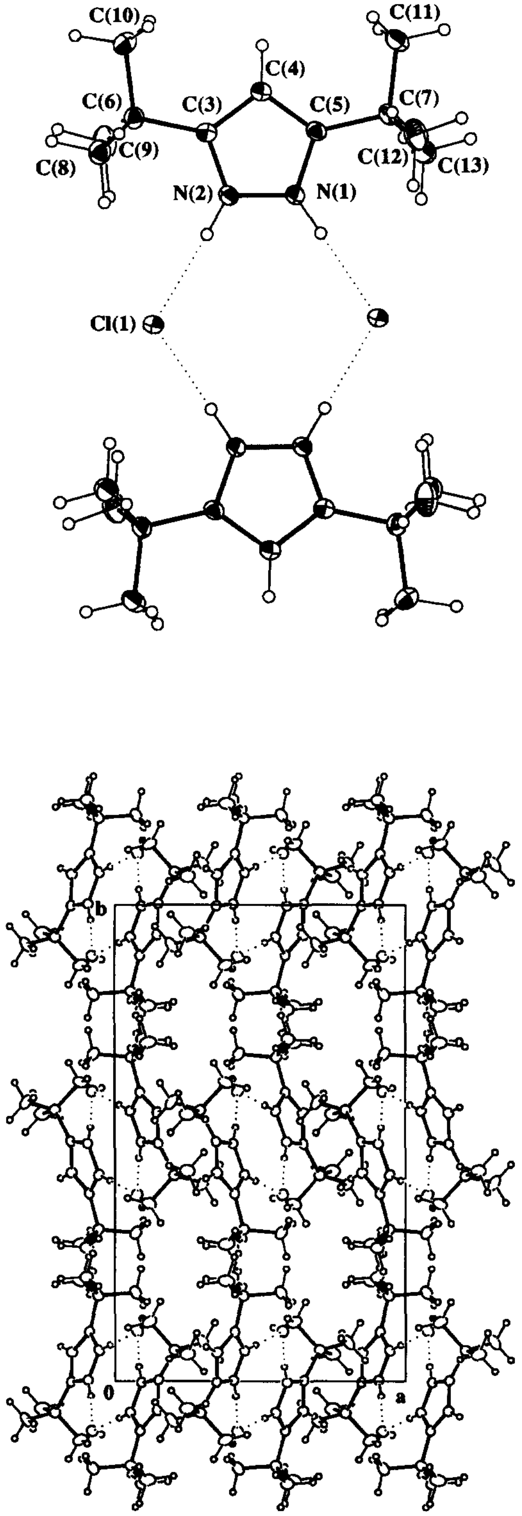

Fig. 1. (a) A view of the dimer showing the atomic numbering scheme. Thermal ellipsoids scaled to 30% probability and the H atoms are denoted by spheres of 0.1 Å in radius. Dotted lines indicate hydrogen bonds. (b) Crystal packing along the *c* axis.

Table 3
Selected geometrical parameters and hydrogen interactions (Å, deg)

N(1)–N(2)	1.353(3)	N(1)–C(5)	1.342(3)
N(2)–C(3)	1.338(3)	C(3)–C(4)	1.386(3)
C(3)–C(6)	1.510(3)	C(4)–C(5)	1.394(3)
C(5)–C(7)	1.506(3)	C(6)–C(8)	1.531(4)
C(6)–C(9)	1.533(4)	C(6)–C(10)	1.534(4)
C(7)–C(11)	1.530(4)	C(7)–C(12)	1.535(4)
C(7)–C(13)	1.529(4)		
N(2)–N(1)–C(5)	109.3(2)	N(1)–N(2)–C(3)	109.4(2)
N(2)–C(3)–C(6)	121.8(2)	N(2)–C(3)–C(4)	107.2(2)
C(4)–C(3)–C(6)	131.0(2)	C(3)–C(4)–C(5)	107.3(2)
N(1)–C(5)–C(4)	106.8(2)	C(4)–C(5)–C(7)	131.2(2)
N(1)–C(5)–C(7)	121.9(2)	C(3)–C(6)–C(10)	108.9(2)
C(3)–C(6)–C(9)	109.1(2)	C(3)–C(6)–C(8)	109.4(2)
C(9)–C(6)–C(10)	110.3(2)	C(8)–C(6)–C(10)	109.6(2)
C(8)–C(6)–C(9)	109.5(2)	C(5)–C(7)–C(13)	109.7(2)
C(5)–C(7)–C(12)	108.3(2)	C(5)–C(7)–C(11)	109.1(2)
C(12)–C(7)–C(13)	110.4(2)	C(11)–C(7)–C(13)	109.5(2)
C(11)–C(7)–C(12)	110.0(2)		
N(2)–C(3)–C(6)–C(8)	55.8(3)	N(2)–C(3)–C(6)–C(9)	-64.0(3)
N(2)–C(3)–C(6)–C(10)	175.5(2)	N(1)–C(5)–C(7)–C(11)	172.0(2)
N(1)–C(5)–C(7)–C(12)	-68.4(3)	N(1)–C(5)–C(7)–C(13)	52.1(3)

X–H···Y	X–H	X···Y	H···Y	X–H···Y	Symmetry
N(1)–H(1)···Cl(1)	0.94(3)	3.057(2)	2.12(3)	175(3)	$-x+1, -y, -z+1$
N(2)–H(2)···Cl(1)	0.91(3)	3.041(2)	2.14(3)	179(3)	x, y, z
C(13)–H(131)···Cl(1)	0.96(4)	3.800(3)	2.90(4)	157(3)	$-x+1, -y, -z+1$
C(13)–H(131)···C(8)	0.96(4)	3.935(4)	3.67(4)	99(2)	$-x+1, y-1/2, -z+3/2$
C(13)–H(132)···C(8)	0.98(4)	3.935(4)	3.76(4)	93(2)	$-x+1, y-1/2, -z+3/2$
C(13)–H(133)···C(8)	1.12(4)	3.935(4)	3.77(4)	90(2)	$-x+1, y-1/2, -z+3/2$
C(10)–H(101)···C(8)	1.03(4)	3.589(4)	3.29(4)	98(2)	$x, -y+1/2, z+1/2$
C(10)–H(103)···C(8)	1.06(4)	3.589(4)	3.12(4)	108(3)	$x, -y+1/2, z+1/2$

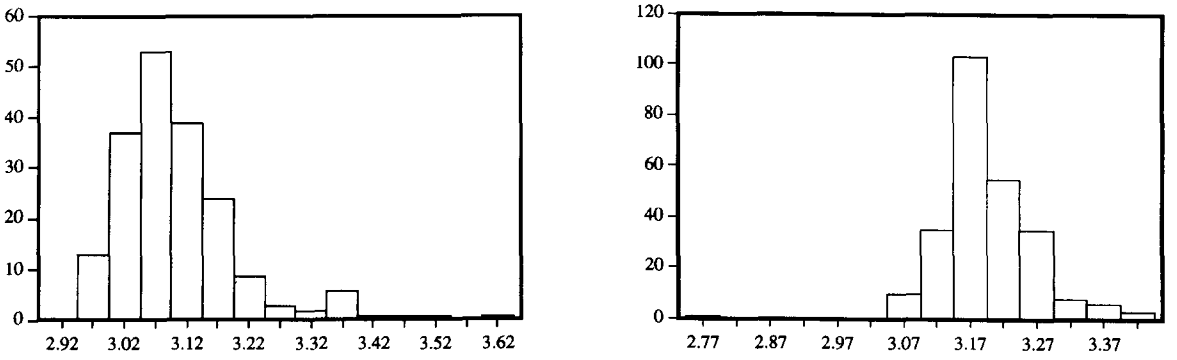

Fig. 2. (a) N···Cl$^-$ and (b) O···Cl$^-$ histograms corresponding to the N$^+$(sp^2)-H···Cl$^-$ interactions and to the water system.

Table 4
Geometrical parameters characterizing the hydrogen bond interactions (Å, deg) (mean values and the standard deviation of the sample in parentheses)[a]

Type	No. data	X/Y–H	X/Y$\cdots$Cl$^-$	H$\cdots$Cl$^-$	X/Y–H$\cdots$Cl$^-$	H$\cdots$Cl$^-\cdots$H	X$\cdots$Cl$\cdots$Y
(i) X=N$^+$	190	0.93(10)	3.12(11)	2.24(19)	162(13)		
(ii) X=N$^+$	59	0.91(11)	3.13(10)	2.28(19)	158(14)	111(22)	111(21)
Y=N		0.91(12)	3.17(10)	2.32(18)	160(13)		
(iii) X=O	64	0.89(12)	3.20(7)	2.34(15)	166(12)	79(10)	78(7)
Y=O							

[a] Average values in H_2O molecule: H–O = 0.89(12) Å and H–O–H = 105(9)°

The most relevant geometrical parameters are summarized in Table 4. Due to the symmetry of the ring in (iii) (D_{2h}) all the equivalent distances and angles were averaged.

The histogram of the N$\cdots$Cl$^-$ distance and the N–H$\cdots$Cl$^-$ angle corresponding to case (i) is shown in Fig. 2(a). The value found for the title compound (Table 3) agrees well with the most probable value.

The angle at the chlorine anion (H$\cdots$Cl$^-\cdots$H = 86(1)°) is similar to the mean value observed when the water molecules replace the pyrazolium cation (79°, Table 4), being close to the most probable value of 98° found in (ii).

The histogram of the O$\cdots$Cl$^-$ distance is shown in Fig. 2(b). The angle distribution is different from that of (iii) with just a few contacts with angles larger than 90°. The O$\cdots$Cl$^-$ range is narrower than that of N$\cdots$Cl$^-$, Fig. 2(a). If the lowest distance of 2.780 Å is excluded, the remaining ones range from 3.051 to 3.351 Å while the N$\cdots$Cl$^-$ contacts show values within 2.952–3.630 Å (four contacts greater than 3.4 Å) and 3.015–3.567 Å for the (i) and (ii) cases, respectively. The most probable distance in (iii) appears to be longer than that in (i) and (ii); the same occurs with the averaged values although they are not significantly different in terms of the standard deviations of the sample.

There are no voids in the crystal and the total packing coefficient amounts to 0.63. The chlorine ions are located in isolated cavities almost oblate spheroidal in shape as tested by the quotients of the specific inertial moments of volume over those of surface [21].

Supplementary material

Lists of the structure factors, thermal components, hydrogen parameters and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

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