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The Relative Basicities of Tris(pyrazol-1-yl)-1,3,5-triazine (TPT), Water and the Picrate Anion in the Solid State

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Abstract

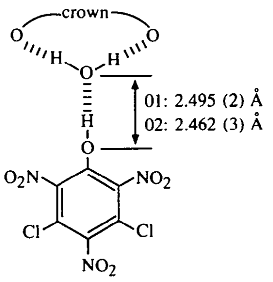
In the solid state, the picrate of tris(pyrazol-1-yl)-1,3,5-triazine (TPT) containing water and chloroform, exists as an oxonium picrate solvated by TPT and chloroform, $H_3O^+.C_6H_2N_3O_7^-.C_{12}H_9N_9.CHCl_3$. The compound shows the shortest $H_3O^+\cdots O^-$ distance ever reported. All H atoms of the oxonium cation are involved in strong hydrogen bonds joining the TPT molecule and the picrate anion. The TPT molecule mimics the crown ethers in stabilizing the H_3O^+ cation.

Comment

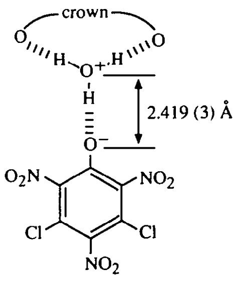
Proton transfer between an acid and a base, both neutral, to produce two charged species (A—H$\cdots B \rightarrow A^-\cdots$H—$B^+$) has never been observed in the gas phase (Abboud, Notario & Botella, 1994), although an appreciable degree of proton transfer has been recently found to exist in the case of the very strong complex $(CH_3)_3N\cdots HCl$ (Legon & Rego, 1989). The situation is completely different in the solid state where the salt-like structures are common (for instance, all NH_4^+ salts). The difference in energy is provided by the lattice, especially by the hydrogen bonds.

The question of proton transfer in crystals arises when the difference in basicity between A^- and B increases, for instance when AH is an organic acid and B is water. Here, we shall examine the case where AH is picric acid (2,4,6-trinitrophenol). Picric acid was the strongest gas acid known (higher acidity than HCl, HBr and HI) (Dzidic, Carrol, Stillwell & Horning, 1974) until very recently (Koppel *et al.*, 1994). Since the solid state compares better with the gas phase than with solution, the situation $C_6H_2(NO_2)_3$—$OH\cdots H_2O$ would be expected to be quite favourable to observe the transfer of the proton to the water, $C_6H_2(NO_2)_3$—$O^-\cdots H_3O^+$, in the crystal.

An examination of the structures reported in the Cambridge Structural Database [CSD; October 1993; $R \leq 0.075$ (Allen *et al.*, 1991)] concerning crystals containing both picric acid (or very close derivatives) and water, shows two situations, (I) (water–picric acid) and (II) (oxonium picrate).



(I) CIRTECT01 and 02

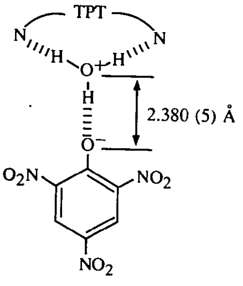


(II) KEPNEY

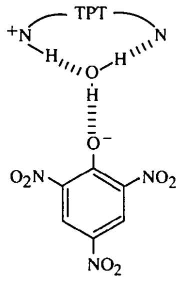
In bis(water–dichloropicric acid)–18-crown-6, (I), two polymorphs CIRTEC01 and CIRTEC02, (Britton, Chantooni, Wang & Kolthoff, 1984; Britton, Chantooni & Kolthoff, 1988), the O$\cdots$O distance is longer than in bis(oxonium dichloropicrate)–dicyclohexano-18-crown-6, (II) (Peiju, Ming & Wenji, 1990) [note that dichloropicric acid is stronger than picric acid in solution (Pearce & Simpkins, 1968)]. The situation is a little more complicated since Peiju, Ming & Wenji (1990) quote the first paper of Britton, Chantooni, Wang & Kolthoff (1984) as an example of oxonium dichloropicrate (protons not found), but subsequently these same authors (Britton, Chantooni & Kolthoff, 1988) described it as a water–dichloropicric acid complex.

The compound described in the present work contains four different chemical entities in the unit cell, namely, picric acid, water, 2,4,6-tris(pyrazol-1-yl)-1,3,5-triazine (TPT) and chloroform. Leaving aside the chlorinated solvent, the acid proton could be located in four positions: (i) on the picric acid, (ii) on the water molecule, (iii) on the pyrazole N atom of TPT, and (iv) on the triazine N atom of TPT. Simple considerations about the relative basicities of these sites could lead to a picrate of $TPTH^+$ with the proton on one of the pyrazole rings [in the gas phase, pyrazole is 40.6 kJ mol^{-1} more basic than ammonia (Abboud *et al.*, 1992) while 1,3,5-triazine is 12.1 kJ mol^{-1} less basic than ammonia (Lias, Liebman & Levin, 1984)].

The molecular structure and the atom-labelling scheme are shown in Fig. 1 (Hall, Flack & Stewart, 1994). The structure found, (III), corresponds to an oxonium picrate with the TPT molecule playing the role of the crown ether. All H atoms of the oxonium cation form strong hydrogen bonds to the N-atom lone pair of each of two pyrazole rings and to the O^- of the picrate ion. To the best of our knowledge, the present $O^+\cdots O^-$ distance is the shortest $H_3O^+\cdots O^-$ hydrogen bond reported (Fig. 1). In a study of these types of interactions (13 structures from the CSD) the shortest distance of 2.419 (3) Å was observed in the closely related structure, (II) (KEPNEY).



(III)



(IV)

This result shows that an adequate hydrogen-bond network can stabilize the oxonium ion sufficiently to overcome the gas-phase difference in energy (water–picric acid complex) and even to prefer the observed structure (III) to other possiblities such as (IV), which would be formed by a simple proton shift.

The *para*- and one of the *ortho*-nitro groups are almost coplanar with the central ring giving rise to a pattern of endo- and exocyclic angular distortions similar to that previously reported (Claramunt *et al.*, 1993). The influence of the strong $O^+—H\cdots O^-$ hydrogen bond is also reflected in the elongation of the $C—O^-$ distance and in the opening of the *ipso* angle [1.269 (5) Å, 113.4 (4)° as opposed to the weighted means (Claramunt *et al.*, 1993) of 1.244 (4) Å and 111.4 (4)°]. These values are rather different from the averaged ones [1.322 (15) Å, 115.7 (4)°] displayed by the picric acid molecule in five structures (CSD). A probability plot (Abrahams & Keve, 1971) indicates that the molecular structure of TPT in the present compound is not significantly different from that of the molecule itself (Echevarría, Elguero, Llamas-Saiz, Foces-Foces, Schultz & Hargittai, 1994) except for the N—C—N—N twists of the pyrazole rings [2.9 (6), −3.1 (5) and 4.4 (5)° in the present compound as opposed to 8.7 (4), 4.3 (4) and −4.0 (3)° in the TPT molecule, see Table 2] and the C(3)—N(21)—C(25) and C(5)—N(31)—C(35) angles, which are greater in the present compound because of the hydrogen bonds [128.7 (4) and 129.1 (4)° as opposed to 124.7 (3) and 126.1 (2)° in the parent compound].

In the crystal packing, partial overlapping of the TPT molecule is observed, the distance between the centroids of the central ring and the N(11)–C(15) (1 + *x*, *y*, *z*) pyrazole ring is 3.487 (2) Å, and the angle between their planes is 3.2 (2)°. The TPT molecule and the ions define a three-dimensional framework in which the channels parallel to the *a* axis are filled by the chloroform molecules. Although the local packing coefficient is slightly low, 0.55 (total packing coefficient = 0.69), all Cl atoms are involved in short $Cl\cdots O$ contacts [3.106 (29)–3.382 (4) Å (Ramasubbu, Parthasarathy & Murray-Rust, 1986)]. The crystal is also stabilized by $C—H\cdots O_2N$ interactions [3.197 (8)–3.554 (25) Å].

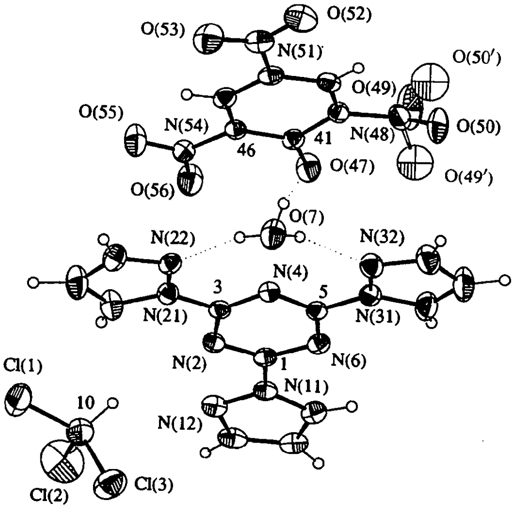


Fig. 1. Crystallographic asymmetric unit with displacement ellipsoids drawn at the 30% probability level.

Experimental

The compound described in the present work was obtained by slow evaporation of an equimolar mixture of TPT and picric acid in chloroform (Echevarría, Elguero, Llamas-Saiz, Foces-Foces, Schultz & Hargittai, 1994).

Crystal data

$H_3O^+.C_6H_2N_3O_7^-.$-
$C_{12}H_9N_9.CHCl_3$
$M_r = 645.76$
Monoclinic
$P2_1/c$
$a = 5.9268\ (2)$ Å
$b = 19.6263\ (15)$ Å
$c = 22.9946\ (24)$ Å
$\beta = 93.853\ (6)°$
$V = 2668.7\ (4)$ Å^3
$Z = 4$
$D_x = 1.607$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 65 reflections
$\theta = 2–45°$
$\mu = 3.782$ mm^{-1}
$T = 295$ K
Plate
0.50 × 0.20 × 0.05 mm
Yellow

Data collection

Philips PW1100 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
4889 measured reflections
4522 independent reflections
3058 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.020$
$\theta_{\rm max} = 65°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 28$
2 standard reflections frequency: 90 min intensity decay: none

Refinement

Refinement on F
$R = 0.062$
$wR = 0.071$
$S = 1.15$
3057 reflections
448 parameters
All H-atom parameters refined
Empirical weighting to give no trends in $\langle w\Delta^2F\rangle$ *versus* $\langle|F_o|\rangle$ and $\langle \sin\theta/\lambda\rangle$

$(\Delta/\sigma)_{\rm max} = 0.16$
$\Delta\rho_{\rm max} = 0.54$ e Å^{-3} [near Cl(2)]
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
C(1)	0.3212 (6)	0.2354 (2)	0.3443 (2)	0.037 (1)
N(2)	0.4123 (5)	0.1754 (2)	0.3574 (1)	0.038 (1)
C(3)	0.6067 (7)	0.1812 (2)	0.3900 (2)	0.037 (1)
N(4)	0.7062 (6)	0.2377 (2)	0.4092 (1)	0.040 (1)
C(5)	0.5951 (7)	0.2933 (2)	0.3917 (2)	0.037 (1)
N(6)	0.4024 (6)	0.2968 (2)	0.3591 (1)	0.041 (1)
N(11)	0.1157 (5)	0.2367 (2)	0.3109 (1)	0.041 (1)
N(12)	0.0059 (6)	0.1783 (2)	0.2941 (2)	0.049 (1)
C(13)	−0.1748 (7)	0.2004 (3)	0.2631 (2)	0.052 (2)
C(14)	−0.1850 (7)	0.2711 (3)	0.2597 (2)	0.053 (3)
C(15)	0.0024 (7)	0.2935 (2)	0.2905 (2)	0.048 (1)
N(21)	0.7200 (6)	0.1209 (2)	0.4046 (2)	0.041 (1)
N(22)	0.9275 (6)	0.1225 (2)	0.4345 (2)	0.043 (1)
C(23)	0.9881 (8)	0.0581 (3)	0.4389 (2)	0.058 (2)
C(24)	0.8242 (10)	0.0157 (3)	0.4130 (3)	0.075 (2)
C(25)	0.6567 (8)	0.0560 (3)	0.3915 (3)	0.063 (2)
N(31)	0.6952 (6)	0.3546 (2)	0.4088 (2)	0.044 (1)
N(32)	0.9032 (6)	0.3551 (2)	0.4384 (2)	0.052 (1)
C(33)	0.9502 (10)	0.4203 (3)	0.4459 (3)	0.068 (2)
C(34)	0.7773 (12)	0.4619 (3)	0.4222 (3)	0.084 (2)
C(35)	0.6179 (9)	0.4195 (3)	0.3993 (3)	0.065 (2)
C(41)	0.6250 (7)	0.2606 (2)	0.5610 (2)	0.040 (1)
C(42)	0.7656 (7)	0.3117 (2)	0.5890 (2)	0.041 (1)
C(43)	0.9682 (7)	0.2994 (2)	0.6185 (2)	0.043 (1)
C(44)	1.0405 (7)	0.2326 (2)	0.6238 (2)	0.042 (1)
C(45)	0.9150 (7)	0.1800 (2)	0.6000 (2)	0.042 (1)
C(46)	0.7120 (6)	0.1934 (2)	0.5690 (2)	0.037 (1)
O(47)	0.4427 (5)	0.2787 (2)	0.5332 (2)	0.063 (1)
N(48)	0.6892 (7)	0.3825 (2)	0.5860 (2)	0.060 (1)
O(49)†	0.4952 (9)	0.3941 (3)	0.5962 (4)	0.103 (3)
O(50)†	0.8282 (9)	0.4271 (2)	0.5788 (3)	0.083 (2)
O(49′)‡	0.582 (4)	0.4019 (12)	0.5412 (11)	0.113 (7)
O(50′)‡	0.715 (5)	0.4166 (14)	0.6220 (13)	0.127 (8)
N(51)	1.2522 (6)	0.2178 (2)	0.6574 (2)	0.054 (1)
O(52)	1.3521 (6)	0.2650 (2)	0.6819 (2)	0.077 (2)
O(53)	1.3202 (6)	0.1592 (2)	0.6588 (2)	0.077 (2)
N(54)	0.5883 (6)	0.1343 (2)	0.5462 (2)	0.045 (1)
O(55)	0.6668 (6)	0.0782 (2)	0.5554 (2)	0.071 (1)
O(56)	0.4102 (6)	0.1425 (2)	0.5178 (2)	0.075 (1)
O(7)	0.1443 (7)	0.2404 (2)	0.4667 (2)	0.067 (1)
C(10)	0.1357 (10)	0.0243 (3)	0.2650 (3)	0.069 (2)
Cl(1)	0.2700 (4)	−0.0481 (1)	0.2948 (1)	0.106 (1)
Cl(2)	0.2992 (3)	0.0607 (1)	0.2131 (1)	0.091 (1)
Cl(3)	−0.1324 (4)	0.0049 (2)	0.2351 (1)	0.138 (1)

† Occupancy 0.77 (1).
‡ Occupancy 0.23 (1).

Table 2. *Selected bond and torsion angles* (°)

N(6)—C(1)—N(11)	114.3 (4)	C(42)—C(41)—C(46)	113.4 (4)
N(2)—C(1)—N(11)	117.9 (4)	C(41)—C(42)—N(48)	118.5 (4)
N(2)—C(3)—N(21)	116.5 (3)	C(43)—C(42)—N(48)	117.0 (4)
N(4)—C(3)—N(21)	116.0 (3)	C(41)—C(42)—C(43)	124.6 (4)
N(4)—C(5)—N(31)	115.7 (4)	C(41)—C(46)—N(54)	121.6 (3)
N(6)—C(5)—N(31)	116.9 (4)	C(45)—C(46)—N(54)	115.8 (4)
C(1)—N(11)—C(15)	126.4 (4)	C(41)—C(46)—C(45)	122.5 (4)
C(3)—N(21)—C(25)	128.7 (4)	C(43)—C(44)—N(51)	119.1 (4)
C(5)—N(31)—C(35)	129.1 (4)	C(45)—C(44)—N(51)	119.2 (4)
O(47)—C(41)—C(42)	118.7 (4)	C(43)—C(44)—C(45)	121.7 (4)
O(47)—C(41)—C(46)	127.9 (4)		

N(2)—C(1)—N(11)—N(12)	2.9 (6)
N(4)—C(3)—N(21)—N(22)	−3.1 (5)
N(4)—C(5)—N(31)—N(32)	4.4 (5)
C(41)—C(42)—N(48)—O(49)	46.7 (6)
C(41)—C(42)—N(48)—O(49)’	−34.7 (14)
C(43)—C(44)—N(51)—O(52)	3.4 (6)
C(41)—C(46)—N(54)—O(56)	2.8 (6)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O(7)—H(71)···N(22$^{\rm i}$)	0.89 (8)	1.86 (8)	2.725 (6)	165 (7)
O(7)—H(72)···N(32$^{\rm i}$)	0.84 (8)	1.93 (8)	2.722 (6)	157 (8)
O(7)—H(73)···O(47)	1.08 (7)	1.31 (6)	2.380 (5)	167 (6)
C(14)—H(14)···O(50)$'^{\rm ii}$	0.91 (5)	2.78 (5)	3.252 (6)	113 (4)
C(34)—H(34)···O(50$^{\rm iii}$)	0.94 (5)	2.75 (5)	3.197 (8)	110 (4)
C(34)—H(34)···O(49$^{\rm iv}$)	0.94 (5)	2.47 (5)	3.268 (8)	143 (4)
C(34)—H(34)···O(49)$'^{\rm iv}$	0.94 (5)	2.81 (6)	3.55 (3)	137 (4)
C(23)—H(23)···O(55$^{\rm v}$)	0.91 (4)	2.74 (5)	3.365 (6)	127 (4)
C(23)—H(23)···O(56$^{\rm vi}$)	0.91 (4)	2.87 (5)	3.419 (6)	120 (4)

Symmetry codes: (i) $x-1, y, z$; (ii) $x-2, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $2-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $2-x, -y, 1-z$; (vi) $1+x, y, z$.

The structure was solved by direct methods (*SIR*92; Altomare *et al.*, 1994). Data processing, refinement and geometrical calculations were carried out on a VAX 6410 computer using the *XRAY*76 program package (Stewart *et al.*, 1976), *PESOS*

(Martìnez-Ripoll & Cano, 1975) and *PARST* (Nardelli, 1983). All H atoms were located in a difference Fourier synthesis. One nitro group of the picrate anion was refined at two sites with 0.77 (1) and 0.23 (1) occupancy factors. The *R* factor probably could not be lowered because of the crystal shape (thin plate), absorption and the disorder of one nitro group.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data, along with details of the weighting scheme, have been deposited with the IUCr (Reference: AB1234). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Unexpected Intermediate in the Synthesis of Substituted Pyridones

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Abstract

The title compound, 8-benzyloxy-8a-methyl-1,2,3,7,8,-8a-hexahydroimidazo[1,2-*a*]pyridin-7-one, (I), is a novel cyclic intermediate in the synthesis of 1-(2-aminoethyl)-3-hydroxy-2-methyl-4(1*H*)-pyridone, (II), a well known Fe^{III} chelator, following a standard route for the synthesis of substituted pyridones. Compound (I) is the major solid intermediate in this reaction and its structural identity has been established conclusively by single-crystal X-ray crystallography. It is a monohydrate in the solid state, $C_{15}H_{18}N_2O_2.H_2O$, and it is obtained upon trituration of the colored oil obtained from the reaction of ethylenediamine with 3-benzyloxy-2-methyl-4-pyrone. Each water molecule bridges two molecules of (I), hydrogen bonding with the carbonyl O atom of one molecule [$O\cdots OW$ 2.796 (4) Å] and with the N atom of the other [$N\cdots OW$ 2.903 (4) Å]. The methyl group at the bridgehead is axially located in a *trans* position with respect to the bulky benzyloxy group. The pyridone ring assumes a slightly distorted half-chair conformation.

Comment

The use of N-substituted 3-hydroxy-2-methyl-4(1*H*)-pyridones as orally active Fe^{III} chelators for possible application in the treatment of iron overload has received considerable attention in recent years (Van der Does, Feng & Bantjes, 1993). Our interest was drawn to the 2-aminoethyl analog, (II), for use as a starting material in the synthesis of substituted pyridones. Compound (II), structurally related to the natural product mimosine, has been reported in numerous papers (Van der Does, Feng & Bantjes, 1992, 1993; Orvig, Nelson, Karpishin & Rettig, 1988; Brady *et al.*, 1989; Kontoghiorghes, 1986). Its synthesis is always performed by adaptations of the maltol route (Orvig, Nelson, Karpishin & Rettig, 1988), wherein maltol is protected as the 3-benzyloxy ether, treated with ethylenediamine to give an uncharacterized intermediate and then deprotected with HCl to yield the desired final product as the dichloride salt. A recent publication (Van der Does, Feng & Bantjes, 1993), applying this chemistry,