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The remarkable stability of the Cl$^-$···(π-system) contacts in 2,3,5-triphenyltetrazolium chloride

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Coordination ability of the title cation to the chloride anion was investigated by XRD analysis of crystal solvates, and DFT calculations were implemented to analyse the nature and binding energy of ion pairs.

Theoretical[1] investigations have revealed that, in addition to conventional H-bonds,[2] anions (such as halides) participate in interactions with the π-system of uncharged[1(a),(d)] or charged[1(b),(c)] molecules. Although the above interactions in a gas phase are energetically favourable, it was shown that their energy falls off sharply upon the increase of medium polarity,[1(a)] thus indicating that anion···(π-system) contacts in crystals are more 'exotic' than a common type of interactions. Indeed, the only experimental evidence for the anion···(π-system) interaction in uncharged aromatic molecules such as tetracyanopyrazine is available.[3]

On the contrary, for formally charged species, such interactions seem more reliable. In particular, an analysis of the Cambridge Structural Database (CSD) has shown that, for NO_3^-, ClO_4^-, BF_4^- and PF_6^- anions, interactions with the π-system in crystals are more frequent for nitrogen-containing heterocycles than for the corresponding aryl systems.[4]

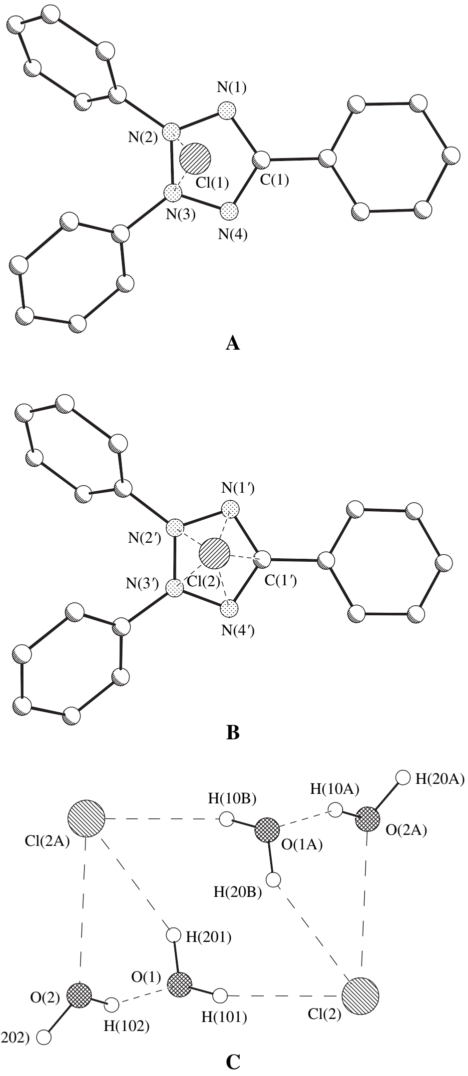

Figure 1 Shortened Cl···N contacts in two independent cation···anion pairs (**A**) and (**B**) and Cl···H_2O bonds (**C**) in the crystal of **1**. The Cl(1)···N(2) 3.303(5) Å, Cl(1)···N(3) 3.213(5) Å, Cl(2)···N(2′) 3.457(4) Å, Cl(2)···N(3′) 3.418(5) Å.

Using analysis of chloride salts within CSD[5] as the starting point to search for the most prominent nitrogen heterocycle with the anion···(π-system) coordination, we found the structural evidence for such interactions in the case of 2,3,5-substituted tetrazolium salts. In particular, in the crystals of bis(2,3-diphenyltetrazolium) dichloride dihydrate, one of the shortest contacts with the π-system [Cl···(ring centroid) is equal to 3.19 Å] was observed.[6]

In order to estimate the stability of Cl···tetrazolium interactions, we performed X-ray diffraction (XRD) and DFT calculation of 2,3,5-triphenyltetrazolium chloride (TTC), which was first synthesised by Pechmann and Runge in 1894,[8] but its crystal structure is still unknown.

Upon the TTC growth we have found that from water (**1**), methanol (**2**) and acetonitrile (**3**) solutions the solvated crystals are formed. According to XRD, all of the crystals of **1**–**3** contain an ion pair and a solvate molecule in a 1:1 ratio.† Note that, in this series, the solvent is characterised by not only different dielectric constants but also principally differs in specific solva-

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† *Crystallographic data for compounds* **1**–**3**.

Crystals of **1**–**3** were prepared upon slow evaporation from solutions. The intensities of reflections for **1** were measured on a Syntex $P2_1$ diffractometer at 220 K [λ(MoKα) = 0.71072 Å, $\theta/2\theta$-scans] for **2**, on a Nonius CAD4 at 298 K [λ(MoKα) = 0.71072 Å, $\theta/2\theta$-scans] and for **3** on a Smart 1000 CCD diffractometer at 120 K [λ(MoKα) = 0.71072 Å, ω-scans] and for **2a**. The structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation.

1 ($C_{19}H_{17}ClN_4O$) at 220 K is triclinic, space group $P\overline{1}$, $a = 9.229(2)$, $b = 12.207(2)$ and $c = 17.008(3)$ Å, $\alpha = 100.79(3)$, $\beta = 98.64(3)$, $\gamma = 103.25(3)°$, $V = 1794.3(6)$ Å^3, $Z = 4$ ($Z' = 2$), $M = 352.82$, $d_{calc} = 1.306$ g cm^{-3}, μ(MoKα) = 2.27 cm^{-1}, $F(000) = 736$, $wR_2 = 0.1514$ and GOF = 1.006 for 6269 independent reflections with $2\theta < 50°$, $R_1 = 0.0651$ for 3618 observed reflections with $I > 2\sigma(I)$.

2 ($C_{21}H_{21}ClN_4O$) at 298 K is orthorhombic, space group $P2_12_12_1$, $a = 10.150(2)$, $b = 12.196(2)$ and $c = 16.318(3)$ Å, $V = 2020.0(7)$ Å^3, $Z = 4$ ($Z' = 1$), $M = 380.87$, $d_{calc} = 1.352$ g cm^{-3}, μ(MoKα) = 2.07 cm^{-1}, $F(000) = 800$, $wR_2 = 0.0808$ and GOF = 1.014 for 4309 independent reflections with $2\theta < 65°$, $R_1 = 0.0425$ for 4545 observed reflections with $I > 2\sigma(I)$.

3 ($C_{21}H_{18}ClN_5$) at 120 K is monoclinic, space group $P2_1/n$, $a = 12.252(2)$, $b = 12.393(2)$ and $c = 12.741(2)$ Å, $\beta = 98.698(5)°$, V = 1912.3(5) Å^3, $Z = 4$ ($Z' = 1$), $M = 375.85$, $d_{calc} = 1.306$ g cm^{-3}, μ(MoKα) = 2.15 cm^{-1}, $F(000) = 784$, $wR_2 = 0.0904$ and GOF = 1.001 for 5566 independent reflections with $2\theta < 60°$, $R_1 = 0.0460$ for 4672 observed reflections with $I > 2\sigma(I)$.

All calculations were performed using SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 289398–289400. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

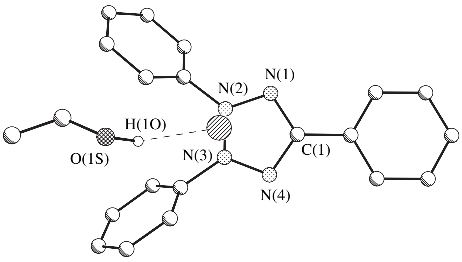

Figure 2 Cation–anion pair in the crystal of **2**.

tion: strong for water and methanol and negligible for acetonitrile. Thus, due to the concurrence of H-bonding between Cl$^-$ and solvate molecule and Cl···(π-system) interactions one can assume that anion···π coordination occurs only in the acetonitrile solvate.

Despite of above differences in solvation mode, the XRD data revealed that in crystals **1**–**3** the chlorine anion is always located above the tetrazolium ring. However, the solvate molecules have a significant influence on the strength and type of the coordination but mainly on the Cl$^-$···(N_4C plane) separation and ring slippage.

In the case of **1**, an asymmetric unit cell contains two independent ion pairs, but only one of which (**A**) forms the shortened N···Cl contacts with anion [Figure 1(**A**)]. In the second ion pair (**B**) anion is also situated above the tetrazolium ring, as well as additionally coordinated by two water molecules *via* strong hydrogen bonds [Cl···O 3.172(3)–3.310(3) Å] [Figure 1(**B**),(**C**)]. This solvation leads to the significant increase of the Cl$^-$ to ring distance from 3.15 to 3.30 Å. However, upon the weakening of the Cl···N interactions the ring slippage decreases from 0.49 to 0.20 Å.

Since methanol can also form strong hydrogen bonds, the crystals of **2** were expected to have similar weak Cl···π interactions. Indeed, owing to the presence of O–H···Cl bonds [3.206(2) Å], the distance from Cl$^-$ to the heterocycle plane is increased up to 3.442(2) Å with the shortest N···Cl contact of 3.472(2) Å. The ring slippage in **2** also attains a maximum value (1.06 Å). Thus, in contrast to **1B**, the increase of the Cl···N distances does not cause the symmetrical disposition of Cl$^-$ anion with respect to the ring (Figure 2).

As expected, the lowest solvation was found in the crystals of **3** with acetonitrile molecule where only a weak Cl(1)···H_3CCN contact with an H···Cl distance of 2.75 Å was observed. Although Cl$^-$ in **3** is poorly coordinated by solvate molecule with no impediments to form a short contact with π-system the Cl···N distances in **3** are slightly longer than those in **1A**. In particular, the distance from Cl$^-$ to N_4C plane is equal to 3.192(2) Å. The reason for the elongation in **3** in respect to **1A** is the presence in the former of additional concurrent Cl···π contact [the distance Cl(1A)···(N_4C plane) is equal to 3.251(2) Å] (Figure 3). Such a type of Cl···tetrazolium interactions in **3** leads to the formation of the infinite Cl···π bonded zig-zag chains along crystallographic axis *b*. The ring slippage for both Cl···π interactions in **3** is approximately equal (0.65 and 0.61 Å) and comparable with **1A**.

In order to estimate the influence of the crystal field on Cl···π contacts in TTC and to analyse the stability of these ion pairs, we performed B3PW91/6-311+G* optimization of TTC in a gas phase without solvate molecules.‡ The geometry of an isolated ion pair is close to the experimentally observed in **1A** and **3** with some decrease of Cl···(N_4C plane) separation (3.076 Å). The latter value is shorter than those found for isolated in Cl$^-$···1,3,5-triazine (3.2 Å)[1(*a*)] complex and comparable with Cl$^-$···s-tetrazine ion pair (2.93 Å).[1(*d*)] The estimated energy of formation for the TTC ion pair with BSSE correction is equal to –85 kcal mol^{-1}, which is close to corresponding values observed for [Be(η^5-C_5H_5)···Cl$^-$] complex (–77 kcal mol^{-1}).[1(*c*)] Such a high value of the formation energy of ion pair is reasonable and results from the separation of charged species [compare values in refs. 1(*a*),(*c*) with 1(*b*),(*d*)] and thus only partly gives information on charge transfer and energy of contacts in the TTC ion pair.

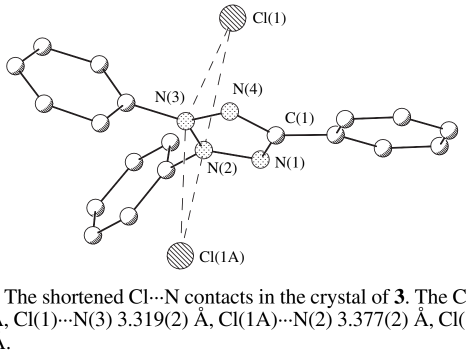

Figure 3 The shortened Cl···N contacts in the crystal of **3**. The Cl(1)···N(2) 3.236(2) Å, Cl(1)···N(3) 3.319(2) Å, Cl(1A)···N(2) 3.377(2) Å, Cl(1A)···N(3) 3.303(2) Å.

The principal difference of the TTC ion pair in respect to triazine and s-tetrazine complexes[1(*a*),(*d*)] is asymmetrical coordination of Cl$^-$ with tetrazolium (ring slippage in the isolated state is 0.60 Å). Both in a crystal and in an isolated ion pair, Cl$^-$ is shifted towards the N(2)–N(3) bond with Cl(1)···N(2) and Cl(1)···N(3) contacts equal to 3.225 and 3.126 Å, respectively.

Clearly, such an asymmetry of Cl$^-$ coordination for isolated TTC is surprising taking into account that N(2) and N(3) atoms are formally equivalent. In order to analyse the reason of such a coordination in TTC, we performed topological analysis of the electron density distribution function $\rho(r)$[9] obtained within B3PW91/6-311+G** calculation. The critical point (CP) search in the vicinity of the Cl$^-$ atom has revealed the presence of the CP (3,–1) of $\rho(r)$ only for the Cl···N(3) contact and for two shortened Cl···H interactions with distances equal to 2.41 and 2.51 Å) (Figure 4). Thus, according to the topological analysis of $\rho(r)$ the Cl(1) in spite of shortened Cl(1)···N distances in the isolated ion pair and apparently in the **1A** and **3** solvates are characterised by the η^1-type of interactions.

All the above contacts involving the chloride anion are characterised by low values of $\rho(r)$ (0.103–0.121 and 0.086 eÅ^{-3} for Cl···H and Cl···N) and positive values of $\nabla^2\rho(r)$ in the CP (3,–1) and thus correspond to the closed-shell type of interactions.[9] The estimation of the Cl···H and Cl···N contact energy in the TTC ion pair using Lecomte's correlation scheme[10] has revealed that the energy of Cl···H interactions (2.63–2.64 kcal mol^{-1}) slightly exceeds the energy of Cl···N one (2.45 kcal mol^{-1}). Thus, the total energy of the Cl···tetrazolium interaction in TTC is approximately equal to –7.7 kcal mol^{-1}, which is close to the energy of the Cl···1,3,5-triazine complex (6.2 kcal mol^{-1})[1(*a*)] obtained within the CBS-Q method.

Thus, the XRD investigations of the solvates and quantum chemical calculations of isolated 2,3,5-triphenyltetrazolium chloride clearly show that the remarkable stability of Cl···(π-system)

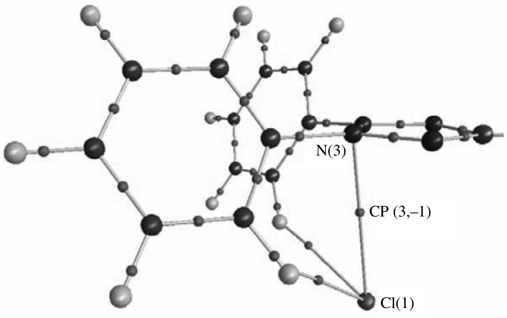

Figure 4 Molecular graph of TTC ion pair according to B3PW91/6-311+G** calculation. The critical points (3,+1), as well as the one of the phenyl rings, are omitted for clarity.

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‡ The *ab initio* calculations of **1** were performed with the Gaussian 98 program package[11] at the B3PW91/6-311+G** level of theory. As convergence criteria, the normal threshold limits of 2×10^{-6} and 6×10^{-6} were applied for the maximum force and displacement, respectively. To enhance the B3LYP calculation accuracy, the pruned (99590) grid was used. Topological analysis of the $\rho(r)$ function was performed using the MORPHY 98 program,[12] basing on the wave functions obtained from the B3LYP calculations.

contacts is the consequence of both a heterocyclic nature of the cation and the presence of phenyl rings, which serve as a pincer, which holds the chlorine anion by means of the Cl···H interactions in the vicinity of the π-system.

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