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# The C–H...$[FBF_3]^-$ Hydrogen Bonds as Origin of the Linear Polytetrameric Self-Organisation of Schiff Base Containing Substituted 1,2,4-Triazole

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The first crystal structure involving Schiff base containing 4-substituted 1,2,4-triazolium cation is reported. The neutral (4-chloro-benzylidene)-[1,2,4] triazol-4-yl-amine (**T**) and protonated (**HT**$^+$) molecules are connected by the strong $[N–H...N]^+$ hydrogen bond forming the discrete dimers. The pair of the dimers and two $BF_4^-$ ions are linked *via* the weak C–H...F interactions and create tetrameric units. $BF_4^-$ ions mediate between succeeding tetramers and as a result double ribbons along [110] are formed. No intermolecular, directional interactions between neighbour ribbons in the crystal were found.

**Key words**: crystal structure, 4-substituted-1,2,4-triazoles, hydrogen bonds

4-Amino-1,2,4-triazole (amtrz) reacts with substituted benzaldehydes to afford a wide family of Schiff-base containing triazoles [1,2]. These compounds were successfully tested for herbicidal activity [3] and some of them are anti-inflammatory agents [4]. The great ability to condensation of amine group of amtrz and aldehydes has been recently used in preparation of chiral synthons [5] and macrocyclic ligands [6]. On the other hand, the 4-substituted-1,2,4-triazole (4-R-trz) coordinate the transition metal ions as bridging ligand and makes the triazoles interesting synthetic targets [7]. It is well known that the magnetic properties of resulting polynuclear transition metal(II) ion complexes highly depend on the chemical character and steric effects of the R substituent [8]. One of the most convenient methods to change the 4-R substituent is the reaction mentioned above. Although the compounds are known for about thirty years only two of them – 9-(4*H*-1,2,4-triazol-4-ylimino)-4,5-diazafluorene [9] and (4-(4-hydroxybenzylidene-amino)-4*H*-1,2,4-triazole hemihydrate [10] – have been characterized structurally by single crystal X-ray study.

Molecules of 4-R-trz, similarly to other 1,2,4-triazoles, can exist in both, the neutral and protonated [11] forms. Surprisingly, a search of the Cambridge Structural Database [12] (release October 2000) failed to reveal any crystal structure containing 4-substituted 1,2,4-triazolium (**HT**$^+$) species.

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This paper deals with synthesis, spectroscopic and single crystal X-ray studies of Schiff bases derived from amtrz and 4-chlorobenzaldehyde. The molecules in protonated and neutral forms co-exist in crystals of title compound.

## EXPERIMENTAL

Commercially available solvents, monohydrate hydrazine, formic acid, and 4-chlorobenzaldehyde were used without further purification. Amtrz was prepared according to literature method [13]. Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. $^1$H NMR spectra were recorded on a Bruker Aspect AM300 spectrometer in $CD_3CN$. ESI MS were performed on a mass spectrometer Finnigan Mat type TSQ700.

*Synthesis of (4-chloro-benzylidene)-[1,2,4] triazol-4-yl-amine (**T**).* To a warm ethanolic solution (25 mL) of 4-amino-1,2,4-triazole (1.69 g, 20 mM) was added an ethanolic solution (30 mL) of 4-chlorobenzaldehyde (2.81 g, 20 mM) and resulting solution was refluxed four hours, then the reaction mixture was cooled to room temperature. Upon standing overnight white crystals separated, which could be isolated by filtration, washed with a small amount of ethanol and diethyl ether and dried under vacuum. For **T**: yield: 65%. M.p.: 190°C (subl.). MS (*m/e*) 207.0. Anal. Calcd for $C_9H_7N_4Cl$: C, 52.31; H, 3.41; N, 27.11. Cl, 17.16. Found: C, 52.40; H, 3.64; N, 26.83; Cl, 17.17. $^1$H NMR ($CD_3CN$, RT; [ppm] (multiplicity, assignment)): 8.77 (s, C-H$_{im}$), 8.69 (s, 2C-H$_{tr}$), 7.84–7.54 (4H, m, *o-,m*-Ph).

*Single crystals of $C_9H_7N_4Cl\cdot C_9H_8N_4Cl^+\cdot BF_4^-$ ($\mathbf{T\cdot HT^+\cdot BF_4^-}$)* were obtained by slow evaporation of ethanolic solution of **T** with few drops of $HBF_4$ at RT. Anal. Calcd for $C_{18}H_{15}N_8Cl_2BF_4$: C, 43.14; H, 3.02; N, 22.36; Cl, 14.15. Found: C, 43.0; H, 3.04; N, 22.43; Cl, 14.17.

*Crystallographic studies*. Crystal data for $C_9H_7N_4Cl\cdot C_9H_8N_4Cl^+\cdot BF_4^-$ are given in Table 1 together with refinement details. The measurement of crystal was performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated MoKα radiation. Crystal was positioned at 65 mm from the KM4CCD camera. 612 frames were measured at 0.75° intervals with a counting time of 20 sec. The data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with Kuma Diffraction (Wrocław) programs. The structure was solved by direct method (program SHELXS97 [14]) and refined by the full-matrix least-squares method on all $F^2$ data using the SHELXL97 [15] program. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from geometry of molecules or $\Delta\rho$ maps and were refined with isotropic thermal parameters. The high values of the displacement parameters for the fluorine atoms suggested disordered positions for the tetrafluoroborate entity. In the next $\Delta\rho$ map the highest three maxima (0.3–0.4 e/Å$^3$) located near the boron atom confirmed the suggestion. The final refinement of the structure including co-ordinates and isotropic displacement parameters of three additional fluorine atoms showed two orientations of the tetrafluoroborate ion with occupancy factors 0.95 and 0.05, respectively.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 164730. Copies of this information may be obtained free of charge from the Director, CCDC, 12 UNION Road, Cambridge 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

**Table 1.** Crystal data and structure refinement.

| | |
|---|---|
| Empirical formula | $C_{18}H_{15}N_8Cl_2BF_4$ |
| Formula weight | 501.09 |
| T/K | 170(2) |
| λ/Å | 0.71073 |
| Crystal system | Triclinic |

Table 1 (continuation)

| | |
|---|---|
| Space group | $P\bar{1}$ |
| $a$/Å | 8.064(2) |
| $b$/Å | 10.057(2) |
| $c$/Å | 14.005(3) |
| $\alpha$/° | 95.50(3) |
| $\beta$/° | 97.74(3) |
| $\gamma$/° | 106.66(3) |
| $V$/Å$^3$ | 1067.3(4) |
| $Z$ | 2 |
| $D_c$/Mg·m$^{-3}$ | 1.559 |
| $\mu$/mm$^{-1}$ | 0.364 |
| $F$(000) | 508 |
| Crystal size/mm | 0.30 × 0.30 × 0.20 |
| Diffractometer | Kuma KM4CCD |
| $\theta$ range for data collection/° | 2.83–25.00 |
| Index ranges | $h$:–8→9, $k$: –11→11, l: –16→11 |
| Reflections collected | 6268 |
| Independent reflections | 3664 |
| Data/parameters | 3664/372 |
| Goodness-of-fit ($F^2$) | 1.109 |
| Final $R_1$/w$R_2$ indices ($I > 2\sigma_I$) | 0.0453/0.1058 |
| Largest diff. peak/hole /e·Å$^{-3}$ | 0.181/–0.219 |

## RESULTS AND DISCUSSION

The numbering scheme and overall conformation of the title compound is shown in Fig. 1. Tables 2 and 3 list selected bond lengths, valence and torsion angles, and geometry of the hydrogen bonds.

The studied crystal is composed of two forms (**T** and **HT**$^+$) of (4-chlorobenzylidene)-[1,2,4] triazol-4-yl-amine and the tetrafluoroborate ion. The first form is neutral and the second one is protonated. Both molecules, **T** and **HT**$^+$ are essentially planar. The hydrogen atom in the **HT**$^+$ is bonded to the N(1′) atom. Some geometric differences are observed between the protonated and neutral form of studied compound. In the protonated form the N(1′)–N(2′) and N(3′)–C(8′) bonds are shorter than N(1)–N(2) and N(3)–C(8) bonds of about 6 and 9$\sigma$, respectively. Simultaneously the N(3′)–C(9′) and N(3′)–N(4′) distances are longer than N(3)–C(9) and N(3)–N(4) in the neutral form of about 6 and 5$\sigma$, respectively. Apparently, concomitant changes are observed for endocyclic valency angles. Protonation increases the endocyclic

N(2′)–N(1′)–C(8′) angle, whereas the adjacent angles at N(2′) and C(8′) undergo opposite variations keeping the ring planar. The geometrical differences presented above show that the neutral 4-substituted triazole ring is more symmetric than that in the protonated form. Although the protonation changes the electron distribution within the ring, it is worthwhile to notice, that only lengths of single bonds are influenced in triazole residue. Similar phenomena were observed for 1-methylimidazole/1-methylimidazolium cation [16].

**Table 2.** Bond lengths (Å), valence, and torsion angles (°).

| | | | |
|---|---|---|---|
| Cl(1)–C(5) | 1.733(2) | Cl(2)–C(5′) | 1.727(2) |
| N(1)–C(8) | 1.292(3) | N(1′)–C(8′) | 1.299(3) |
| N(1)–N(2) | 1.377(3) | N(1′)–N(2′) | 1.360(3) |
| N(2)–C(9) | 1.299(3) | N(2′)–C(9′) | 1.291(3) |
| N(3)–C(8) | 1.351(3) | N(3′)–C(8′) | 1.324(3) |
| N(3)–C(9) | 1.347(3) | N(3′)–C(9′) | 1.365(3) |
| N(3)–N(4) | 1.395(2) | N(3′)–N(4′) | 1.405(2) |
| N(4)–C(1) | 1.257(3) | N(4′)–C(1′) | 1.252(3) |
| C(1)–C(2) | 1.457(3) | C(1′)–C(2′) | 1.456(3) |
| C(2)–C(3) | 1.383(3) | C(2′)–C(3′) | 1.389(3) |
| C(2)–C(7) | 1.391(3) | C(2′)–C(7′) | 1.388(3) |
| C(3)–C(4) | 1.375(3) | C(3′)–C(4′) | 1.377(3) |
| C(4)–C(5) | 1.375(3) | C(4′)–C(5′) | 1.380(3) |
| C(5)–C(6) | 1.379(3) | C(5′)–C(6′) | 1.368(3) |
| C(6)–C(7) | 1.373(3) | C(6′)–C(7′) | 1.374(3) |
| F(1)–B(1) | 1.383(4) | | |
| F(2)–B(1) | 1.353(4) | | |
| F(3)–B(1) | 1.366(3) | | |
| F(4)–B(1) | 1.374(3) | | |
| C(8)–N(1)–N(2) | 106.03(18) | C(8′)–N(1′)–N(2′) | 111.0(2) |
| C(9)–N(2)–N(1) | 108.14(19) | C(9′)–N(2′)–N(1′) | 104.4(2) |
| C(9)–N(3)–C(8) | 104.80(19) | C(8′)–N(3′)–C(9′) | 105.9(2) |
| C(9)–N(3)–N(4) | 133.02(18) | C(8′)–N(3′)–N(4′) | 120.34(19) |
| C(8)–N(3)–N(4) | 122.03(18) | C(9′)–N(3′)–N(4′) | 133.69(19) |
| C(1)–N(4)–N(3) | 116.48(18) | C(1′)–N(4′)–N(3′) | 116.31(19) |
| N(4)–C(1)–C(2) | 121.1(2) | N(4′)–C(1′)–C(2′) | 121.0(2) |
| C(3)–C(2)–C(7) | 118.7(2) | C(7′)–C(2′)–C(3′) | 118.7(2) |
| C(3)–C(2)–C(1) | 119.08(19) | C(7′)–C(2′)–C(1′) | 118.7(2) |

Table 2 (continuation)

| | | | |
|---|---|---|---|
| C(7)–C(2)–C(1) | 122.2(2) | C(3′)–C(2′)–C(1′) | 122.6(2) |
| C(4)–C(3)–C(2) | 121.3(2) | C(4′)–C(3′)–C(2′) | 120.5(2) |
| C(5)–C(4)–C(3) | 118.8(2) | C(3′)–C(4′)–C(5′) | 119.6(2) |
| C(4)–C(5)–C(6) | 121.3(2) | C(6′)–C(5′)–C(4′) | 120.7(2) |
| C(4)–C(5)–Cl(1) | 119.29(18) | C(6′)–C(5′)–Cl(2) | 119.02(18) |
| C(6)–C(5)–C(1) | 119.44(17) | C(4′)–C(5′)–Cl(2) | 120.24(18) |
| C(7)–C(6)–C(5) | 119.4(2) | C(5′)–C(6′)–C(7′) | 119.7(2) |
| C(6)–C(7)–C(2) | 120.5(2) | C(6′)–C(7′)–C(2′) | 120.8(2) |
| N(1)–C(8)–C(3) | 111.3(2) | N(1′)–C(8′)–N(3′) | 107.6(2) |
| N(2)–C(9)–N(3) | 109.7(2) | N(2′)–C(9′)–N(3′) | 111.0(2) |
| F(2)–B(1)–F(3) | 110.4(3) | | |
| F(2)–B(1)–F(4) | 110.3(3) | | |
| F(3)–B(1)–F(4) | 109.2(2) | | |
| F(2)–B(1)–F(1) | 108.3(2) | | |
| F(3)–B(1)–F(1) | 108.4(3) | | |
| F(4)–B(1)–F(1) | 110.2(2) | | |
| C(9)–N(3)–N(4)–C(1) | –16.2(3) | | |
| N(3)–N(4)–C(1)–C(2) | 178.98(18) | | |
| N(4)–C(1)–C(2)–C(7) | 5.9(3) | | |
| C(9′)–N(3′)–N(4′)–C(1′) | 5.5(4) | | |
| N(3′)–N(4′)–C(1′)–C(2′) | 177.69(19) | | |
| N(4′)–C(1′)–C(2′)–C(7′) | 178.5(2) | | |

The protonated and neutral molecules are connected *via* the linear N–H...N hydrogen bond (Table 3) forming discrete dimers (**T...HT**$^+$), where two proton bridged molecules are oriented head-to-head. The N...N and H...N distances [2.689(3) and 1.71(3) Å, respectively] are typical for strong [N–H...N]$^+$ hydrogen bonds [17–19]. The pair of the dimers and two BF$_4^-$ ions are linked through the weak C–H...F hydrogen bonds. These molecules create discrete, centrosymmetric, cyclic tetrameric units in the studied crystals. Three fluorine atoms from each tetrafluoroborate ion are involved in formation of six hydrogen bonds with both **T** and **HT**$^+$ triazole moieties inside the tetramer (Fig. 2). This is well known, that participation of BF$_4^-$ ions in the hydrogen bond systems is a main reason of some geometrical deformations (especially bond lengths) of these ions. This is also observed in the system under investigation. The shortest B–F bond [1.353(4) Å] is that to the F(2) atom, which is not involved in hydrogen bond and is directed outside of the tetramer. The lengths of other B–F bonds to the fluorine atoms are very similar. Such geometry of the BF$_4^-$ ion suggests that the most charged atoms are placed inside the tetrameric unit.

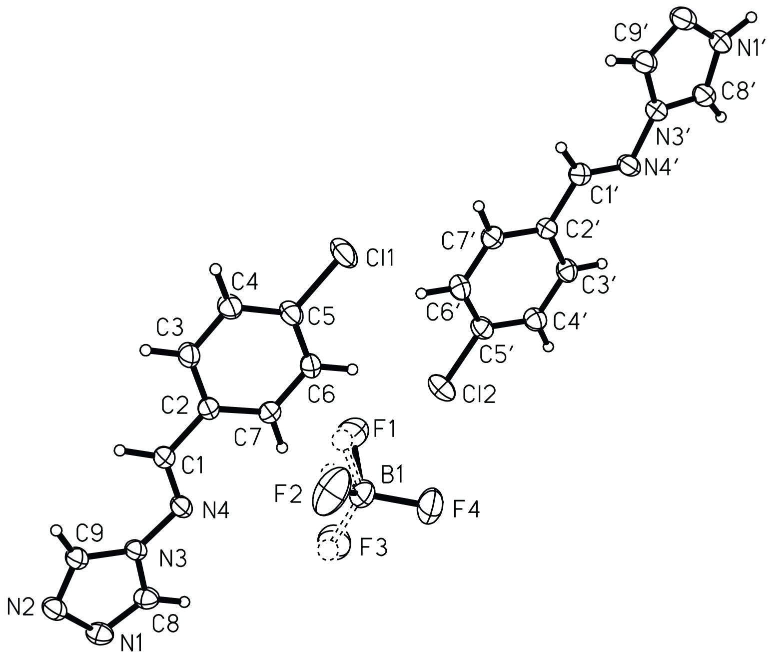

**Figure 1.** The structure of **T·HT$^{+}$BF$_4^{-}$** showing 30% probability displacement ellipsoids with the numbering scheme. The broken lines present a minor component of disordered BF$_4^{-}$ ion.

**Table 3.** Lengths (Å) and angles ($^{o}$) of the hydrogen bonds.

| D–H...A | D–H | H...A | D...A | ∠ D–H...A |
|---|---|---|---|---|
| N(1′)–H(1N)...N(2$^{\text{i}}$) | 0.98(3) | 1.71(3) | 2.689(3) | 175(3) |
| C(1)–H(1)...F(1$^{\text{ii}}$) | 0.99(3) | 2.34(3) | 3.329(3) | 178(2) |
| C(3)–H(3)...F(3$^{\text{iii}}$) | 0.94(3) | 2.53(3) | 3.418(3) | 159(2) |
| C(9)–H(9)...F(1$^{\text{ii}}$) | 0.90(2) | 2.38(2) | 3.222(3) | 157(2) |
| C(1′)–H(1′)...F(4$^{\text{iv}}$) | 0.91(3) | 2.35(3) | 3.254(3) | 173(2) |
| C(7′)–H(7′)...F(3$^{\text{iv}}$) | 0.95(3) | 2.50(3) | 3.320(3) | 145(2) |
| C(9′)–H(9′)...F(4$^{\text{iv}}$) | 0.93(3) | 2.44(3) | 3.318(3) | 156(2) |
| C(3′)–H(3′)...F(1$^{\text{v}}$) | 0.96(2) | 2.55(3) | 3.457(3) | 159(2) |
| C(8′)–H(8′)...F(3$^{\text{v}}$) | 0.92(3) | 2.54(3) | 3.194(4) | 129(2) |
| C(4)–H(4)...N(1$^{\text{vi}}$) | 0.94(3) | 2.47(3) | 3.398(3) | 174(2) |

Symmetry transformations used to generate equivalent atoms: (none) x, y, z; (i) x – 1, y – 2, z – 1; (ii) 1 – x, 1 – y,1 – z; (iii) 1 – x, 1 – y, 1 – z; (iv) x, –1 + y, z; (v) 1 – x, –y, –z; (vi) –1 + x, –1 + y, z.

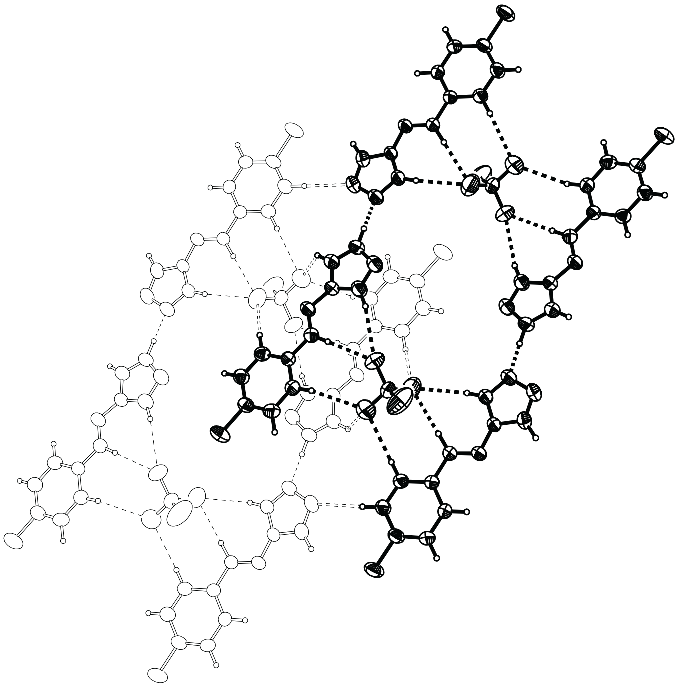

**Figure 2.** View of two succeeding tetrameric units along the [100] direction. The hydrogen bonds are depicted by broken lines.

The tetramer units are shifted along the [110] direction forming additional four C–H...F and two C–H...N weak hydrogen bonds. The **HT**$^+$ molecules of succeeding tetramers overlap in the head-to-tail mode. Each of the overlapped triazolium cation arranges two C–H...F bonds. These interactions are additionally stabilized by $\pi$-$\pi$ interactions between aromatic and triazolium rings. The perpendicular distance between them is 3.38 Å and the offset between centres of these rings is 0.76 Å. As a result of the interactions mentioned above a double linear ribbon is formed. All intermolecular interactions observed in the crystal are involved in formation of the ribbons. There are neither hydrogen bonds nor other directional interactions between parallel ribbons.

## CONCLUSIONS

The 4-substituted triazoles form the hydrogen bonded triazole-triazolium dimers. Two pairs of the dimers and two $BF_4^-$ anions arrange discrete tetrameric unit. These basal units produce linear ribbons along the [110] direction. This self-organization of the crystal is a result of expanded net of intermolecular hydrogen bonds. Most of them (80%) are realized with contribution of the C–H donors and fluorine atoms from the $BF_4^-$ ions as acceptors. These rather weak interactions are driving force of poly-tetrameric self-organization in studied crystals.

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