CRYSTAL STRUCTURE AND QUANTUM CHEMICAL INVESTIGATION OF 4-(3,4-DICHLORPHENYL)-1,2,4-TRIAZOLE

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1,2,4-Triazole derivative substituted in the 4th position — 4-(3,4-dichlorphenyl)-1,2,4-tirazole — has been synthesized. Crystal and molecular structure of the compound were determined by single crystal X-ray diffraction. Molecular geometry optimization and effective charge calculations were performed by DFT methods.

Keywords: 1,2,4-triazole, synthesis, crystal structure, quantum chemical calculations.

1,2,4-Triazole derivatives are applied as medicinal and photosensitive materials, as well as agents influencing plant growth and development. Polynitrogen heterocycles, 1,2,4-triazole derivatives in particular, are potential ligands for the preparation of magnetically active coordination compounds. 4-substituted 1,2,4-triazole derivatives are of special interest. The absence of substituents at the N(1) and N(2) positions in the heterocycle provides bidentate — bridging coordination making it possible to synthesize oligo- and polynuclear coordination compounds. Co(II), Ni(II) and Cu(II) complexes of these types manifest ferro- and antiferromagnetic interactions between the paramagnetic centers [1-5]. Thermally induced spin crossover ${}^{1}A_{1} \Leftrightarrow {}^{5}T_{2}$ [6-8] is observed in a number of Fe(II) complexes with these ligands, which is accompanied by the thermochromism (color change pink \Leftrightarrow white). This contribution presents the synthesis and crystal structure of 4-(3,4diclorphenyl)-1,2,4-triazole (Clphtrz) — a potential ligand for the preparation of complexes possessing the above features.

Experimental. Synthesis of Clphtrz. 9.8 g (0.06 mole) of 3,4-dichloraniline and 5.3 g (0.06 mole) of diformylhydrazine were placed in a round-bottom flask equipped with reflux, heated to 195°C and kept at this temperature for 40 min. Then the flask was cooled to 80°C, and 20 ml of ethanol was added. The reaction mixture was transferred to a beaker and cooled in a refrigerator after the addition of 100 ml of dry ether. The precipitate formed was filtered off (3.5 g). Additional 2.7 g of the product were obtained by ether precipitation from ethanol. The total yield of Clphtrz was 6.2 g or 50%.

Found, %: C 44.6; H 2.4; Cl 32.8; N 20.0. Calculated for C₈H₅Cl₂N₃, %: C 44.6; H 2.3; Cl 33.2; N 19.6.

IR spectrum (cm⁻¹): 1500, 1560, 1600 (aromatic ring valence vibrations); 1685 (C=N); 1130 (C-N); 630, 670, 790 (C-Cl); 3100 (C-H).

NMR ¹H, ppm: 9.18 (s, 2H, H–3.5); 8.14 (d, 1H, H–2_{Ph}, ⁴*J* = 2.5 Hz); 7.83 (d, 1H, H–5_{Ph}, ³*J* = 8.8 Hz); 7.76 (dd, 1H, H–6_{Ph}, ³*J* = 8.8 Hz, ⁴*J* = 2.5 Hz).

NMR ¹³C, ppm: 141.32 (C–3.5); 133.80 (C–1_{Ph}); 132.44 (C–Cl); 131.76 (C–5_{Ph}); 130.39 (C–Cl); 123.11 (C–2_{Ph}); 121.28 (C–6_{Ph}).

Single crystals of Clphtrz suitable for X-ray diffraction study were obtained by the slow crystallization from ethanol solutions.

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Research techniques. IR spectrum of Clphtrz was recorded in KBr pellets with a Specord 75 IR spectrophotometer. ¹H and ¹³C NMR spectra were obtained using a Bruker DPX-400 spectrometer (400.13 MHz ¹H; 100.61 MHz ¹³C) in DMSO-*d*₆.

Structural investigation. A colorless needle-like single crystal of $0.62 \times 0.16 \times 0.14$ mm size was mounted on a automated four-circle diffractometer Enraf Nonius CAD-4 for the unit cell measurement and intensity data collection (Mo K_a , graphite monochromator, room temperature, standard technique). The crystal is monoclinic, the space group $P2_1/c$; a = 7.235(3) Å, b = 14.139(9) Å, c = 8.986(5) Å; $\beta = 102.65(4)^\circ$, V = 896.9(8) Å³, Z = 4, $\rho_{calc} = 1.585$ g/cm³ for the composition C₈H₅Cl₂N₃, $\mu = 0.673$ mm⁻¹. Adsorption correction appeared to be negligible and was not considered. A total of 2592 reflections were measured within $2\theta = 50^\circ$. The structure was solved by the direct method and refined anisotropically for non-hydrogen atoms in the full-matrix approximation using SHELX-97 program [9]. Hydrogen atoms were set into idealized positions. The final agreement factors were: $R_1 = 0.0692$, $wR_2 = 0.1602$ for 850 $F_{hkl} \ge 4\sigma(F)$, $R_1 = 0.1179$, $wR_2 = 0.1918$, GOOF = 0.853 for all 1570 independent reflections. Atomic coordinates are reported in Table 1, bond lengths and selected valence angles — in Table 2.

Quantum chemical study. The quantum chemical calculations were made with GAUSSIAN-98 package [10] using the exchange-correlation functionals B3LYP and B3PW91. 6-311+G(2d, p) wave function set [10] was used as the basis. Charge calculations on the atoms were performed according to Mulliken [11], Merz–Kollman–Singh [12,13] and Breneman [14] schemes after complete molecular geometry optimization done.

Discussion. The structure of Clphtrz molecule is shown in Fig. 1. Both cycles of the molecule are planar and inclined to each other at the angle of $45.5(2)^{\circ}$ that is apparently caused by sterical reasons. Bond lengths and angles have usual values. The interatomic distances in the triazole fragment suggest the presence of two double bonds N1–C1 and N2–C2.

The molecular packing is shown in Fig. 2. Non-valence contacts N...H(C) of 2.46 Å and 2.59 Å length are found in the crystal, which are likely to indicate the presence of weak hydrogen bonds.

Calculated bond lengths and angles are reported in Table 2. In general, they are in a good agreement with the experimental structural data. Minor mismatches can be due to the functional choice and packing effects.

Atomic charges are given in Table 3. It is seen that the charges calculated by the methods [12-14] match well mutually, but differ significantly from that calculated according to the scheme [11]. Thus, atoms N(1) and N(2) gain the largest and virtually equal negative charges favoring the bidentate bridging coordination of Clphtrz to metal atoms in the complex

Atom	x	У	Z	$U_{ m eq}*$
Cl1	6036(2)	-571(1)	-8151(2)	67(1)
C12	5361(3)	1612(1)	-7703(2)	74(1)
C1	9987(9)	2011(3)	-1868(6)	57(2)
C2	8816(9)	914(4)	-756(6)	56(1)
C3	8112(8)	798(3)	-3599(5)	45(1)
C4	8298(8)	-174(3)	-3758(5)	49(1)
C5	7627(8)	-585(3)	-5154(6)	48(1)
C6	6771(8)	-46(4)	-6385(5)	49(1)
C7	6543(8)	926(3)	-6204(6)	51(1)
C8	7230(8)	1340(3)	-4798(6)	49(1)
N1	10532(8)	2164(3)	-429(5)	61(1)
N2	9745(8)	1448(3)	299(5)	64(1)
N3	8881(6)	1226(3)	-2161(4)	46(1)

TABLE 1. Non-Hydrogen Atom Coordinates (×10⁴) and Equivalent Thermal Parameters (Å²×10³) in the Clphtrz Structure

 U_{eq} is set to one third of the normalized U_{ij} tensor trace.

	Length, Å				Length, Å		
Bond	Experiment	Optim	ization	Bond	Experiment	Optimization	
		B3LYP	B3PW91			B3LYP	B3PW91
N(1)–N(2)	1.393(6)	1.384	1.375	C(3)–N(3)	1.424(6)	1.419	1.414
C(1)–N(1)	1.285(7)	1.302	1.301	C(4)–C(5)	1.371(7)	1.386	1.384
C(1)–N(3)	1.361(6)	1.374	1.369	C(5)–C(6)	1.374(7)	1.391	1.389
C(2)–N(2)	1.281(7)	1.302	1.301	C(6)–C(7)	1.399(7)	1.395	1.394
C(2)–N(3)	1.348(6)	1.373	1.369	C(7)–C(8)	1.382(7)	1.390	1.388
C(3)–C(4)	1.391(7)	1.393	1.391	Cl(1)–C(6)	1.727(5)	1.741	1.728
C(3)–C(8)	1.362(7)	1.391	1.388	Cl(2)–C(7)	1.726(5)	1.741	1.728
	AngleExperimentOptimization			Value			
Angle			ization	Angle	Experiment	Optimization	
		B3LYP	B3PW91			B3LYP	B3PW91
C(1)–N(1)–N(2)	106.5(4)	107.3	107.4	N(1)-C(1)-N(3)	111.7(4)	110.9	110.7
C(2)–N(2)–N(1)	106.4(4)	107.3	107.4	N(2)-C(2)-N(3)	112.3(5)	110.9	110.8
C(1)-N(3)-C(3)	128.2(4)	128.2	128.2	C(4)–C(3)–N(3)	119.0(5)	120.2	120.2
C(2)–N(3)–C(1)	103.0(4)	103.6	103.7	C(8)–C(3)–C(4)	120.9(5)	120.1	120.1
C(2)–N(3)–C(3)	128.6(4)	128.1	128.1	C(8)-C(3)-N(3)	120.1(4)	119.7	119.6

TABLE 2. Experimental and Calculated Bond Lengths, Å, and Selected Valence Angles, deg, in the Structure of Clphtrz



Fig. 1. Structure of Clphtrz molecule; ellipsoids of 50% probability.

compounds. Chlorine atom charges are small in absolute value that, taking also into account the charges on the neighboring atoms C(6) and C(7), enables one to postulate a comparatively small polarity of Cl–C bonds. Atoms C(4), C(5) and C(8) bear a minor negative charge. Allowing for the fact that the charges on hydrogen atoms equal approximately 0.1 (for all calculation techniques), this promotes the formation of weak intermolecular hydrogen bonds with N(1) and N(2) atoms of neighboring Clphtrz molecules.

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Fig. 2. Crystal molecular packing as viewed along the a axis. Contacts N...H of 2.46 Å and 2.59 Å lengths are shown as dashed lines.

Atom	Scheme [11]		Scheme [12, 13]		Scheme [14]	
	B3LYP	B3PW91	B3LYP	B3PW91	B3LYP	B3PW91
N(1)	-0.195	-0.194	-0.323	-0.315	-0.343	-0.335
N(2)	-0.193	-0.191	-0.327	-0.319	-0.341	-0.331
C(1)	0.027	-0.009	0.138	0.121	0.278	0.254
C(2)	0.019	-0.019	0.152	0.133	0.270	0.243
N(3)	0.083	0.215	0.212	0.198	-0.039	-0.026
C(3)	-0.423	-0.663	-0.191	-0.152	0.049	0.049
C(4)	-0.045	-0.020	-0.038	-0.073	-0.116	-0.128
C(5)	-0.970	-1.062	-0.121	-0.111	-0.083	-0.090
C(6)	0.923	0.967	0.052	0.035	0.087	0.080
C(7)	0.476	0.411	0.046	0.043	0.080	0.070
C(8)	-0.536	-0.482	-0.008	-0.035	-0.094	-0.103
Cl(1)	0.094	0.156	-0.066	-0.056	-0.094	-0.085
Cl(2)	0.102	0.165	-0.064	-0.054	-0.084	-0.074

TABLE 3. Effective Atomic Charges for the Optimized Molecular Geometry of Clphtrz

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