*ISSN 0022-4766, Journal of Structural Chemistry, 2021, Vol. 62, No. 10, pp. 1522-1530. © Pleiades Publishing, Ltd., 2021.*
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# CRYSTAL STRUCTURE OF 3-*tert*-BUTYL-PYRAZOLO[5,1-*c*][1,2,4]TRIAZINE-3,4-DIYL DICARBOXYLATES

**L.M. Mironovich[1†*], S.M. Ivanov[2], and D.S. Koltun[2]**

By single crystal X-ray diffraction the structures of (*trans*-)7-$R^1$-8-methyl-3-*tert*-butyl-3,4-dihydropyrazolo[5,1-*c*][1,2,4]triazine-3,4-diyl dibenzoates **3a, 4a** ($R^1$ = H, Br) and diacetate **3b** ($R^1$ = H) are studied for the first time. The compounds are synthesized by oxidative bromination of respective 1,4-dihydropyrazolo[5,1-*c*][1,2,4]triazines in the presence of carboxylic acids. Dicarboxylates adopt a *twist*-conformation with the equatorial (**3a**) or axial (**3b, 4a**) orientation of *tert*-butyl groups relative to the heterocycle. In the case of diacetate **3b**, a decrease in the thermal motion of the O4–C16–C17 fragment along with a decrease in the unit cell volume are observed on cooling from 300 K to 200 K. Bond lengths, torsion angles, and molecular packings in the crystals are discussed.

**DOI:** 10.1134/S0022476621100061

**Keywords:** 1,2,4-triazines, pyrazolo[5,1-*c*][1,2,4]triazines, chirality, X-ray crystallographic analysis.

## INTRODUCTION

Qualitative and quantitative structural characteristics of heterocyclic compounds are significant in studying reaction mechanisms as well as in the synthesis of novel biologically active materials [1-4]. It is well known that the majority of saturated six-membered heterocycles adopt the *chair* conformation whereas the structure of aromatic derivatives is almost planar [5-9]. Deviations from the planarity may arise due to a set of various steric and electronic factors [10].

Conformational features of polycyclic triazines largely depend on the nature of the annelated cycle. Azolo[1,2,4]triazines [11] is an important class of biologically active compounds applied as effective antiviral drugs, such as triazavirin (1,2,4-triazolo[5,1-*c*][1,2,4]triazine) and remdesivir(pyrrolo[2,1-*f*][1,2,4]triazine) [12, 13]. Nonetheless, the structural features of hydrogenated azolotriazines still remain poorly studied. We have previously considered the chemical properties and structures of several aromatic and partially saturated azolo[1,2,4]triazines [14-18]. In this work, for the first time we investigated the structures of a series of 3-*tert*-butyl-3,4-dihydropyrazolo[5,1-*c*][1,2,4]triazine-3,4-diyl dicarboxylates by single crystal X-ray diffraction (XRD) and discussed their bond lengths and bond angles together with molecular packings in the crystals.

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## EXPERIMENTAL

**Materials and methods.** The melting point was determined on a STUART Melting point SMP30 apparatus. IR spectra were recorded on an Agilent Cary 660 FTIR spectrometer with KBr as a thin layer or pellets. NMR spectra were obtained on Bruker AM-300 or Bruker AV-600 spectrometers with working frequencies of 300 MHz ($^1$H), 75 MHz, or 125 MHz ($^{13}$C). $CHCl_3$ ($^1$H) and $CDCl_3$ ($^{13}$C) were used as the internal standards. High resolution spectra were measured on a Bruker MicroTOF II instrument with electronic sputtering ionization. The measurements were performed on positive ions (capillary voltage 4500 V); solvents were methanol or acetonitrile. The elemental analysis was performed on a PerkinElmer Series II 2400 Elemental Analyzer. Merck 60 (200 μm) silica gel was used for chromatography. Initial compounds **1** and **2a** were prepared by the procedure described previously [19].

**Single crystal XRD.** For the study the crystals of compounds **3a,b** and **4a** were grown by slow evaporation of the solvent from their saturated solutions in EtOAc at room temperature.

Reflections were collected on a Quest D8 Bruker single crystal diffractometer (Photon-III detector, graphite monochromator, $\lambda(\mathrm{Mo}K_\alpha) = 0.71073$ Å) at 100 K. Reflection intensity data were obtained using the SAINT program [20] and crystal absorption correction was applied semi-empirically based on equivalent reflections using SADABS/TWINABS [20, 21]. The structures were solved by direct methods using SHELXS [22] and refined by the least squares technique in the anisotropic (isotropic for hydrogen atoms) full-matrix approximation on $F^2$ using the SHELXL-2018 program [23]. Positions of all ordered hydrogen atoms in **3a,b** and **4a** are found from the electron density difference map. For molecular graphics we employed the SHELXTL program [20].

A crystal of compound **3a** is a two-component twin with a domain ratio of 0.533(2):0.467(2) and the [–1 0 0, 0 –1 0, 0.191 0 –1] twinning law. The rotating group model was applied for methyl groups. Since the crystal of compound **3b** completely decomposed at 100 K (the temperature was lowered by 60 K/h), it was coated with epoxy resin. The reflections of **3b** were recorded at 300 K and 200 K (the temperature was lowered by 120 K/h). The crystal also slowly decomposed at 200 K, which caused an increase in $R_{int}$ and $R_1$ values (for independent reflections). At 300 K the C16, C17, and O4 atoms are disordered over two positions with a ratio of 0.742(6):0.258(6). At 200 K the disordering of only O4 atom was modeled (0.891(6):0.109(6)) because the amount of residual electron density is insufficient to model well the disordering of C16, C17 atoms and hydrogen atoms at C17.

Crystallographic data for **3a,b** and **4a** structures have been deposited with the Cambridge Crystallography Data Center. Deposition numbers and the most important characteristics are listed in Table 1.

**General synthesis procedure for compounds 3a and 3b.** One portion of compound **2a** (0.5 g, 2.6 mmol) was added to a mixture of EtOAc (5.0 mL), benzoic acid (3.0 g, 24.57 mmol, for **3a**) or acetic acid (5 g, 83.3 mmol, for **3b**), and NBS (10.0 g, 56.19 mmol). The mixture was refluxed at 60 °C (**3a**) or 30-35 °C (**3b**) for 5 h. After cooling to room temperature, EtOAc (50.0 mL) and heptane (10.0 mL) were added. The mixture obtained was added with a portion of a mixture of $K_2CO_3$ (10.0 g, 72.36 mmol) and $N(n\text{-Bu})_4^+Br^-$ (10 mg, $3.1\cdot10^{-5}$ mmol) in water (100.0 mL), and the heterogeneous mixture obtained was vigorously stirred for 1 h at room temperature. The organic phase was separated, washed with water (3×100 mL), dried with crystalline $K_2CO_3$ and anhydrous $MgSO_4$, and filtered off. After the evaporation of solvents the precipitate was purified chromatographically (eluent EtOAc:heptane = 1:50-1:30), and 0.81 g of compound **3a** (72%) or 0.75 g of **3b** (94%) were obtained.

**(±)(3*S*,4*S*)-7-Bromo-3-*tert*-butyl-8-methyl-3,4-dihydropyrazolo[5,1-*c*][1,2,4]triazine-3,4-diyl dibenzoate (4a).** To a mixture of compound **1** (3.0 g, 10.74 mmol) with TMSBr (3.0 mL, 22.73 mmol) in acetonitrile (20.0 mL) *t*-BuONO (6.0 mL, 50.44 mmol) was added dropwise with stirring for 20 min. The reaction mixture was heated to 80 °C for 1 h; the reaction course was controlled by thin layer chromatography (TLC). After the evaporation of solvents the precipitate was dissolved in $Et_2O$ (20.0 mL), $BF_3\cdot Et_2O$ (10.0 mL, 81.03 mmol) was added, and cooled to 0 °C in an ice bath. After cooling, small portions of $LiBH_4$ (1.5 g, 68.87 mmol) were added to the reaction mixture during 2 h. The mixture obtained was left

**TABLE 1.** Crystallographic Data and Single Crystal *XRD* Details

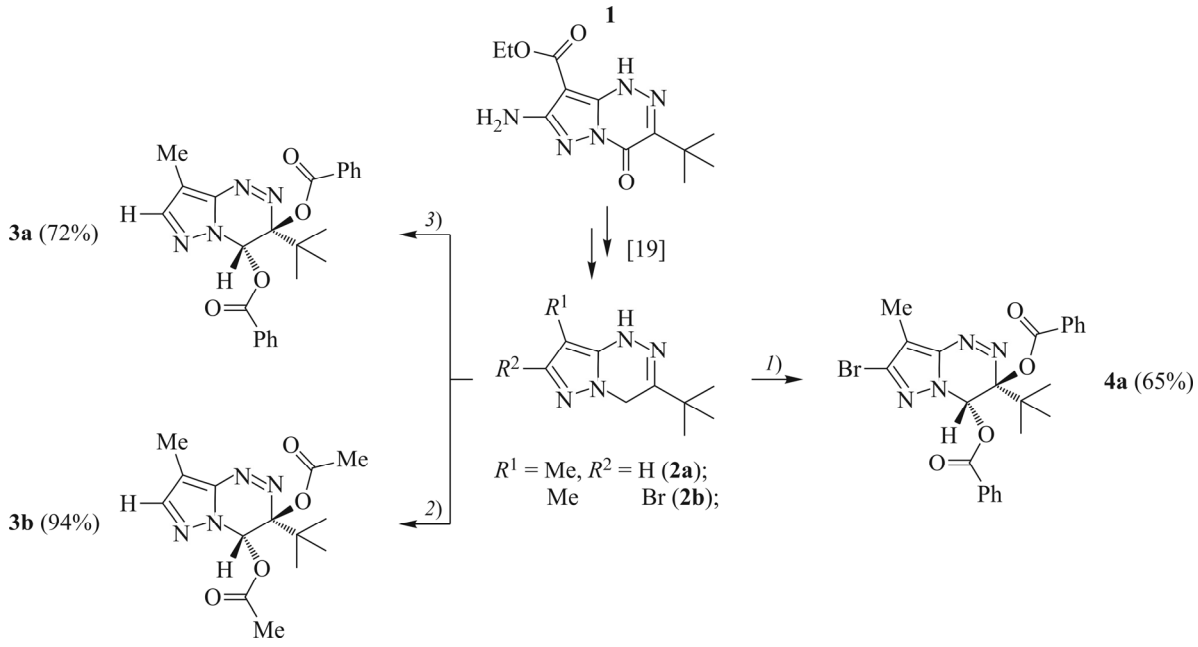
| Parameter | **4a** | **3b** (200 K) | **3b** (300 K) | **3a** |
|---|---|---|---|---|
| Chemical formula | $C_{24}H_{23}BrN_4O_4$ | $C_{14}H_{20}N_4O_4$ | $C_{14}H_{20}N_4O_4$ | $C_{24}H_{24}N_4O_4$ |
| Weight | 511.37 | 308.34 | 308.34 | 432.47 |
| Crystal system | Triclinic | Triclinic | Triclinic | Monoclinic |
| Space group; $Z$ | $P\bar{1}$; 2 | $P\bar{1}$; 2 | $P\bar{1}$; 2 | $P2_1$ |
| Cell parameters: $a$, $b$, $c$, Å | 9.6586(2), 10.61255(2), 11.8280(3) | 8.3371(8), 10.1693(8), 11.8280(3) | 8.5021(15), 10.177(2), 11.133(2) | 6.0886(7), 8.9675(10), 19.732(2) |
| α, β, γ, deg | 83.1991(6), 68.3645(6), 77.8837(6) | 86.793(3), 69.290(3), 67.435(3) | 85.442(8), 68.399(5), 67.235(5) | 90, 91.693(3), 90 |
| $V$, Å$^3$ | 1100.75(4) | 797.31(12) | 823.6(3) | 1076.9(2) |
| Crystal dimensions, mm | 0.33×0.22×0.13 | 0.46×0.38×0.32 | 0.46×0.38×0.32 | 0.33×0.17×0.09 |
| $d_{calc}$, g/cm$^3$ | 1.543 | 1.284 | 1.243 | 1.334 |
| μ, mm$^{-1}$ | 1.908 | 0.096 | 0.093 | 0.093 |
| θ range, deg | 2.306-32.500 | 2.818-31.551 | 2.766-28.323 | 3.070-29.997 |
| Reflections measured / independent | 28793 / 7970 | 28186 / 5335 | 32500 / 4087 | 4723 / 4723 |
| $R_{int}$ | 0.0446 | 0.0815 | 0.0412 | 0 |
| Observed reflections with $I > 2\sigma(I)$ | 6738 | 2780 | 2656 | 3957 |
| $R_1$, $wR_2$ for $I > 2\sigma(I)$ | 0.0341, 0.0723 | 0.0670, 0.1244 | 0.0538, 0.1258 | 0.0643, 0.1544 |
| $R_1$, $wR_2$ for independent reflections | 0.0460, 0.0793 | 0.1459, 0.1568 | 0.0895, 0.1481 | 0.0875, 0.1693 |
| *GOOF* | 1.026 | 1.011 | 1.038 | 1.023 |
| CCDC | 2072875 | 2072878 | 2072877 | 2072874 |

overnight at room temperature (the formation of compound **2b** was controlled by TLC). Then water cooled to 0 °C was added dropwise (100.0 mL) and EtOAc (20.0 mL), and the mixture was stirred for 30 min. To the heterogeneous mixture obtained KOH (10.0 g, 178.24 mmol) and $N(n\text{-Bu})_4^+Br^-$ (0.5 g, 1.55 mmol) were added and heated with stirring to 70-80 °C for 1 h. After cooling, it was extracted with $CHCl_3$/EtOAc (2:1, 4 × 50 mL). The combined organic phase was dried with anhydrous $MgSO_4$, filtered off, and the filtrate was evaporated in a vacuum. To the precipitate obtained EtOAc (5.0 mL), benzoic acid (3.0 g, 24.57 mmol), and NBS (12.0 g, 67.42 mmol) were added. The mixture was refluxed at 100 °C for 5 h. After cooling to room temperature, EtOAc (50.0 mL), heptane (10.0 mL), water (100.0 mL), $K_2CO_3$ (10.0 g, 72.36 mmol), $N(n\text{-Bu})_4^+Br^-$ (10 mg, $3.1\cdot10^{-5}$ mmol) were successively ordered. The heterogeneous mixture obtained was vigorously stirred for 1 h at room temperature. The organic phase was separated, washed with water (3×100 mL), dried with anhydrous $K_2CO_3$ and $MgSO_4$, filtered off, and the filtrate was evaporated in a vacuum. The precipitate was purified by double flash-chromatography (eluent EtOAc:heptane = 1:50-1:30), and 3.57 g of compound **4a** (65%) were obtained: yellow crystals, m.p. 186-187 °C. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, $J$, Hz): 8.08 (d, 4H, 4 *o*-CH Ph, $^3J$ = 7.7), 7.88 (s, 1H, C4H), 7.50-7.63 (m, 6H, 2 *p*- and 4 *m*-CH Ph), 2.44 (s, 3H, C8$CH_3$), 1.35 (s, 9H, C($CH_3$)$_3$). $^{13}$C NMR spectrum ($CDCl_3$, δ, ppm): 164.80, 164.31 (2 COPh), 141.42 (C3), 134.24, 133.90 (2 *p*-CH Ph), 132.22 (C7Br), 130.54, 130.13, 129.39, 128.84 (2 *m*- and 2 *o*-CH Ph), 128.72, 128.33 (2 *ipso*-C Ph), 120.38 (C8a), 97.51 (C8), 77.59 (C4H), 41.57 (<u>C</u>($CH_3$)$_3$), 26.30 (C(<u>C</u>$H_3$)$_3$), 8.27 (C8$CH_3$). IR, cm$^{-1}$: 3013, 2994, 2978, 2940 (CH), 1752, 1717 (2 CO), 1600, 1583, 1565, 1481, 1493, 1434, 1451, 1399, 1350, 1369, 1316, 1264, 1240, 1180, 1194, 1133, 1065, 1085, 1055, 1025, 997, 938, 875, 843, 800, 705, 686, 668, 638, 611. Found $[M]^+$ 511.0964. Calculated $[M]^+$ for $C_{24}H_{23}BrN_4O_4$ 511.0975. Found (%): C 56.32, H 4.55, N 10.98. Calculated for $C_{24}H_{23}BrN_4O_4$ (%): C 56.37, H 4.53, N 10.96.

**7,8-Dibromo-3-*tert*-butyl-3,4-dihydropyrazolo[5,1-*c*][1,2,4]triazine-3,4-diyl dibenzoate (4b).** One portion of compound **2d** (1 g, 3 mmol) was added to a mixture of benzoic acid (3.0 g, 24.57 mmol) and NBS (5.0 g, 28.09 mmol) in EtOAc (10 mL). The solution obtained was heated to 100 °C for 2 h. After cooling to room temperature the precipitate was dissolved in a mixture of EtOAc (30 mL) and heptane (10 mL). To the organic phase a mixture of $K_2CO_3$ (10 g, 72.36 mmol) and $N(n\text{-}Bu)_4^+Br^-$ (10 mg, $3.1\cdot10^{-5}$ mmol) in water (100 mL) was added and stirred for 1 h. The organic phase was separated, washed with water (3×100 mL), dried with anhydrous $MgSO_4$, filtered off, and the filtrate was evaporated in a vacuum. The precipitate was purified chromatographically (eluent EtOAc:heptane = 1:50-1:40) and 1.14 g (66%) of compound **4b** were obtained: yellow viscous fluid, m.p. < 0 °C. $^1$H NMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 8.11-8.07 (m., 4H, 4 *o*-CH Ph), 7.91 (s, 1H, C4H), 7.51-7.66 (m, 6H, 2 *p*- and 4 *m*-CH Ph), 1.35 (s, 9H, $C(CH_3)_3$). $^{13}$C NMR spectrum ($CDCl_3$, δ, ppm): 164.88, 164.20 (2COPh), 141.13 (C3), 134.45, 134.09 (2 *p*-CH Ph), 132.33 (C7Br), 130.56, 130.16, 128.92, 128.79 (2 *m*- and 2 *o*-CH Ph), 129.08, 127.98 (2 *ipso*-C Ph), 101.96, 98.04 (C8a, C8), 77.36 (C4H), 41.75 ($C(CH_3)_3$), 26.21 ($C(CH_3)_3$). IR, $cm^{-1}$: 3063, 3014, 2994, 2978, 2941 (CH), 1758, 1716, 1691 (2 CO), 1675, 1652, 1642, 1623, 1599, 1583, 1560, 1546, 1521, 1494, 1480, 1448, 1400, 1366, 1348, 1316, 1294, 1257, 1269, 1238, 1174, 1126, 1083, 1066, 1052, 1023, 996, 938, 870, 888, 845, 799, 707, 685, 644, 619, 565, 544, 464. Found $[M]^+$ 574.9915. Calculated $[M]^+$ for $C_{23}H_{20}Br_2N_4O_4$ 574.9924. Found (%): C 47.87, H 3.48, N 9.75. Calculated for $C_{23}H_{20}Br_2N_4O_4$ (%): C 47.94, H 3.50, N 9.72.

## RESULTS AND DISCUSSION

3-*tert*-Butyl-3,4-dihydropyrazolo[5,1-*c*][1,2,4]triazine-3,4-diyl dicarboxylates **3a,b** were previously synthesized [24] by the interaction of aromatic 3-*tert*-butyl-pyrazolo[5,1-*c*][1,2,4]triazines with N-bromosuccinimide in the presence of respective carboxylic acids. We found that 3-*tert*-butyl-8-methyl-1,4-dihydropyrazolo[5,1-*c*][1,2,4]triazine **2a** is readily brominated in the presence of acetic or benzoic acids. Thus, prolonged heating of cyclic hydrazone **2a** with NBS in the BzOH/EtOAc mixture or in an excess of glacial AcOH results in good yields of dicarboxylates **3a** and **3b** respectively (Scheme 1).




**Scheme 1.** Preparation of dicarboxylates **3a** and **3b**, and compound **4a**. Reagents and conditions: NBS, $PhCO_2H$, EtOAc, 100 °C, 5 h (*1*); NBS, AcOH, 30-35 °C (*2*); NBS, $PhCO_2H$/EtOAc, 60 °C, 5 h (*3*).

The XRD results for compounds **3a** and **3b** are summarized in Table 1. The triazine ring of the **3a** heterocycle adopts the *twist*-conformation with the equatorial arrangement of the *tert*-butyl group as a conformational *anchor* and axial carboxylate moieties fixed in the *trans*-configuration. The molecular packing in the **3a** crystal represents 1D extended chains along the *c* axis (Fig. 1). The crystal of compound **3b** decomposed on cooling to 100 K. The crystal coated with epoxy resin also slowly decomposed at 200 K, which caused an appreciable increase in $R_{int}$ and $R_1$ values (based on independent reflections) at this temperature. We have experimentally observed a 26.3 $Å^3$ decrease in the unit cell volume on cooling from 300 K to 200 K (3.2%), which can be explained by a decrease in the thermal motion of the O4–C16–C17 fragment: the distance between disordered O4A and O4B shortened from 0.99(1) Å to 0.93(3) Å (Fig. 2). The most significant structural change is an increase in the acetate torsion angle at the C4 position (by 5.6° for C16A–O3–C4–H4 and by 22.3° for C16B–O3–C4–H4). At different temperatures changes in the crystal structure of **3b** were also revealed in the structure of the triazine ring: N1–N2–C3–O1, N1–N2–C3–C10, and N1–N2–C3–C4 torsion angles decrease by approximately 2° (Fig. 2, Table 2).

We managed to covert readily available compound **1** into dibenzoate **4a** without isolating intermediate products. The synthesis involves diazotization of the C7 position, reduction of the ring and the side chain under the influence of $BH_3/BF_3$ [15, 19], and in situ oxidation of intermediate **2b** with a NBS/BzOH mixture (Scheme 1). Target compound **4a** was obtained in a good yield.

The single crystal XRD results for compound **4a** are summarized in Table 1. In the **4a** molecule, the aromatic pyrazole ring and substituents are located in one plane with a deviation of 1-3° (Table 2), while the triazine ring is in the *twist*-conformation. Unlike analogue **3a**, not containing a bromine atom, in **3b** and **4a**, the *tert*-butyl group takes the position close to axial, with the equatorial carboxylate groups being in the *trans*-configuration (Fig. 3). The molecular packing in the

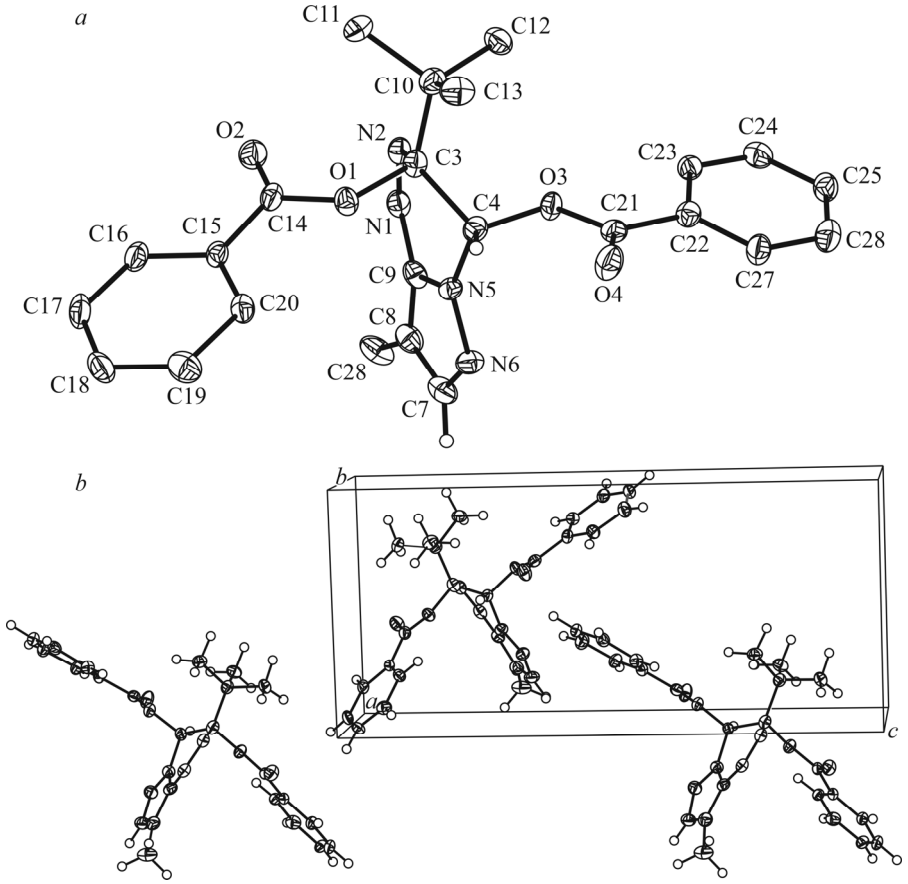



**Fig. 1.** Molecular structure of compound **3a** and its packing in the crystal. Hydrogen atoms of Me and Ph groups are omitted.

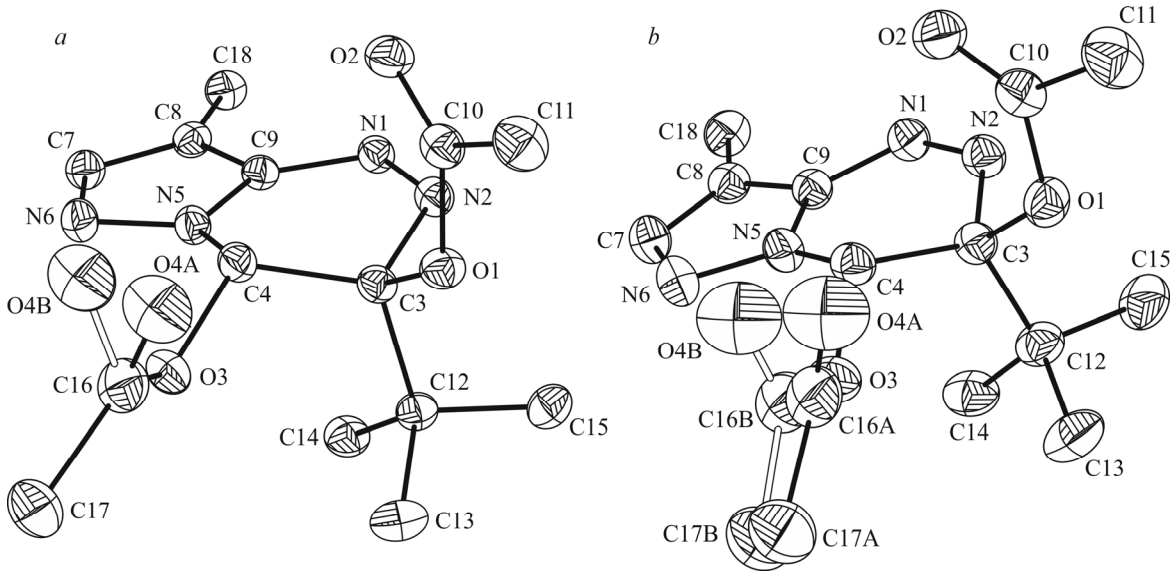



**Fig. 2.** Molecular structure of compound **3b** at 200 K (*a*) and 300 K (*b*). Hydrogen atoms are omitted.

**TABLE 2.** Torsion Angles in Compounds **3a,b** and **4a**, deg

| Torsion angle | **4a** | **3a** | **3b** (200 K) | **3b** (300 K) |
|---|---|---|---|---|
| C9–N1–N2–C3 | 5.9(2) | –3.4(6) | 6.9(2) | 6.4(2) |
| N1–N2–C3–O1 | –143.16(14) | –72.2(5) | –149.08(15) | –147.62(14) |
| N1–N2–C3–C4 | –23.9(2) | 36.4(6) | –31.1(2) | –29.7(2) |
| N1–N2–C3–C10 | 106.88(16) | 166.4(4) | 99.85(18) | 101.16(17) |
| N2–C3–C4–O3 | 145.79(12) | 70.4(5) | 156.28(14) | 155.37(13) |
| N2–C3–C4–N5 | 28.76(16) | –46.5(5) | 37.8(2) | 36.35(17) |
| Br1–C7–C8–C9 | –178.00(11) | - | - | - |
| Br1–C7–C8–C11 | –2.9(2) | - | - | - |
| N6–C7–C8–C11 | 178.28(15) | 179.3(5) | –179.92(19) | –179.82(18) |

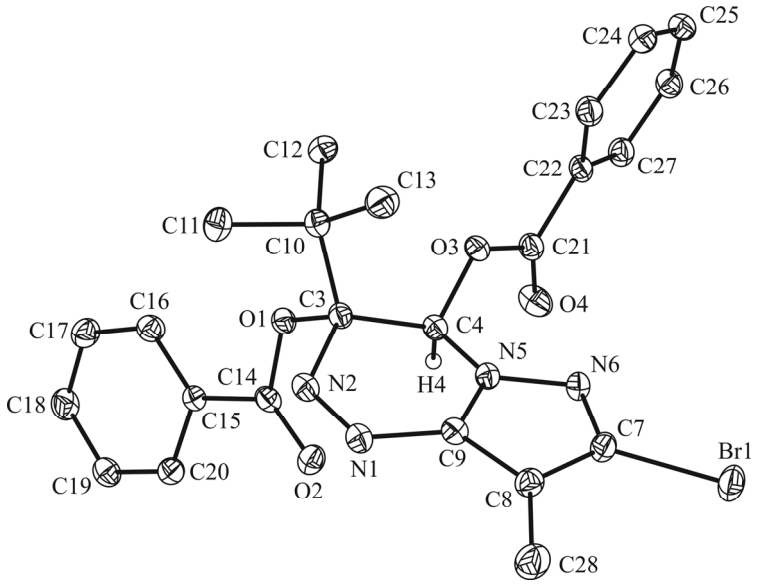
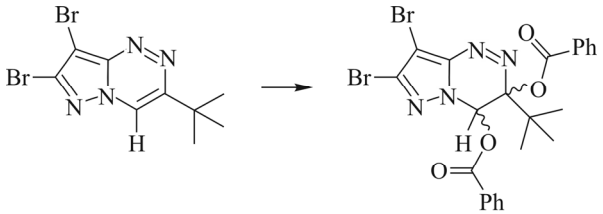



**Fig. 3.** Molecular structure of compound **4a**. Hydrogen atoms of alkyl and phenyl groups are omitted.

**4a** crystal is shown in Fig. 4. Compound **4a** forms intermolecular halogen bonds [25] between Br and O2 atoms of the neighboring molecules with a length of 3.086(1) Å, the C7–Br–O2 angle being 161.12(6)°.

The removal of the bromine atom from the C7 position of compound **4a** led to an insignificant (0.01-0.02 Å) decrease in C8–C11, C7–C8, and N5–N6 bond lengths and C9–C8–C11 and N6–C7–C8 bond angles (1-2°). It is worth noting that on passing from phenyl groups in compound **3a** to methyl ones in **3b**, a decrease in C3–O1 and C4–O3 bond lengths from 1.459(6) Å and 1.435(2) Å to 1.435(2) Å and 1.422(2) Å, respectively, is observed (Table 3). On the contrary, due to a change in the volume of the substituent, a weakening of C3–C10 and N5–N6 bonds is observed: by 0.03 Å and 0.01 Å respectively. In diacetate **3b**, the N2–C3–O1 and O1–C3–C(*t*-Bu) bond angles decreased by 5-6° in comparison with similar ones in dibenzoate **3a**. In turn, the N1–N2–C3–O1 and N2–C3–C4–O3 torsion angles increased by ~6° and ~10° respectively, which may be explained by some relaxation of steric hindrance in the **3b** molecule.

Due to pronounced structural features of carboxylate **4a** brominated at the C7 position, it was interesting to investigate by single crystal XRD the structure of similar compound **4b** containing bromine atoms at C7 and C8 positions. Previously undescribed compound **4b** was isolated in treating aromatic 7,8-dibromopyrazolotriazine **5** [26] with N-bromosuccinimide in the presence of benzoic acid (Scheme 2).




**5** **4b** (66%)

**Scheme 2.** Preparation of compound **4b**. Reagents and conditions: NBS, $PhCO_2H$/EtOAc, 100 °C, 2 h.

The IR spectrum of dibenzoate **4b** contains intense characteristic bands at 1758 $cm^{-1}$ and 1716 $cm^{-1}$, which we assigned to stretching vibrations of two carbonyl groups. In the $^1H$ NMR spectrum, we observed signals of C4–H hydrogen atoms at 7.91 ppm (C4H) and also two phenyl groups at 7.51-8.11 ppm. The $^{13}C$ NMR spectrum (experiment - test for bound

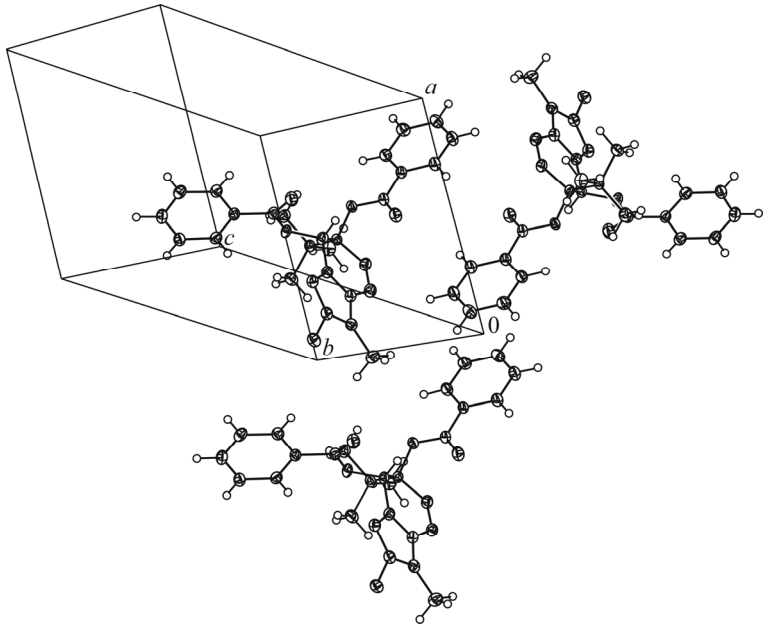



**Fig. 4.** Molecular packing of compound **4a** in the crystal.

**TABLE 3.** Selected Bond Lengths in Compounds **3a**,**b** and **4a** (Å)

| Bond | **4a** | **3a** | **3b** (200 K) | **3b** (300 K) |
|---|---|---|---|---|
| Br1–C7 | 1.8635(14) | - | - | - |
| N1–N2 | 1.2555(18) | 1.259(6) | 1.261(2) | 1.2596(19) |
| N1–C9 | 1.3904(19) | 1.405(6) | 1.397(2) | 1.394(2) |
| N2–C3 | 1.5062(19) | 1.508(6) | 1.500(2) | 1.499(2) |
| C3–O1 | 1.4344(17) | 1.459(6) | 1.435(2) | 1.436(2) |
| C3–C4 | 1.561(2) | 1.543(6) | 1.546(2) | 1.549(2) |
| C3–C10 | 1.572(2) | 1.543(7) | 1.574(3) | 1.571(2) |
| C4–O3 | 1.4168(17) | 1.435(6) | 1.422(2) | 1.4180(19) |
| C4–N5 | 1.4509(19) | 1.431(6) | 1.441(2) | 1.437(2) |
| N5–C9 | 1.3492(19) | 1.359(6) | 1.353(2) | 1.350(2) |
| N5–N6 | 1.3537(17) | 1.339(6) | 1.351(2) | 1.352(2) |
| N6–C7 | 1.338(2) | 1.333(7) | 1.337(3) | 1.331(2) |
| C7–C8 | 1.401(2) | 1.392(7) | 1.401(3) | 1.400(3) |
| C8–C9 | 1.387(2) | 1.375(7) | 1.377(3) | 1.376(2) |
| C8–C(Me) | 1.490(2) | 1.511(8) | 1.488(3) | 1.488(3) |

protons, APT) and the high-resolution mass spectrum corresponded to the expected ones. Product **4b** was isolated as a viscous fluid which we failed to crystallize under diverse experimental conditions.

## CONCLUSIONS

The structures of 7-$R^1$-8-methyl-3-*tert*-butyl-3,4-dihydropyrazolo[5,1-*c*][1,2,4]triazine-3,4-diyl diacetate ($R^1$ = H) and dibenzoates ($R^1$ = H, Br) are studied by single crystal XRD for the first time. The observed conformations of the triazine ring largely depended on the nature of substituents in the heterocyclic core, which may be explained by the combined action of spatial effects and intermolecular non-valent interactions. The *trans*-arrangement of carboxylate moieties was confirmed in all compounds studied. A decrease in the unit cell volume of the diacetate crystal on cooling from 300 K to 200 K is experimentally found. Bond lengths and bond angles as well as the molecular packing in the crystals are considered.

## ACKNOWLEDGMENTS

The single crystal XRD analysis was performed in the Department of Structural studies of the Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow.

## CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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