ORIGINAL RESEARCH



Crystal structure and thermal expansion of N,N,N',N'-tetrakis-[(1H,2,4-triazol-1-yl)methyl]-ethane-1,2-diamine

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Abstract The crystal structure of N,N,N',N'-tetrakis-[(1H,2,4-triazol-1-yl)methyl]-ethane-1,2-diamine has been fully determined at six different temperatures by X-ray single-crystal diffraction, and the thermal expansion has been determined from 100 K to ambient temperature. The expansion is anisotropic, and it is negative in one direction of the unit cell. The supramolecular structure formed by weak hydrogen bonds of the type C–H…N resembles a trellis analogous to that observed in other organic systems with strong hydrogen bonds.

Keywords Crystal \cdot Negative thermal expansion \cdot Triazole derivative \cdot C-H \cdots N hydrogen bonds

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Introduction

Identification of recurring patterns in crystal structures is important for crystal engineering in order to design new solids with specific physical and chemical properties [1]. Crystal structures are governed by a combination of a large number of intermolecular interactions. A specific combination of molecular functionalities may lead to a particular supramolecular synthon, which in turn may lead to a large number of similar crystal structures. In neutral molecular solids, hydrogen bonds (traditionally $O-H\cdots O$ and $N-H\cdots O$) are generally considered as important building blocks for supramolecular synthons and networks.

The ability of the C–H group to act as a proton donor in hydrogen bonds has been the subject of controversy for many years. The possibility was first described in 1935 [2], and it was for the first time systematically studied in purines and pyrimidines in the 1960's [3]. In 1999, the weak C-H-O hydrogen bond has been treated in a book [4], but the interaction is broadly applicable to other hydrogen bond acceptors. Neutron diffraction data have provided conclusive evidence for the existence of C-H···A hydrogen bonds [4]. They are known to be rather long and weak. In spite of their weakness, they can be important as secondary interactions and in certain cases even as primary ones defining the crystal structure. They also play an important role in biological systems [5]. Typically, criteria to establish the presence of this type of hydrogen bonds are based on geometrical or spectral observations [4]. Theoretical calculations show that the proton-donor property of the C-H groups varies with C hybridization ($Csp > Csp^2 > Csp^3$) [6]. The energy of the C-H...A interactions (A being O, N or F) can vary from 0.6 to 3.6 kcal/mol, the strongest being C-H...N. However, the energies are often difficult to evaluate experimentally.

N,N,N',N'-tetrakis-[(1H,2,4-triazol-1-yl)methyl]-ethane-1,2-diamine (TTYED) has been prepared in the framework of a study on triazole derivatives with novel modes of action in their antifungal properties [7, 8]. Considering the molecular structure of this neutral molecular compound (Fig. 1), only weak intermolecular interaction was expected. The molecular structure was confirmed by singlecrystal X-ray diffraction using crystals found in the powder obtained after synthesis. The crystal structure clearly demonstrated the presence of $C(sp^2)$ –H…N hydrogen bonds.

In addition to the structure determination, lattice expansion was studied by collecting X-ray diffraction data and solving the crystal structure at different temperatures from 100 to 297 K. Intermolecular interactions can be studied with the isobaric expansion tensor derived from these results [9–11]. The thermal expansion of the compound is presented in this paper, and it will be demonstrated that it exhibits uniaxial shrinking with increasing temperature. Most materials tend to expand in all directions when heated. Unusual and nonuniform thermal expansion in crystals has recently attracted attention as it is of interest for technological applications and from the fundamental point of view.

Materials with negative thermal expansion (NTE) have the counterintuitive property to expand on cooling. NTE is generally considered rare and even more rare in organic materials. Mechanisms that give rise to this phenomenon are still poorly documented, but several mechanisms have been reported: torsional vibrations in polymers, ordering of water molecules in organic crystals or cooperative movements involving strong hydrogen bonds in, for example, hydrated methanol [12], (S,S')-octa-3,5-duyin-2,7-diol [13] and tienoxolol [10].

Uniaxial NTE (contraction in one direction whereas the total volume increases with temperature) is expected to be



Fig. 1 Chemical structure of N,N,N',N'-tetrakis-[(1H,2,4-triazol-1-yl)methyl]-ethane-1,2-diamine, $C_{14}H_{20}N_{14}$, M = 384.44 g mol⁻¹

more prevalent than overall NTE, i.e., the decrease in the entire unit-cell volume, but reports on this subject are rare, whereas it will certainly contribute to our understanding of strong and weak interactions in crystal structures.

In the present paper, the NTE mechanism involving C– H…N hydrogen bonds is discussed. To our knowledge, this is the first time that an NTE mechanism is reported involving such weak hydrogen bonds.

Materials and methods

Materials

Synthesis of (1H-1, 2, 4-triazol-1-yl) methanol

The compound was synthesized with some modifications compared to Ref. [14]: (1.2.4)-triazole [98 % (Aldrich),1,73 g, 25 mmol] in 20 ml of ethanol (absolute ethanol, ≥99.8 %, Sigma-Aldrich) and 3.5 ml of formaldehyde solution (>36,5 %, Sigma-Aldrich) were stirred, refluxed for 1 h, and mixing was continued at room temperature for 12 h. After the elimination of the solvent under reduced pressure, the obtained residue was treated with cold water. A white solid appeared, which was collected by filtration, washed with diethyl ether (99 %, Sigma-Aldrich) and dried under vacuum to yield the pure product (79 %).

Synthesis of N,N,N',N'-tetrakis-[(1H,2,4-triazol-1yl)methyl]-ethane-1,2-diamine

This compound was prepared from the condensation of four equivalents of 1H-(1, 2, 4)-triazol-1-yl methanol (10 mmol, 1 g) with one equivalent of ethane-1,2-diamine (\geq 99,0 %, **Fluka**, 2,5 mmol, 0,15 g) in anhydrous acetonitrile (\geq 99,8 %, **Sigma-Aldrich**) as the solvent. The mixture was stirred under reflux for 4 h. Then, the solution was dried over anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure and the obtained residue was washed with a mixture of dichloromethane (99.8 %, **Sigma-Aldrich**) and diethyl ether (3/1 ratio) to give an oily product, which was recrystallized with ethanol to yield white crystals.

Single-crystal X-ray diffraction

A single crystal (Fig. 2) was mounted on a glass rod. Single-crystal X-ray diffraction data were collected on an X-CALIBUR-2 CCD four-circle diffractometer (Oxford Diffraction) at 100, 150, 170, 200, 250 and 297 K. Data collections, unit-cell determinations and data reductions were carried out with Mo K α radiation ($\lambda = 0.710$ 73 Å) and performed with the CRYSTALIS program suite [15]



Fig. 2 Optical microscopy photograph of single crystals of N,N,N',N'-tetrakis-[(1H,2,4-triazol-1-yl)methyl]-ethane-1,2-diamine (TTYED)

on the full data set. The structures were solved by direct methods and successive Fourier difference calculations with the ShelxS97 program [16] and refined on F^2 by weighted anisotropic full-matrix least-squares methods using the SHELXL-2014 program [17]. Nonhydrogen

Table 1 Crystal data and structure refinement

atoms were refined with anisotropic thermal parameters. The hydrogen atoms were positioned geometrically. Both programs were used within the WINGX package [12]. Empirical absorption correction using spherical harmonics was carried out using the SCALE3 ABSPACK program [18]. The cooling device was a CryoJet[®] from Oxford Instruments (UK). The crystal was allowed to equilibrate in the nitrogen flux for 30 min before starting each isothermal data collection. Crystallographic data at different temperatures are given in Table 1.

Isobaric thermal expansion tensor

Intermolecular interactions can be studied with the isobaric thermal expansion tensor, which is a measure for how intermolecular distances change with temperature. A small value for a tensor eigenvalue is commonly referred to as a 'hard' direction and a large value as a 'soft' direction [19]. The tensor has been calculated by the PASCAL software [20].

Common details							
Formula	C ₁₄ H ₂₀ N	14 Wavelength/Å		0.71073			
Formula weight/g mol ⁻¹	384.44		ystal size/mm	$0.40 \times 0.30 \times 0.08$			
Crystal system	Monoclinic		niting indices	ces $-24 < h < 24; -11 < k < 11; -15 < l <$			
Space group	C 2/c		F (000) 808				
Z	4 Refinement metho		finement method	Full-matrix least squares on F^2			
Temperature/K	100	150	170	200	250	297	
Cell parameters as a function	of temperature						
Unit-cell dimensions/Å, °	a = 18.6498 (9)	a = 18.6598 (6)	a = 18.6696 (8)	a = 18.654 (1)	a = 18.673 (1)	a = 18.667 (1)	
	b = 8.5225 (5)	b = 8.5656 (3)	b = 8.5776(5)	b = 8.5988 (5)	b = 8.6470 (6)	b = 8.6944 (7)	
	c = 11.3310 (6)	c = 11.3354 (4)	c = 11.3343 (6)	c = 11.3266 (6)	c = 11.3388 (7)	c = 11.3376 (8)	
	$\beta = 100.680(5)$	$\beta = 100.595$ (4)	$\beta = 100.532(5)$	$\beta = 100.511$ (6)	$\beta = 100.441$ (7)	$\beta = 100.365$ (7)	
Volume/Å ³	1769.8 (2)	1780.9 (1)	1784.5 (2)	1786.3 (2)	1800.5 (2)	1810.1 (2)	
$d_c/g \ cm^{-3}$	1.443	1.434	1.431	1.429	1.418	1.411	
μ/mm^{-1}	0.101	0.101	0.100	0.100	0.100	0.099	
$\theta_{\rm max}$ /°	28.280	28.280	28.277	28.282	28.272	28.277	
Reflections collected/unique	7633/2197	7683/2208	7707/2211	7660/2215	7680/2236	7688/2246	
	$[R_{\rm int} = 0.0603]$	$[R_{\rm int} = 0.0260]$	$[R_{\rm int} = 0.0294]$	$[R_{\rm int} = 0.0656]$	$[R_{\rm int} = 0.0729]$	$[R_{\rm int} = 0.0821]$	
Completeness (%)	99.9	99.9	99.9	99.9	99.9	99.9	
Data/restraints/parameters	2197/0/128	2208/0/127	2211/0/128	2215/0/128	2236/0/128	2246/0/128	
Goodness of fit on F^2	1.038	1.030	1.046	1.014	1.032	0.991	
<i>R</i> indices $[I > 2\sigma (I)]$	$R_1 = 0.0490$	$R_1 = 0.0367$	$R_1 = 0.0365$	$R_1 = 0.0511$	$R_1 = 0.0534$	$R_1 = 0.0548$	
	$wR_2 = 0.0854$	$wR_2 = 0.0860$	$wR_2 = 0.0839$	$wR_2 = 0.0780$	$wR_2 = 0.0703$	$wR_2 = 0.0778$	
R indices (all data)	$R_1 = 0.0931$	$R_1 = 0.0513$	$R_1 = 0.0565$	$R_1 = 0.1173$	$R_1 = 0.1432$	$R_1 = 0.1612$	
	$wR_2 = 0.1031$	$wR_2 = 0.0940$	$wR_2 = 0.0905$	$wR_2 = 0.1017$	$wR_2 = 0.1071$	$wR_2 = 0.1209$	
Extinction coefficient	0.0004 (4)	0.0000 (4)	0.0000 (5)	0.0007 (3)	0.0010 (2)	0.0017 (3)	
$\Delta ho_{ m max} / \Delta ho_{ m min}$, e Å $^{-3}$	0.256/-0.283	0.231/-0.172	0.248/-0.181	0.194/-0.212	0.198/-0.188	0.196/-0.177	



Fig. 3 a Ortep of N,N,N',N'-tetrakis-[(1H,2,4-triazol-1-yl)methyl]ethane-1,2-diamine (TTYED) with thermal ellipsoids at 297 K (20 % probability level). Only the atoms of the asymmetric unit are labelled. **b** Crystal structure of TTYED projected on plane *ac* (H atoms omitted for clarity)

Table 2 Isobaric thermal tensor coefficients (in MK^{-1}) and the orientation of the tensor in the unit cell

Eigenvalues		Eigen	Eigenvectors				
			а	b	С		
α11	-7.6 (9)	e1	0.4258	0	-0.9048		
α22	20 (1)	e2	0.5864	0	0.8100		
α33	101 (3)	e3	0	-1	0		

Results

Crystal structure

TTYED crystallizes in the monoclinic system, space group C 2/c, and the molecule is located on the twofold rotational axis; thus, only half of the molecule is found in the asymmetric unit. Crystal and structure-refinement data at different temperatures are compiled in Table 1. Supplementary crystallographic data can be found in the CCDC deposit (CCDC 1036547–1036552) and obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/. The molecular structure and atomic numbering are shown in Fig. 3.

Influence of the temperature on the crystal structure

Expansivity

The unit-cell parameters determined from 100 to 297 K are compiled in Table 2. The specific volume v (in cm³ g⁻¹) of TTYED as a function of temperature *T* (in K) can be fitted to a straight line, with $r^2 = 0.986$:

$$v = 0.68489 + 7.9588 \times 10^{-5} \times T \tag{1}$$

It demonstrates that the volume increases linearly with temperature in the range from 100 K up to 297 K. It corresponds to an expansivity α_v of 1.16 \times 10⁻⁴ K⁻¹.

Thermal expansion tensor

The eigenvalues of the thermal expansion tensor, calculated with the PASCAL program [20], are compiled in Table 2. Because the cell is monoclinic, the principal axis e3 is parallel to the b axis of the unit cell and the axes e1 and e2 can be found in the ac plane (Table 2). The tensor parameters are constant, because the volume and the cell parameters depend linearly on the temperature between 100 and 297 K. The maximum expansion can be found along e3 [101 (3) MK⁻¹], the minimum expansion along e1 [-7.6 (9) MK⁻¹].

 Table 3 Selected torsion

 angles (°) as a function of the

 temperature

	100 K	150 K	170 K	200 K	250 K	297 K	
C3-N2-C2-N3	133.7 (2)	133.6 (1)	133.4 (1)	133.2 (2)	133.2 (3)	133.3 (3)	
N2-C2-N3-C7	151.4 (2)	150.9 (1)	150.9 (1)	150.7 (2)	150.3 (2)	149.7 (2)	
C6-N1-C7-N3	107.9 (2)	107.7 (1)	107.7 (1)	107.7 (2)	107.2 (3)	107.9 (3)	
N1-C7-N3-C2	67.7 (2)	67.8 (1)	67.8 (1)	67.8 (2)	68.1 (3)	67.6 (3)	
N3-C1-C1-N3	49.5 (2)	50.2 (1)	50.4 (1)	50.4 (2)	50.4 (3)	51.2 (3)	
C2-N3-C1-C1 ^a	119.1 (2)	118.8 (1)	118.6 (1)	118.4 (2)	118.4 (3)	117.8 (3)	

Equivalent atom by symmetry transformation -x + 1, y, -z + 1/2



Fig. 4 Changes in selected torsion angles as a function of temperature

Discussion

Molecular conformation

Because a twofold axis parallel to the b axis intersects the central C–C bond of the molecule, the asymmetric unit consists of half a molecule.

Table 4 Evolution of the intramolecular hydrogen bond as a function of temperature

D–H…A	D–H, Å	H…A, Å	D…A, Å	DHA,°
100 K				
C7–H7B…N4	0.99	2.71	3.573 (2)	146
150 K				
C7–H7B…N4	0.99	2.72	3.593 (2)	146
170 K				
C7–H7B…N4	0.98	2.73	3.587 (2)	146
200 K				
C7−H7B…N4	0.99	2.72	3.594 (3)	146
250 K				
C7–H7B…N4	0.98	2.74	3.592 (3)	146
297 K				
C7–H7B…N4	0.97	2.74	3.596 (3)	147

The molecule is rather flexible with 11 torsion angles of which 6 are independent due to the twofold axis (Table 3). The torsion angles C3–N2–C2–N3 and N2–C2–N3–C7 define the orientation of the second crystallographically independent triazole group (see Fig. 3), whereas the torsion angles C6–N1–C7–N3 and N1–C7–N3–C2 define the orientation of the first triazole group. The torsion angles N3–C1–C1–N3 and C2–N3–C1–C1 define the orientation of half of the molecule relative to the other half.

The mean plane of the molecule is approximately parallel to the $(0\ 1\ 0)$ plane. The first triazole group is parallel to the mean plane, and the second triazole forms an angle of 59.634 (49)° to the mean plane.

The two torsions, N1–C7–N3–C2 and C6–N1–C7–N3 (Table 3; Fig. 3), defining the orientation of the first triazole group remain virtually constant with the temperature. All the other torsion angles vary linearly with the temperature (Fig. 4). However, the variation is relatively small (Fig. 4) and the conformation remains virtually the same from 100 K up to ambient temperature.

Considering geometrical criteria [4], two intramolecular hydrogen bonds can be identified in the molecule. Due to

D–H…A	D–H, Å	H…A, Å	D…A, Å	DHA, °	Symmetry
100 K					
C2-H2A…N5	0.99	2.69	3.387 (2)	128	-x + 3/2, -y + 1/2, -z + 1
C3-H3N7	0.95	2.44	3.242 (2)	141	$-x + 3/2, y - 1/2, -z + \frac{1}{2}$
C4-H4N6	0.95	2.37	3.317 (2)	177	x, y, z + 1
C7-H7BN3	0.99	2.62	3.193 (2)	117	$-x + 1, y, -z + \frac{1}{2}$
150 K					
C3-H3N7	0.95	2.46	3.256 (2)	141	-x + 3/2, y - 1/2, -z + 1/2
C4-H4N6	0.95	2.38	3.328 (2)	177	x, y, z + 1
C7–H7B…N3	0.99	2.62	3.197 (2)	117	-x + 1, y, -z + 1/2
170 K					
C3-H3N7	0.94	2.48	3.263 (2)	141	-x + 3/2, y - 1/2, -z + 1/2
C4-H4N6	0.94	2.39	3.330 (2)	177	x, y, z + 1
C7-H7B…N3	0.98	2.62	3.198 (2)	118	-x + 1, y, -z + 1/2
200 K					
C3-H3N7	0.95	2.47	3.270 (3)	141	-x + 3/2, y - 1/2, -z + 1/2
C4-H4N6	0.95	2.38	3.330 (3)	177	x, y, z + 1
C7-H7BN3	0.99	2.61	3.196 (2)	118	$-x + 1, y, -z + \frac{1}{2}$
250 K					
C3-H3N7	0.94	2.50	3.292 (3)	142	-x + 3/2, y - 1/2, -z + 1/2
C4-H4N6	0.94	2.40	3.337 (4)	177	x, y, z + 1
C7-H7BN3	0.98	2.63	3.201 (3)	118	$-x + 1, y, -z + \frac{1}{2}$
297 K					
C3-H3N7	0.93	2.52	3.298 (4)	142	-x + 3/2, y - 1/2, -z + 1/2
C4-H4N6	0.93	2.41	3.343 (4)	178	x, y, z + 1
C7-H7B…N3	0.97	2.63	3.206 (3)	118	-x + 1, y, -z + 1/2



Fig. 5 View perpendicular to the infinite chain of hydrogen bonds C(10) interconnected with infinite chain of C(11) weak hydrogen bonds. The trellis-like structure made up by hydrogen bonds can be recognized

its symmetry, only one hydrogen bond needs to be defined: C7–H7B…N4 between the $C(sp^3)H_2$ group attached to the first triazole group and one of the N atoms of the second triazole group (see Table 4). This may explain why the conformation of the first triazole group does not change with temperature in relation to the second triazole group.

Crystal packing and intermolecular interactions at 297 K

Each molecule of TTYED is involved in eight intermolecular hydrogen bonds $C(sp^2)$ -H···N with 6 different molecules. Due to the symmetry of the molecule and the fact that the molecule can be donor and acceptor, only two hydrogen bonds are independent (see Table 5). A weak intermolecular close contact can also be identified at each temperature (C7-H7B···N3 in Table 5).

The hydrogen bonds C4–H4···N6 form cyclic dimers [graph set notation [21] $\mathbf{R}_2^2(12)$] and an infinite chain [graph set notation C(10), figure S1 in supplementary materials]. All the C(10) chains present in the crystal are parallel to each other and parallel to the crystallographic c axis and connected to each other via the C3–H3···N7 hydrogen bonds (see Fig. 5; Table 5).

The C3-H3...N7 hydrogen bonds form also infinite chains of hydrogen bonds interlocked [graph set notation



Fig. 6 Changes in the values of the 2 independent intermolecular hydrogen bonds and the close contact as a function of temperature (see Table 5)

C(11), Fig. 5]. Consequently, one C(10) chain is then connected to 4 different C(10) chains by these C3–H3 \cdots N7 hydrogen bonds. One can recognize the scissor- or trellis-like structure, which is similar to the one observed in tienoxolol [10] or methanol hydrate [12].

Influence of the temperature on the crystal structure

From Table 5 and Fig. 6, it can be seen that the C4– H4…N6 hydrogen bond giving rise to the C(10) chains is the strongest hydrogen bond in the system: Its angle is closest to 180°, and the donor–acceptor distance is the smallest [4]. Moreover, the D–H–A angle and the donor– acceptor distance do not change significantly with temperature. It corresponds also to the hydrogen bond making up the infinite hydrogen bond parallel to the *c* axis, made of cyclic dimers $\mathbf{R}_2^2(12)$ (figure S1 in supplementary materials).

The second hydrogen bond (defined by its geometry) is C3–H3…N7 [giving rise to the C(11) chains], but its distance donor-acceptor exhibits the greatest variation (Table 5; Fig. 6).

The anisotropy of the thermal expansion is shown in Fig. 7 (see also Table 2). The thermal expansion along *e1* is negative, but small in comparison with the expansion along *e2* and *e3*. Therefore, the specific volume of the title compound increases with temperature. However, its expansivity $(1.15 \times 10^{-4} \text{ K}^{-1})$ is found to be twice as small as the mean value for expansivity mentioned by Gavezzotti for organic molecular crystals ($\alpha_V = 2 \times 10^{-4} \text{ K}^{-1}$) [15]. It is even smaller than the one observed in another uncharged organic molecule: $1.54 \times 10^{-4} \text{ K}^{-1}$ in tienoxol [10], which contained strong O–H…N hydrogen bonds.

The major part of the expansion in TTYED is along e3 (Fig. 7); indeed, the coefficient is about $101 \times 10^{-6} \text{ K}^{-1}$. It is smaller than in the innocolol ($123 \times 10^{-6} \text{ K}^{-1}$ [10]), but greater than in the zwitterionic form of L-citrulline



Fig. 7 The three major components of the thermal expansion tensor and the respective projections of the crystal structure. Negative thermal expansion is marked in *red*. Hydrogen atoms omitted for clarity (Color figure online)

 $(73 \times 10^{-6} \text{ K}^{-1} \text{ in forms } \alpha \text{ and } \delta$ [11]). The high value along the *e3* axis indicates the soft direction in the crystal with the weakest intermolecular interactions. It corresponds to a direction perpendicular to the infinite chain of the strongest hydrogen bonds in the crystal (Fig. 5).

Along *e1*, the expansion is negative in TTYED. The contraction $(-7.5 \times 10^{-6} \text{ K}^{-1})$ is smaller than in citrulline $(-10 \times 10^{-6} \text{ K}^{-1})$ in the δ form and $-18 \times 10^{-6} \text{ K}^{-1}$ in the α form) and larger than in tienoxolol $(-5 \times 10^{-6} \text{ K}^{-1})$. In tienoxolol, the contraction was related to the decrease in the cell parameter *b* with temperature. In TTYED, the observed contraction is due to the decrease in the cell parameter β with temperature, whereas all the other cell parameter β with temperature, whereas all the other cell parameters increase (Table 1). The infinite chains of the strongest hydrogen bonds in the crystal remain parallel to the *c* axis at each temperature, but the angle between *c* and *a* decreases with increasing temperature; thus, along one direction, a contraction can be observed.

Moreover, a scissors or trellis effect is observed analogous to the one in tienoxolol. There are two interlocked infinite chains of weak hydrogen bonds C(11) (Fig. 5), and an expansion along the *b* axis mechanically induces a contraction perpendicular to *b* (along *e1* in TTYED).

Conclusion

The crystal structure of N,N,N',N'-tetrakis-[(1H,2,4-triazol-1-yl)methyl]-ethane-1,2-diamine (TTYED) has been solved to unambiguously characterize the compound. Moreover, it has been solved at 6 different temperatures by single-crystal X-ray diffraction.

Uniaxial contraction is observed, or uniaxial NTE, which is rarely reported for organic compounds. The architecture of the intermolecular interactions in TTYED is similar to the architecture observed in tienoxolol and methanol monohydrate: The two types of hydrogen bond chains in the crystal form a trellis. The weak hydrogen bond chains are positioned in such a way that they induce a contraction in one direction with increasing temperature. Another chain of slightly stronger hydrogen bonds functions as the rotational axis for the mechanism. This scissor or trellis effect has previously only been observed for stronger hydrogen bonds such as $O-H\cdots O$ and $N-H\cdots O$. To our knowledge, this is the first time such a mechanism is reported for weak $C-H\cdots N$ hydrogen bonds.

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