Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Regulated molecular rotor in phase transition materials with switchable dielectric and SHG effect

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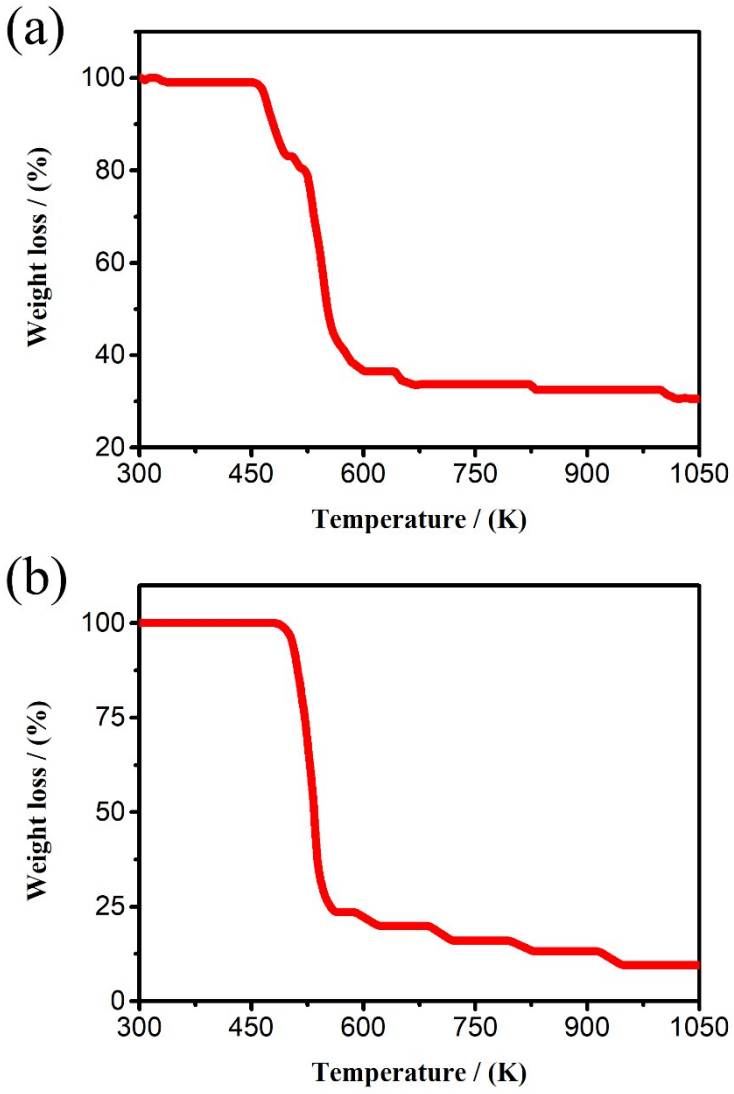

Fig. S1 The thermogravimetric analyses curves of compound (a) Ⅰ and (b) Ⅱ.

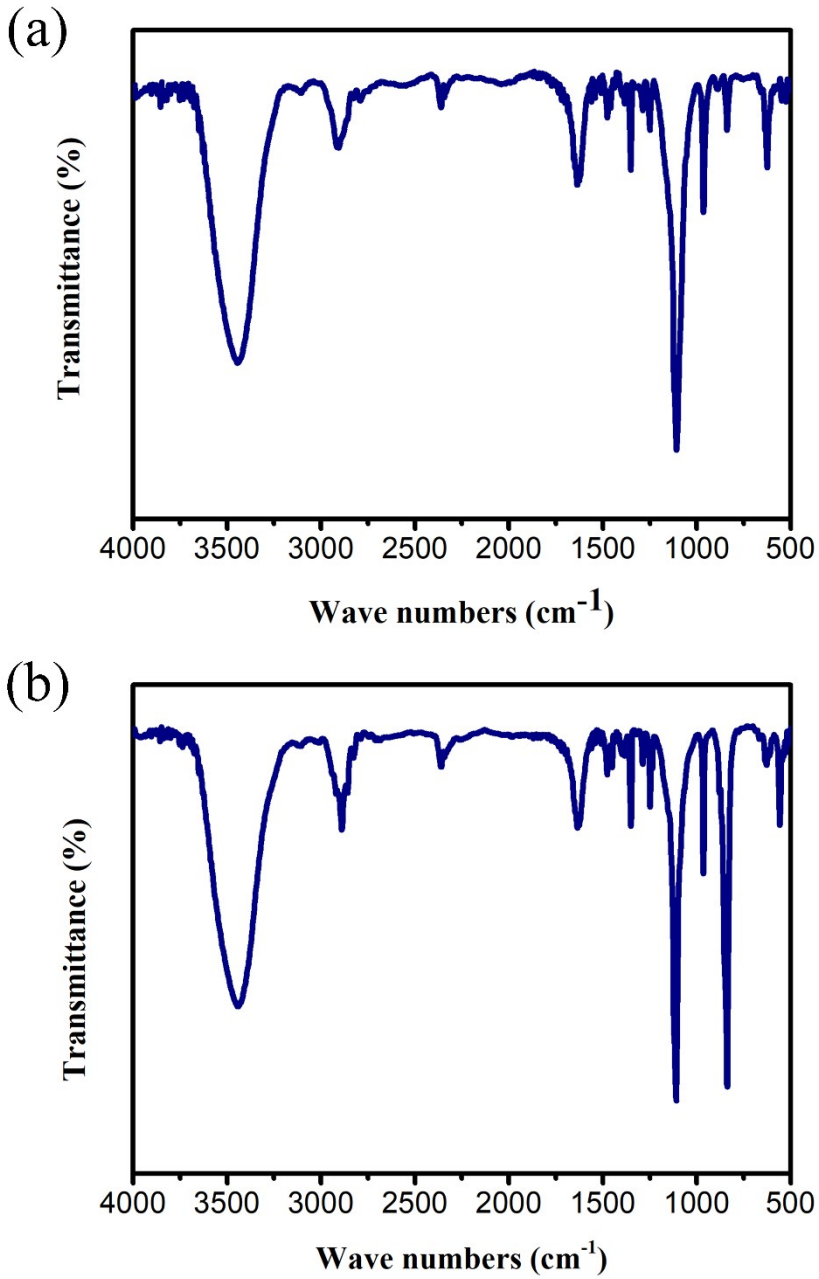

Fig. S2 The IR spectra of compound (a) Ⅰ and (b) Ⅱ.

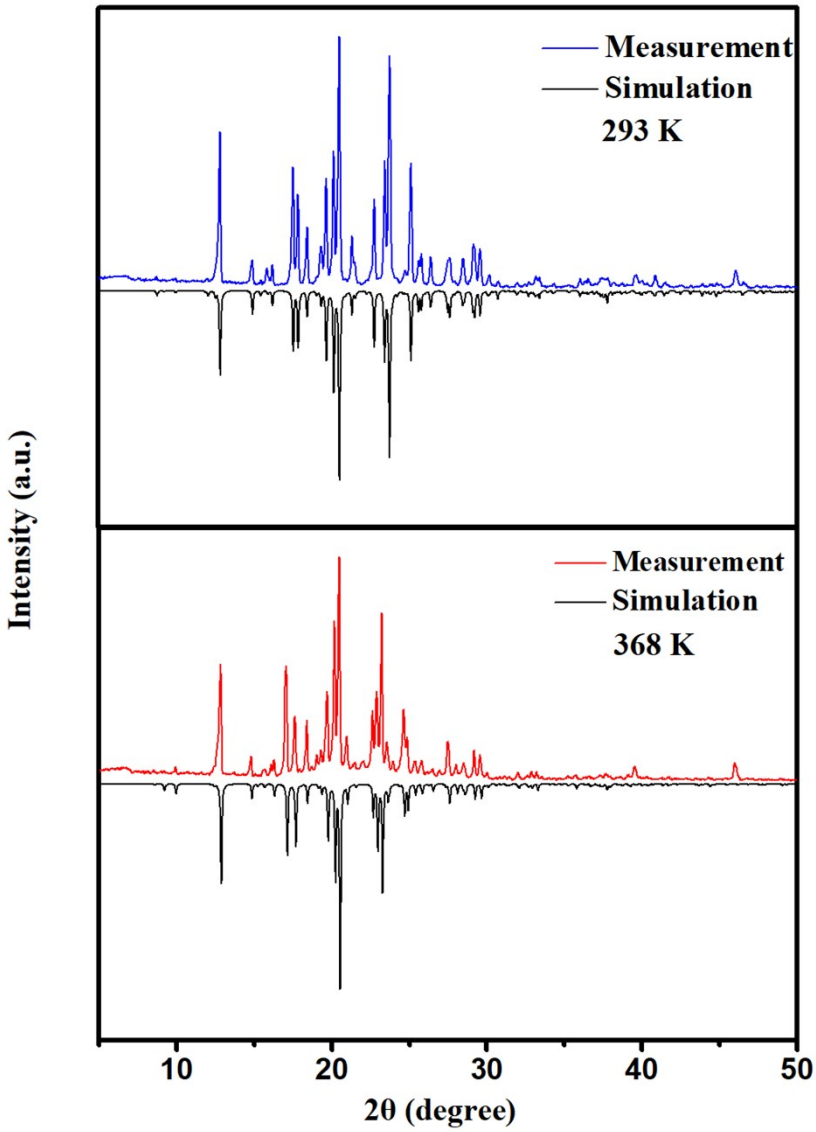

Fig. S3 The PXRD patterns of **Ⅰ** at 293 K and 368 K.

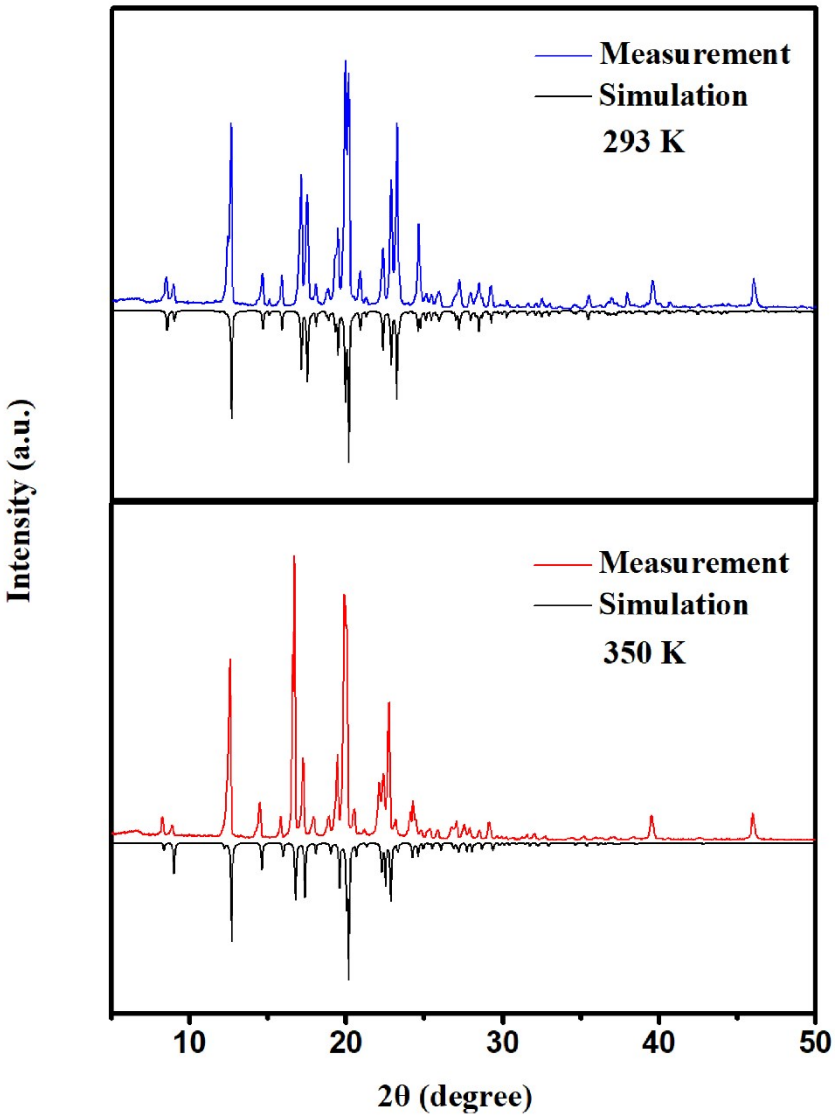

Fig. S4 The PXRD patterns of Ⅱ at 293 K and 350 K.

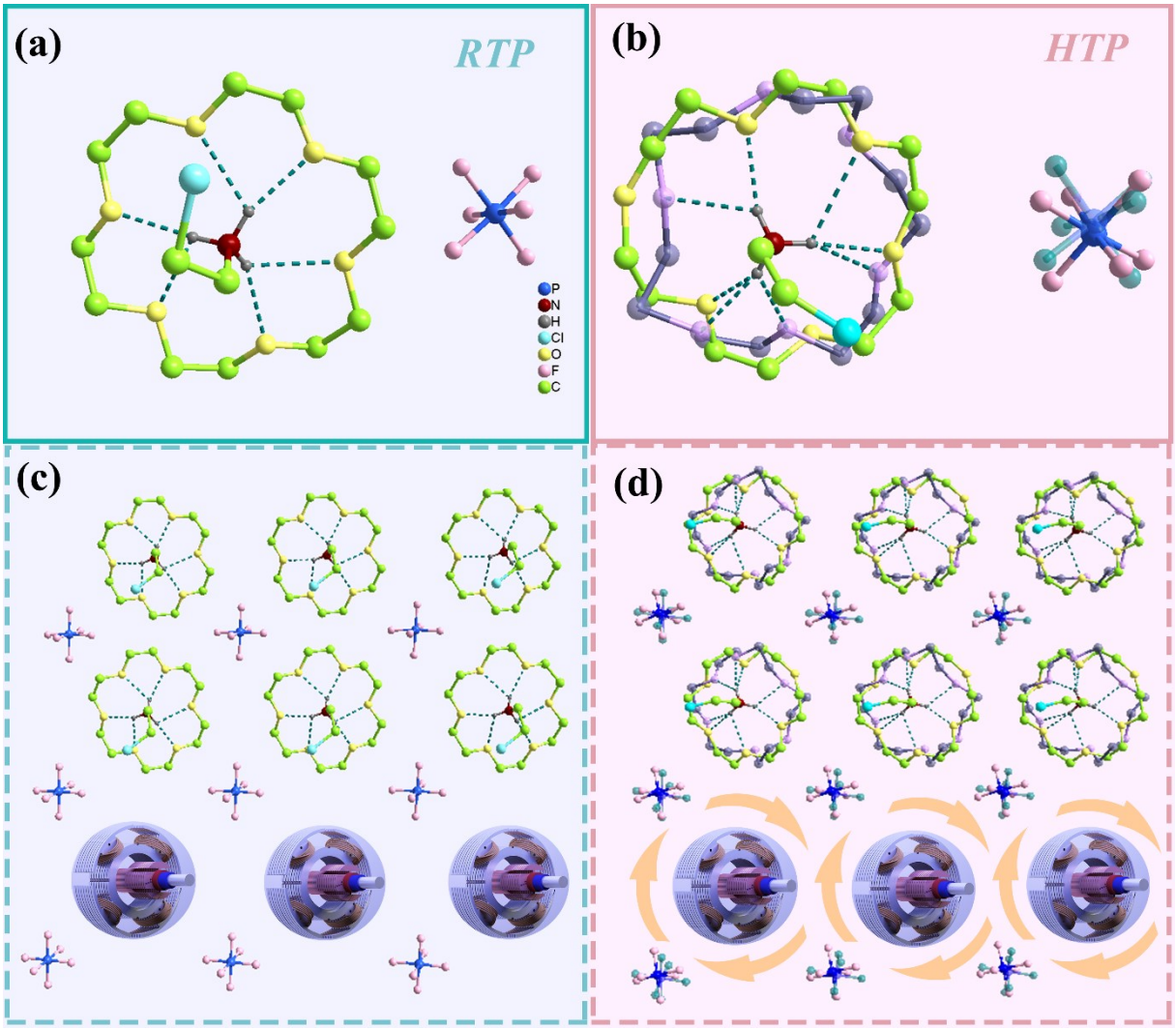

Fig. S5 The asymmetric unit diagrams of compound Ⅱ at (a) 293 K and (b) 350 K, and structural packing diagrams of Ⅱ at (c) 293 K and (d) 350 K. All hydrogen atoms were omitted for clarity.

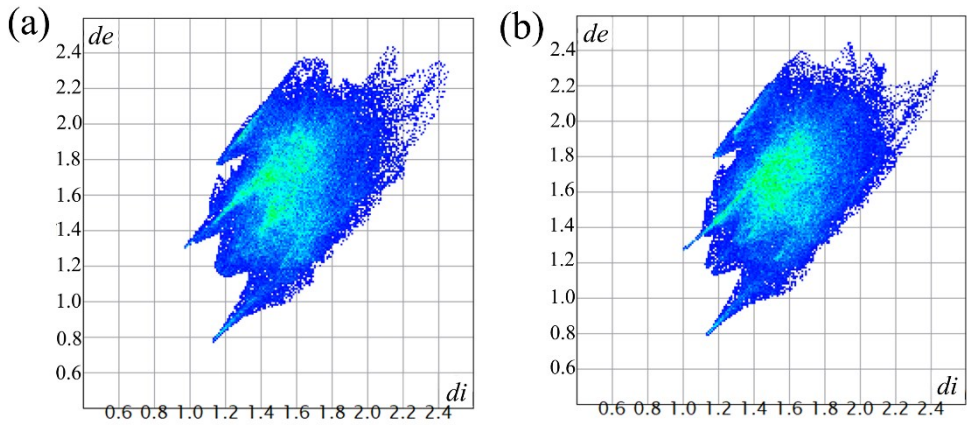

Fig. S6 The 2D fingerprint plots of crown ether ring for (a) Ⅰ and (b) Ⅱ at 293 K.

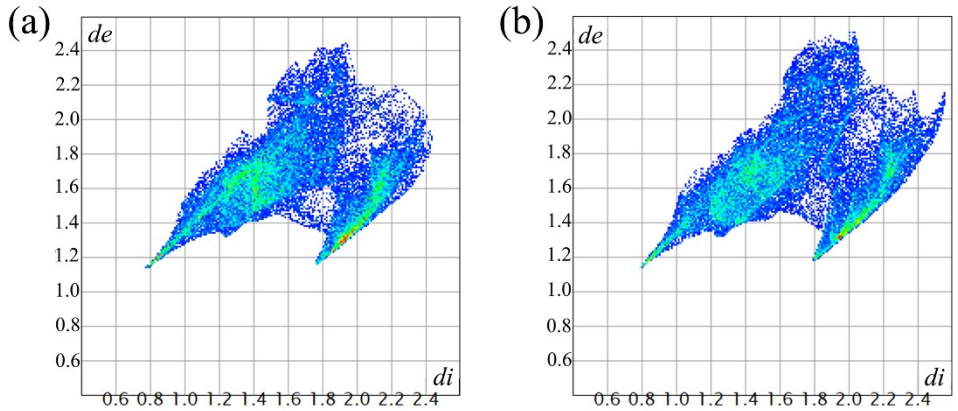

Fig. S7 The 2D fingerprint plots of 2-chloroethylamine cation for (a) Ⅰ and (b) Ⅱ at 293 K.

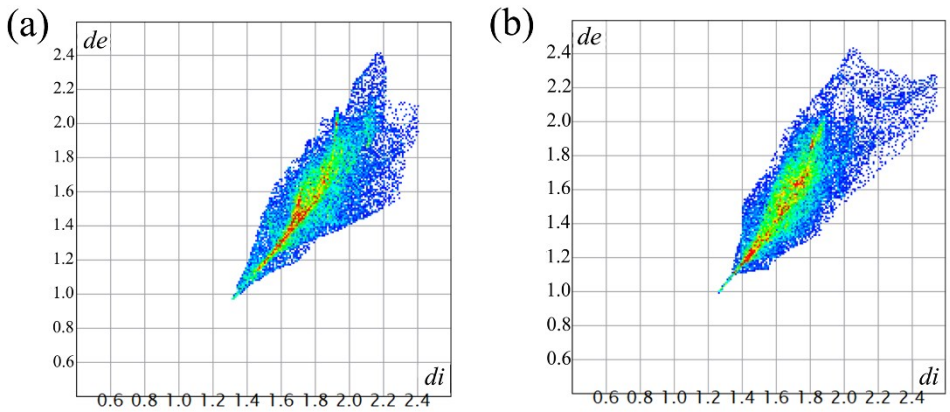

Fig. S8 The 2D fingerprint plots of (a) $[ClO_4]^-$ and (b) $[PF_6]^-$ at 293 K.

Table S1. Crystal data and structure refinements of Ⅰ at 293K and 368K

	RTP(293K)	**HTP(368K)**
Empirical formula	$C_{14}H_{31}O_{10}NCl_2$	$C_{14}H_7O_{10}NCl_2$
Formula weight	444.30	420.11
Temperature(K)	293 K	368 K
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$Pna2_1$
a/Å	9.9191(6)	9.8711(9)
b/Å	10.9587(6)	20.732(3)
c/Å	20.2561(11)	10.8819(19)
Volume/Å^3	2201.8(2)	2226.9(5)
Z	4	4
Radiation type	Mo-Kα	Mo-Kα
Absorption correction	Semi-empirical	Semi-empirical
D_{calc} / g cm−3	1.340	1.232
F(000)	944.0	820.0
GOF	1.039	0.833
R1[I > 2σ(I)]	0.0829	0.1024
wR2[I > 2σ(I)]	0.2679	0.2047

Table S2. Crystal data and structure refinements of Ⅱ at 293K and 350K

	RTP(293K)	**HTP(350K)**
Empirical formula	$C_{14}H_{31}O_6NClPF_6$	$C_{14}H_7O_6NClPF_6$
Formula weight	489.82	465.63
Temperature(K)	293 K	350 K
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$Pna2_1$
a/Å	9.9996(5)	9.9318(8)
b/Å	11.1621(8)	21.1187(17)
c/Å	20.7524(12)	11.087(1)
Volume/Å^3	2316.3(2)	2325.5(3)
Z	4	4
Radiation type	Mo-Kα	Mo-Kα
Absorption correction	Semi-empirical	Semi-empirical
D_{calc} / g cm−3	1.405	1.330
F(000)	1024.0	928.0
GOF	1.032	1.060
R1[I > 2σ(I)]	0.0890	0.1209
wR2[I > 2σ(I)]	0.2970	0.2400

Table S3. The Hydrogen-bond parameters for Ⅰ at 293 K and 368 K

	D—H···A (Å)	H···A (Å)	D···A (Å)	∠(DHA)(°)
293 K	N1-H1A···O1	2.08	2.940(4)	161.1
	N1-H1A···O2	2.40	2.949(4)	120.4
	N1-H1B···O3	2.04	2.921(4)	169.3
	N1-H1B···O4	2.53	2.960(4)	110.2
	N1-H1C···O5	2.12	2.901(4)	146.6
	N1-H1C···O6	2.40	2.905(4)	116.1
368 K	N1-H1A···O1	2.52	3.394(6)	169.2
	N1-H1A···O1′	2.00	2.847(4)	157.8
	N1-H1A···O2	2.41	2.750(6)	103.2
	N1-H1B···O2′	2.43	3.037(5)	125.3
	N1-H1B···O3	2.06	2.909(3)	159.7
	N1-H1C···O5	1.90	2.757(6)	162.4
	N1-H1C···O5′	2.51	3.394(7)	169.5
	N1-H1A···O6	2.54	3.004(5)	112.9
	N1-H1C···O6′	2.43	2.964(5)	118.9

Table S4. The Hydrogen-bond parameters for Ⅱ at 293 K and 350 K

	D—H···A (Å)	H···A (Å)	D···A (Å)	∠(DHA)(°)
293 K	N1-H1A···O1	2.06	2.943(5)	172.6
	N1-H1A···O2	2.46	2.908(5)	111.6
	N1-H1B···O3	2.40	2.961(5)	121.7
	N1-H1B···O4	2.12	2.902(5)	146.0
	N1-H1C···O5	2.48	2.960(5)	114.0
	N1-H1C···O6	2.05	2.898(5)	158.8
350 K	N1-H1A···O1	2.20	3.075(7)	169.0
	N1-H1A···O1′	2.23	2.997(7)	144.7
	N1-H1A···O2	2.53	3.012(9)	114.4
	N1-H1B···O3	2.01	2.795(4)	146.1
	N1-H1B···O4′	2.27	2.855(6)	123.2
	N1-H1C···O5	2.00	2.815(6)	152.4
	N1-H1C···O5′	2.08	2.954(8)	165.6
	N1-H1C···O6′	2.10	2.789(5)	133.6