Ferroelectricity and Switching Polarization on the C-H···π Bond in Pure Organic Molecular Crystal – 1,3,5-Trimethylnitrobenzene

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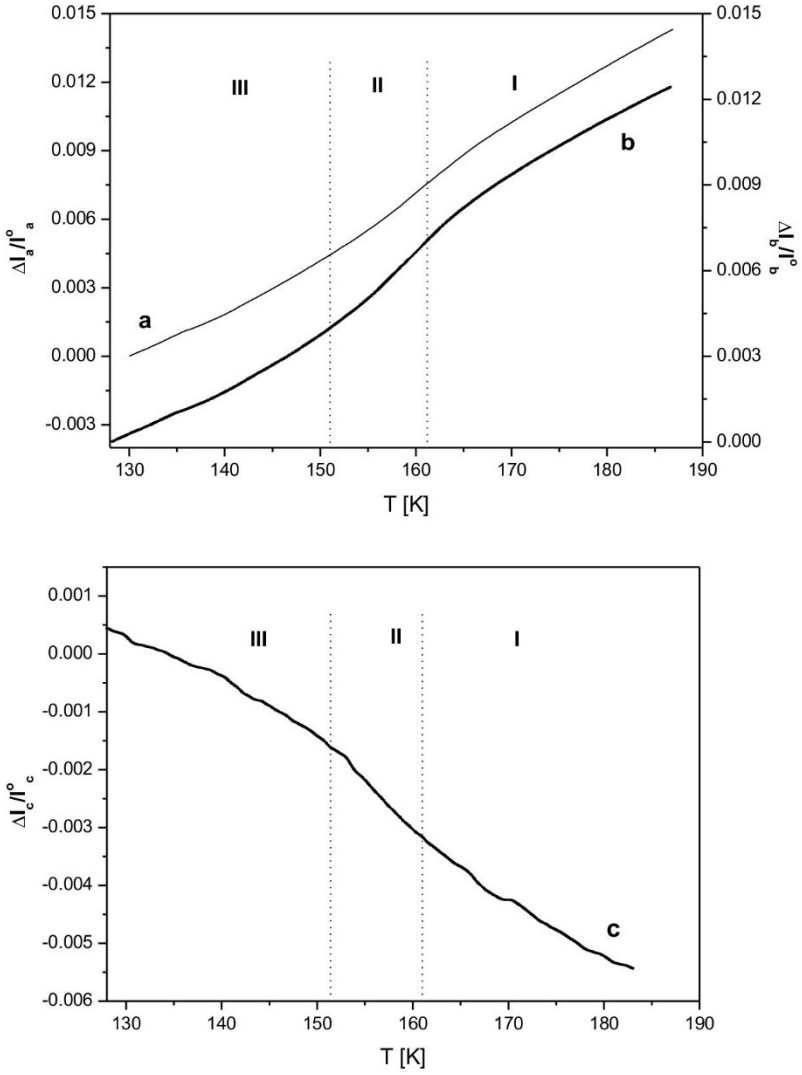

Figure S1. The linear thermal expansion (TMA) measurements results for TMNB.

Table S1. Crystal data, data collection and refinement of **TMNB** in phase **I.**

Crystal data	
Chemical formula	$C_9H_{11}NO_2$
M_r	165.19
Crystal system, space group	Orthorhombic, *Pnma*
Temperature (K)	250
a, b, c (Å)	15.113 (9), 7.205 (4), 8.356 (4)
V (Å^3)	909.9 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.70 × 0.36 × 0.25
Data collection	
Diffractometer	Xcalibur, Atlas
Absorption correction	Analytical
T_{min}, T_{max}	0.961, 0.986
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13691, 1285, 832
R_{int}	0.028
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.691
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.165, 1.06
No. of reflections	1285
No. of parameters	82
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.13, −0.21

Table S2. Crystal data, data collection and refinement of **TMNB** in phase **III.**

Crystal data	
Chemical formula	$C_9H_{11}NO_2$
M_r	165.19
Crystal system, space group	Orthorhombic, $Pca2_1$
Temperature (K)	100
a, b, c (Å)	16.306 (5), 6.980 (2), 15.165 (6)
V (Å^3)	1725.9 (10)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.70 × 0.36 × 0.25
Data collection	
Diffractometer	Xcalibur, Atlas
Absorption correction	Analytical
T_{min}, T_{max}	0.960, 0.985
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25698, 4396, 3554
R_{int}	0.030
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.689
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.120, 1.06
No. of reflections	4396
No. of parameters	223
No. of restraints	1

$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.21
Absolute structure parameter	1.4 (8)

Table S3. Hydrogen-bond geometry (Å, º) for TMNB in phase **I**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O1^{i}	0.94	2.70	3.582 (5)	157
C7—H7*A*···O2^{ii}	0.97	2.67	3.514 (5)	146
C8—H8*B*···C$_g$^{iii}	0.97	2.71	3.634 (2)	160

Symmetry codes: (i) *x*+1/2, *y*, −*z*+3/2; (ii) −*x*, *y*−1/2, −*z*+2; (iii) −*x*, *y*+1/2, −*z*+1.

Table S4. Hydrogen-bond geometry (Å, º) for TMNB in phase **III**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6*A*—H6*A*···O1*A*^{i}	0.95	2.53	3.443 (6)	162
C7*A*—H7*AB*···O2*B*^{ii}	0.98	2.50	3.466 (4)	171
C7*A*—H7*AC*···O1*B*^{iii}	0.98	2.78	3.685 (4)	153
C8*A*—H8*AC*···C$_g$*B*	0.98	2.68	3.593 (3)	155
C6*B*—H6*B*···O1*B*^{iv}	0.95	2.55	3.467 (6)	162
C7*B*—H7*BA*···O2*A*^{v}	0.98	2.58	3.556 (4)	172
C7*B*—H7*BC*···O1*A*^{vi}	0.98	2.72	3.625 (4)	153
C8*B*—H8*BC*···C$_g$*A*	0.98	2.70	3.612 (3)	155

Symmetry codes: (i) −*x*, −*y*+1, *z*+1/2; (ii) *x*−1/2, −*y*, *z*; (iii) *x*−1/2, −*y*+1, *z*; (iv) −*x*+1/2, *y*, *z*−1/2; (v) *x*+1/2, −*y*+1, *z*; (vi) *x*+1/2, −*y*, *z*.