Supporting Information

Steric Guided Anomalous Thermal Expansion in a Dimorphic Organic System

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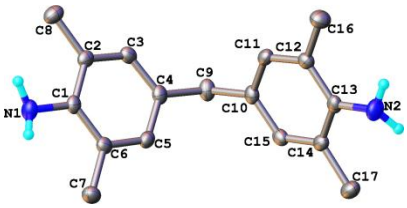
Contents

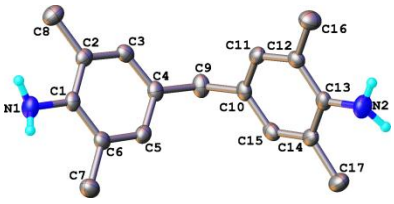
Experimental Details:

Crystallization: Both the polymorphic forms were formed concomitantly when a 2:3 stoichiometric mixture of the **b**enzene-1,3,5-**t**ricarboxylic **a**cid (**BTA**) and 4,4'-**M**ethylene-**b**is(2,6-**d**imethyl**a**niline) (**MBDA**) were crystallized from ethanol. However, the major product of the experiment was a 1:1:1 cocrystal solvate of **BTA**, **MBDA** and ethanol.

X-Ray crystallography:X-ray crystal data were collected on Xcalibur Eos Oxford Diffraction Ltd. with Mo-K_α radiation (λ = 0.71073 Å). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm were applied.[S1] Structure solution and refinement were performed with SHELXS-97[S2] and XL[S3] respectively. Diffraction quality single crystal for both forms I and II polymorphs of **MBDA**, were chosen for the experiments. The crystals were mounted and six data sets were collected for each by cooling the crystals gradually from 298 K to 148 K at 30 K interval. The Form II triclinic crystal could not be cooled below 135 K without avoiding disintegration. The temperature control was performed by cryojet controlling a liquid nitrogen flow. In both the forms, the carbon bonded hydrogen atoms were placed in calculated positions where as the amine hydrogen atoms were isotropically refined. CCDC 948909 – 948920.



MBDA Form I-148 K



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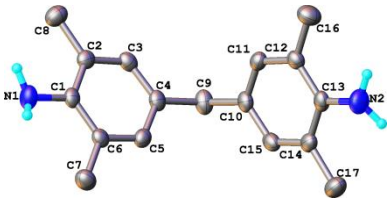

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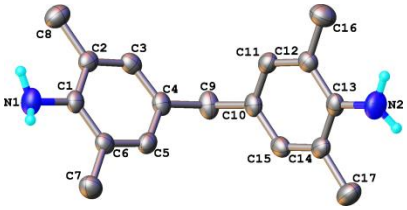
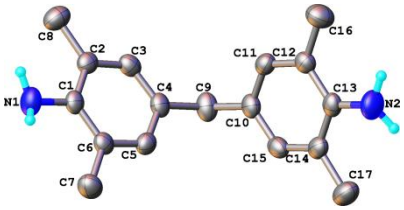
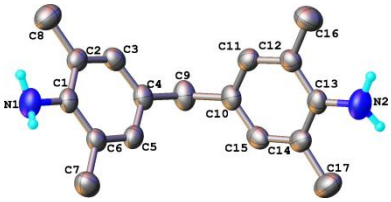


MBDA Form I-238 K

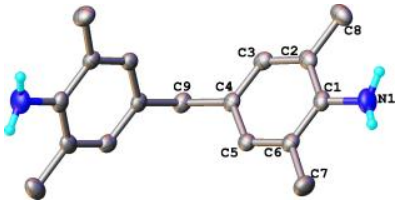


MBDA Form I-268 K

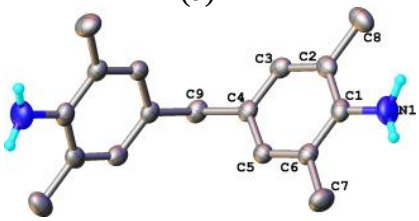


MBDA Form I-298 K

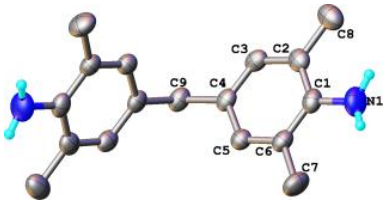
(a)



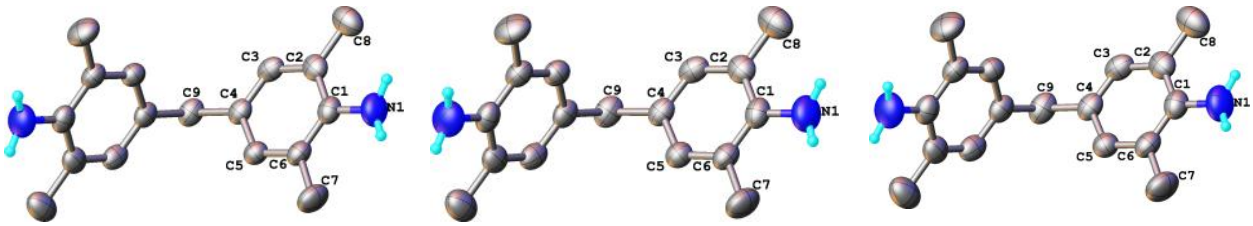
MBDA Form II-148 K



MBDA Form II-178 K



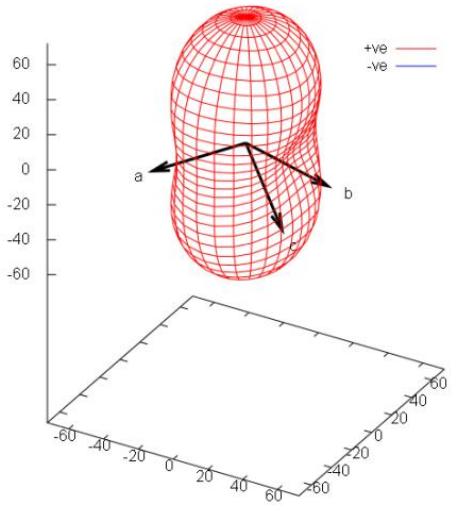
MBDA Form II-208 K



MBDA Form II-238 K **MBDA** Form II-268 K **MBDA** Form II-298 K

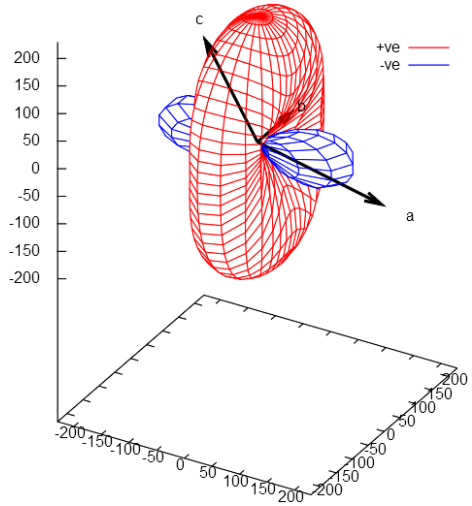
(b)

Figure S1: ORTEP plots for the data at 50 % probability.



α_{X1} 24(6) ($4\bar{2}\bar{3}$)
α_{X2} 43(4) ($2\bar{2}3$)
α_{X3} 70(5) (552)
α_V 146(16)

(a)



α_{X1} -174 (8) (301)
α_{X2} 174 (3) (010)
α_{X3} 229 (3) (102)
α_V 235 (9)

(b)

Figure S2: Thermal expansivity indicatrix for the (a) **MBDA** Form I (triclinic) (b) **MBDA** Form II (monoclinic) systems which is a hypothetical surface obtained by joining the tip of the expansion vectors of the system along every direction. The indicatrix has a unit of MK^{-1}.

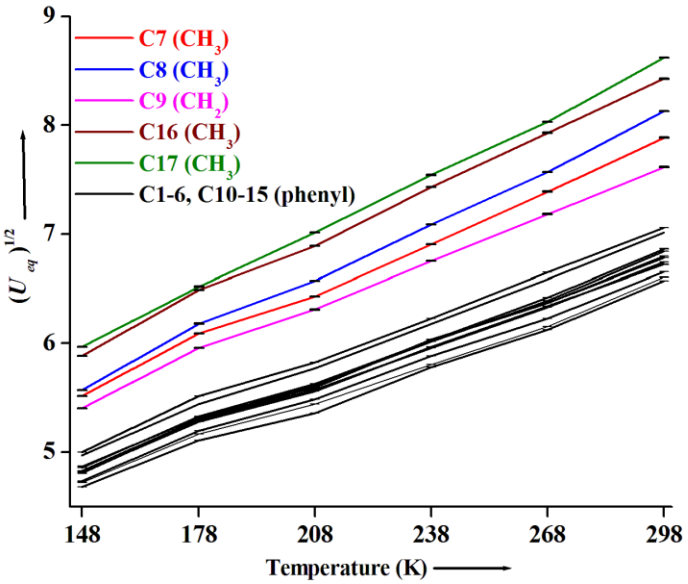


Figure S3: The change in $\sqrt{U_{eq}}$ values with temperature for the different carbon atoms of **MBDA** in Form I. C1-6 and C10-15 (phenyl) represents the carbon atoms forming the aromatic ring of **MBDA**

Table S1:N2–H2A···N1Hydrogen bond interaction inMBDA Form I (Triclinic)						
	148	178	208	238	268	298
N–H *d* *D* *θ*	0.89(2) 2.405(19) 3.2265(18) 154(2)	0.90(2) 2.398(19) 3.233(2) 155(2)	0.89(2) 2.418(19) 3.238(2) 152(2)	0.93(2) 2.39(2) 3.242(2) 153(2)	0.92(2) 2.41(2) 3.252(2) 152(2)	0.95(2) 2.40(2) 3.254(3) 150(2)

Table S2: Aspherism Index (*A*) calculations for the systems	
$A = \frac{2}{3}\left(1 - \frac{3\beta}{\alpha_v^2}\right)^{1/2}$	*A*=Aspherism Index $\beta = \alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_1\alpha_3$ α_i=Coefficient of Expansion (MK^{-1})
MBDA Triclinic Form I $\beta = \alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_1\alpha_3$ = (24x43 + 43x70 + 71x24) = 5722 MK^{-2} α_v^2 = 21316 MK^{-2} $A = \frac{2}{3}\left(1 - \frac{3\times5722}{21316}\right)^{1/2}$ =0.294	**MBDA** Monoclinic Form II $\beta = \alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_1\alpha_3$ = (-174x174 + 174 x 229 + 229 x (-174)) =-30276MK^{-2} α_v^2 = 54756 MK^{-2} $A = \frac{2}{3}\left(1 - \frac{3\times(-30276)}{54756}\right)^{1/2}$ =1.087

Table S3: Anisotropy and volumetric thermal expansion for some reported sets of polymorphs			
Polymorphic modification		Temp. Range (K)	Ratio of volumetric coefficients
α -*p*-Nitroohenol	*β* -*p*-Nitroohenol[S5a]		
α_{X1} = -1 MK^{-1} α_{X2} = 47 MK^{-1} α_{X3} = 109 MK^{-1} α_{v} = 156 MK^{-1}	α_{X1} = 25 MK^{-1} α_{X2} = 28 MK^{-1} α_{X3} = 147 MK^{-1} α_{v} = 203 MK^{-1}	120 to 198	1.30
γ-hexanitrohexaazaisowurtzitane	*ε*-hexanitrohexaazaisowurtzitane[S5b]		
α_{X1} = -6(1) MK^{-1} α_{X2} = 22(1) MK^{-1} α_{X3} = 84(4) MK^{-1} α_{v} = 103(7) MK^{-1}	α_{X1} =20(2) MK^{-1} α_{X2} = 46(2) MK^{-1} α_{X3} = 54(3) MK^{-1} α_{v} = 123(3) MK^{-1}	100 to 298	1.19
CBTA•BPE Form I	CBTA•BPE Form I[S5c]		
α_{X1} = 4(5) MK^{-1} α_{X2} = 25(4) MK^{-1} α_{X3} = 147(8) MK^{-1} α_{v} = 183(14) MK^{-1}	α_{X1} = -4(5) MK^{-1} α_{X2} = 18(5) MK^{-1} α_{X3} = 136(5) MK^{-1} α_{v} = 158(15) MK^{-1}	120 to 298	1.16
(S,S)-3,5-octadiyn-2,7-diol(HT)[S5d]	(S,S)-3,5-octadiyn-2,7-diol(LT)[S5e]		
α_{X1} = -205(24) MK^{-1} α_{X2} = -77(16) MK^{-1} α_{X3} = 562(49) MK^{-1} α_{v} = 271(10) MK^{-1}	α_{X1} = -15(8) MK^{-1} α_{X2} = 22(1) MK^{-1} α_{X3} = 191(22) MK^{-1} α_{v} = 202(13) MK^{-1}	225 to 315	1.34
MBDA Form I	**MBDA** Form II*		
α_{X1} = 24(6) α_{X2} = 43(4) α_{X3} = 70(5) α_{v} = 146(16)	α_{X1} = -174 (8) α_{X2} = 174 (3) α_{X3} = 229 (3) α_{v} = 234 (9)	148 to 298	1.60
*Work discussed in this report.			

Table S4: Crystallographic details for the systems at different temperatures						
MBDA Form I, Triclinic						
Temperature (K)	**148**	**178**	**208**	**238**	**268**	**298**
Formula	$C_{17}H_{22}N_2$	$C_{17}H_{22}N_2$	$C_{17}H_{22}N_2$	$C_{17}H_{22}N_2$	$C_{17}H_{22}N_2$	$C_{17}H_{22}N_2$
*M*r	254.37	254.37	254.37	254.37	254.37	254.37
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.2122(7)	8.2145(7)	8.2268(7)	8.2384(8)	8.2565(8)	8.2504(9)
b (Å)	9.0548(5)	9.0601(6)	9.0703(6)	9.0950(6)	9.1147(6)	9.1159(7)
c (Å)	11.4228(7)	11.4225(8)	11.4426(8)	11.4600(8)	11.4695(8)	11.4622(9)
α(°)	93.672(5)	93.690(6)	93.691(5)	93.700(6)	93.722(5)	93.800(7)

β (°)	110.255(7)	110.215(7)	110.218(7)	110.161(8)	110.153(8)	110.087(9)
γ(°)	108.406(6)	108.361(7)	108.335(6)	108.267(7)	108.221(7)	108.151(9)
V (Å^3)	741.63(9)	742.67(10)	746.06(9)	750.96(10)	755.11(10)	754.71(12)
Crystal size	0.42 x 0.38 x 0.36	0.42 x 0.38 x 0.36	0.42 x 0.38 x 0.36	0.42 x 0.38x 0.36	0.42 x 0.38 x 0.36	0.42 x 0.38 x 0.36
ρ (g/cc)	1.139	1.137	1.132	1.125	1.119	1.119
T (K)	148 (2)	178 (2)	208 (2)	238 (2)	268 (2)	298 (2)
Z	2	2	2	2	2	2
F(000)	276	276	276	276	276	276
μ(mm^{-1})	0.067	0.067	0.067	0.066	0.066	0.066
Ref. collected/unique	6918/3356	7177/3399	7125/3372	7096/3406	6901/3386	7173/3453
Parameters	192	192	192	192	192	192
Final R indices [I>2σ(I)]	0.0435	0.0450	0.0461	0.0483	0.0488	0.0516
R indices (all data)	0.1123	0.1174	0.1221	0.1282	0.1322	0.1420
Goodness of fit on F^2	1.027	1.052	1.032	1.023	1.031	1.042

MBDA Form II, Monoclinic						
Temperature (K)	**148**	**178**	**208**	**238**	**268**	**298**
Formula	C_{17} H_{22} N_2	C_{17} H_{22} N_2	C_{17} H_{22} N_2	C_{17} H_{22} N_2	C_{17} H_{22} N_2	C_{17} H_{22} N_2
*M*r	254.37	254.37	254.37	254.37	254.37	254.37
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C2/c*	*C2/c*	*C2/c*	*C2/c*	*C2/c*	*C2/c*
a (Å)	17.9670(12)	17.9037(14)	17.8536(16)	17.7463(14)	17.6512(18)	17.5602(17)
b (Å)	7.9756(6)	8.0121(8)	8.0700(6)	8.0930(7)	8.1468(5)	8.1816(6)
c (Å)	14.0251(8)	14.0696(9)	14.1329(11)	14.1825(9)	14.2338(10)	14.2820(10)
α(°)	90.00	90.00	90.00	90.00	90.00	90.00
β (°)	133.571(4)	133.440(4)	133.271(5)	133.117(4)	132.931(6)	132.800(5)
γ(°)	90.00	90.00	90.00	90.00	90.00	90.00
V (Å^3)	1456.11(17)	1465.4(2)	1482.65(19)	1486.85(19)	1498.6(2)	1505.5(2)
Crystal size	0.44 x 0.34 x 0.3	0.44 x 0.34 x 0.3	0.44 x 0.34 x 0.3	0.44 x 0.34 x 0.3	0.44 x 0.34 x 0.3	0.44 x 0.34 x 0.3
ρ (g/cc)	1.160	1.153	1.140	1.136	1.127	1.122
T (K)	148 (2)	178 (2)	208 (2)	238 (2)	268 (2)	298 (2)
Z	4	4	4	4	4	4
F(000)	552	552	552	552	552	552

μ(mm^{-1})	0.068	0.068	0.067	0.067	0.066	0.066
Ref. collected/unique	3828/1675	3773/1701	3663/1696	3700/1712	3909/1728	3767/1732
Parameters	97	97	97	97	97	97
Final R indices [I>2σ(I)]	0.0426	0.0497	0.0530	0.0584	0.0544	0.0563
R indices (all data)	0.1115	0.1451	0.1393	0.1662	0.1361	0.1663
Goodness of fit on F^2	1.041	1.051	1.035	1.021	1.014	1.019

Reference:

S1.CrysAlisPro, Version 1.171.33.66; Oxford Diffraction Ltd.: Abingdon, U.K., 2010.

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S5.(a) N. B. Bolotina, M. J. Hardie, R. L. Speer Jr and A. A. Pinkerton, *J. Appl. Cryst.*, 2004, **37**, 808 – 814. (b) G. Wójcik and I. Mossakowska, *ActaCryst.*, 2006, **B62**, 143 – 152. (c) S. Bhattacharya and B. K. Saha, *Cryst.Growth Des.*, 2013, **13**, 3299 – 3302.(d) D. Das, T. Jacobs and L. J. Barbour**,** *Nat. Mater.*, 2010, **9**, 36 – 39. (e) D. Das, T. Jacobs, A. Pietraszko and L. J. Barbour, *Chem. Commun.*, 2011, **47**, 6009 – 6011.