Supporting information

Understanding the elastic bending mechanism in anthraquinone crystal through thermal expansion study

Sumair A. Rather and Binoy K. Saha*

Contents:

Experimental: X-ray crystallography.

Table S1. Crystallographic details of the Anthraquinone at different temperatures.

Table S2. Thermal expansion coefficient values along the principal axes and volumetric thermal expansion coefficients calculated using PASCal program.

Table S3. Angles (θ) between the molecular planes during the process of actual thermal expansion experimentally obtained, calculated for hypothetical thermal expansion and bending for different *b*-axis lengths (b) in case of $Cu(acac)_2$.

Table S4. Angles (θ) between the molecular planes during the process of actual thermal expansion experimentally obtained and calculated for hypothetical thermal expansion for different *b*-axis lengths (b) in case of 9,10-anthraquinone.

Fig. S1 (a) Molecular stacking along the bending axis (a-axis) of 4-chlorobenzonitrile. (b) Schematic diagram of thermal expansion along the bending axis in 4-chlorobenzonitrile crystal structure.

Fig. S2 Similarity in the molecular packing diagrams of $Cu(acac)_2$ and 9,10-anthraquinone.

Experimental

X-ray crystallography: X-ray crystal data analysis were performed on Xcalibur Eos Oxford-Rigaku Diffraction Ltd. With Mo- Kα radiation (λ = 0.71073 A). Temperature was mentained with an Oxford Cryojet HT instrument. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm were applied.[S1] Structural analysis and refinement were performed with SHELXS[S2] and SHELXL[S2] respectively using Olex2-1.1 software package[S3]. Hydrogen atoms attached to the carbon atoms were placed in the calculated positions using riding model.

Table S1. Crystallographic details of the anthraquinone at different temperatures.

Identification code	Anthraquinone-163K	Anthraquinone-178K	Anthraquinone-193K	Anthraquinone-208K	Anthraquinone-223K
Empirical formula	$C_{14}H_8O_2$	$C_{14}H_8O_2$	$C_{14}H_8O_2$	$C_{14}H_8O_2$	$C_{14}H_8O_2$
Formula weight	208.20	208.20	208.20	208.20	208.20
Temperature/ K	163	178	193	293	223
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	7.8780(6)	7.8729(8)	7.8702(9)	7.8846(8)	7.8876(7)
b/Å	3.9147(4)	3.9195(5)	3.9302(6)	3.9372(5)	3.9434(4)
c/Å	15.6886(14)	15.7126(18)	15.732(2)	15.754(2)	15.7578(19)
α/°	90	90	90	90	90
β/°	102.569(7)	102.604(10)	102.573(12)	102.594(12)	102.624(11)
γ/°	90	90	90	90	90
Volume/Å^3	472.24(7)	473.18(9)	474.93(12)	477.29(11)	478.28(9)
Z	2	2	2	2	2
ρ_{calc}g/cm^3	1.464	1.461	1.456	1.449	1.446
μ/mm^{-1}	0.098	0.098	0.097	0.097	0.097
F(000)	216.0	216.0	216.0	216.0	216.0
Crystal size/mm^3	0.62 × 0.2 × 0.16	0.62 × 0.26 × 0.16	0.62 × 0.26 × 0.16	0.62 × 0.26 × 0.16	0.62 × 0.26 × 0.16
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.642 to 58.518	6.638 to 58.09	6.636 to 58.044	6.624 to 58.62	6.622 to 58.598
Index ranges	$-9 \le h \le 10$, $-5 \le k \le 5$, $-20 \le l \le 19$	$-10 \le h \le 4$, $-4 \le k \le 5$, $-19 \le l \le 20$	$-10 \le h \le 4$, $-4 \le k \le 5$, $-19 \le l \le 20$	$-10 \le h \le 5$, $-4 \le k \le 5$, $-20 \le l \le 20$	$-10 \le h \le 5$, $-4 \le k \le 5$, $-20 \le l \le 20$
Reflections collected	4856	2132	2118	2138	2167

Independent reflections	1137 [R_{int} = 0.0315, R_{sigma} = 0.0307]	1029 [R_{int} = 0.0248, R_{sigma} = 0.0477]	1034 [R_{int} = 0.0241, R_{sigma} = 0.0482]	1046 [R_{int} = 0.0496, R_{sigma} = 0.0937]	1049 [R_{int} = 0.0319, R_{sigma} = 0.0541]
Data/restraints /parameters	1137/0/73	1029/0/73	1034/0/73	1046/0/73	1049/0/73
Goodness-of-fit on F^2	1.054	1.008	0.995	0.890	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.1146	R_1 = 0.0512, wR_2 = 0.1230	R_1 = 0.0520, wR_2 = 0.1191	R_1 = 0.0554, wR_2 = 0.0911	R_1 = 0.0533, wR_2 = 0.1138
Final R indexes [all data]	R_1 = 0.0624, wR_2 = 0.1295	R_1 = 0.0773, wR_2 = 0.1443	R_1 = 0.0841, wR_2 = 0.1411	R_1 = 0.1259, wR_2 = 0.1103	R_1 = 0.0904, wR_2 = 0.1367
CCDC no.	2075695	2075696	2075697	2075698	2075699

Cont…

Identification code	Anthraquinone-238K	Anthraquinone-253K	Anthraquinone-268K	Anthraquinone-283K	Anthraquinone-298K
Empirical formula	$C_{14}H_8O_2$	$C_{14}H_8O_2$	$C_{14}H_8O_2$	$C_{14}H_8O_2$	$C_{14}H_8O_2$
Formula weight	208.20	208.20	208.20	208.20	208.20
Temperature/ K	238	293	268	293	298
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	7.8864(7)	7.8758(8)	7.8728(7)	7.8868(10)	7.8662(4)
b/Å	3.9488(5)	3.9534(5)	3.9608(5)	3.9718(5)	3.9660(3)
c/Å	15.774(2)	15.7573(16)	15.7845(19)	15.822(2)	15.7823(11)
α/°	90	90	90	90	90
β/°	102.624(10)	102.653(10)	102.664(9)	102.719(13)	102.696(6)
γ/°	90	90	90	90	90
Volume/$Å^3$	479.35(9)	478.71(9)	480.23(10)	483.47(11)	480.32(6)
Z	2	2	2	2	2
$\rho_{calc}g/cm^3$	1.443	1.444	1.440	1.430	1.440
μ/mm^{-1}	0.096	0.097	0.096	0.096	0.096
F(000)	216.0	216.0	216.0	216.0	216.0
Crystal size/mm^3	0.62 × 0.26 × 0.16	0.62 × 0.26 × 0.16	0.62 × 0.26 × 0.16	0.62 × 0.26 × 0.16	0.62 × 0.26 × 0.16
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)

2Θ range for data collection/°	6.618 to 58.716	6.626 to 58.474	6.62 to 57.748	6.604 to 58.25	6.622 to 58.3
Index ranges	$-5 \le h \le 10$, $-4 \le k \le 5$, $-20 \le l \le 20$	$-10 \le h \le 5$, $-5 \le k \le 5$, $-20 \le l \le 21$	$-8 \le h \le 10$, $-4 \le k \le 5$, $-21 \le l \le 15$	$-8 \le h \le 10$, $-4 \le k \le 5$, $-21 \le l \le 13$	$-10 \le h \le 10$, $-5 \le k \le 5$, $-20 \le l \le 20$
Reflections collected	2164	2125	2169	2223	4877
Independent reflections	1052 [R_{int} = 0.0250, R_{sigma} = 0.0414]	1072 [R_{int} = 0.0264, R_{sigma} = 0.0534]	1078 [R_{int} = 0.0303, R_{sigma} = 0.0561]	1086 [R_{int} = 0.0337, R_{sigma} = 0.0614]	1172 [R_{int} = 0.0283, R_{sigma} = 0.0253]
Data/restraints/parameters	1052/0/73	1072/0/73	1078/0/73	1086/0/73	1172/0/73
Goodness-of-fit on F^2	1.036	1.022	1.003	1.005	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0489, wR_2 = 0.1093	R_1 = 0.0551, wR_2 = 0.1230	R_1 = 0.0547, wR_2 = 0.1249	R_1 = 0.0572, wR_2 = 0.1209	R_1 = 0.0467, wR_2 = 0.1153
Final R indexes [all data]	R_1 = 0.0800, wR_2 = 0.1304	R_1 = 0.0956, wR_2 = 0.1554	R_1 = 0.1077, wR_2 = 0.1601	R_1 = 0.1200, wR_2 = 0.1616	R_1 = 0.0724, wR_2 = 0.1374
CCDC no.	2075700	2075701	2075702	2075703	2075704

Table S2. Thermal expansion coefficient values along the principal axes and volumetric thermal expansion coefficients calculated using PASCal program.

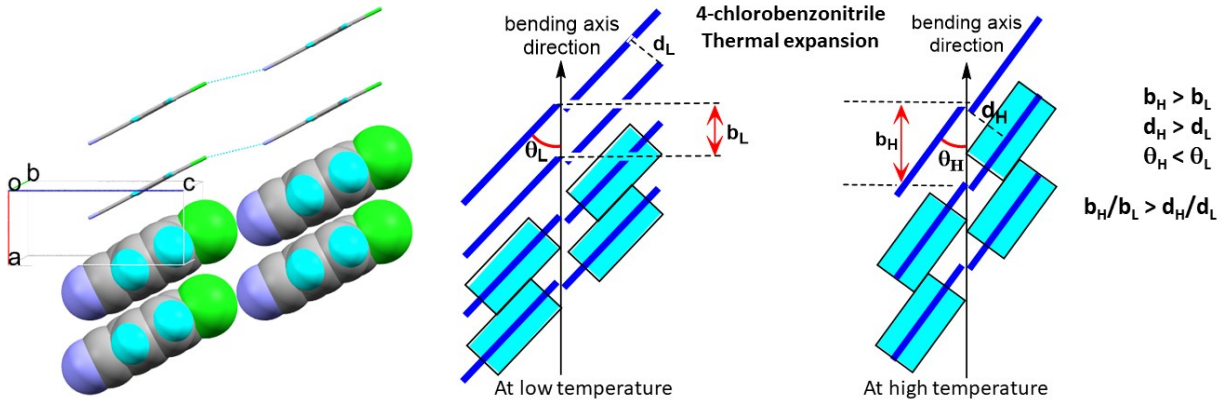
	$\alpha_{X1}(\sigma)$ [direction]	$\alpha_{X2}(\sigma)$ [direction]	$\alpha_{X3}(\sigma)$ [direction]	$\alpha_V(\sigma)$
Anthraquinone	-1(5) [100]	46(5) [105]	104(6) [010]	160(13)

Table S3. Angles (θ) between the molecular planes during the process of actual thermal expansion experimentally obtained, calculated for hypothetical thermal expansion and bending for different *b*-axis lengths (b) in case of $Cu(acac)_2$.

	Thermal expansion of $Cu(acac)_2$					Bending of $Cu(acac)_2$		
Temperature (K)	*b*-axis length (b)	Interplanar distance (d)	Molecular plane to the *b*-axis angle (θ)			*b*-axis length (b)	θ	points
			Actual thermal expansion	Hypothetical Thermal expansion				
100	4.6106	2.993	40.48	40.48		4.708	40.21	a
110	4.6401	3.011	40.47	40.17		4.700	39.60	b
120	4.6276	2.993	40.29	40.30		4.691	39.70	c
130	4.632	3.000	40.38	40.26		4.683	39.93	d
140	4.6387	3.007	40.41	40.19		4.674	40.09	e
150	4.6481	3.015	40.45	40.09		4.664	40.10	f
160	4.6522	3.018	40.45	40.05		4.654	40.16	g
170	4.6599	3.027	40.51	39.97		4.643	40.33	h
180	4.6583	3.021	40.44	39.99		4.629	40.50	i
190	4.6684	3.031	40.49	39.89		4.618	40.64	j
200	4.6743	3.035	40.49	39.82		4.605	40.73	k
210	4.6771	3.037	40.49	39.79		4.594	40.68	l
220	4.6813	3.042	40.54	39.75		4.58	40.88	m
230	4.6853	3.044	40.52	39.71		4.573	41.10	n
240	4.689	3.048	40.51	39.67		4.563	41.12	o
250	4.6944	3.051	40.54	39.62		4.558	41.21	P
260	4.6956	3.05	40.52	39.60				
270	4.6971	3.055	40.58	39.59				
280	4.7013	3.063	40.65	39.55				
290	4.7032	3.063	40.64	39.53				
300	4.7121	3.071	40.68	39.44				

Table S4. Angles (θ) between the molecular planes during the process of actual thermal expansion experimentally obtained and calculated for hypothetical thermal expansion for different *b*-axis lengths (b) in case of 9,10-anthraquinone.

Temperature (K)	*b*-axis length (b)	Interplanar distance (d)	Molecular plane to the *b*-axis angle (θ)	
			Actual thermal expansion	Hypothetical Thermal expansion
163	3.915	3.495	63.22	64.46
178	3.92	3.499	63.22	64.30
193	3.93	3.508	63.19	64.00
208	3.937	3.512	63.12	63.80
223	3.943	3.517	63.11	63.62
238	3.949	3.521	63.08	63.44
253	3.953	3.524	63.06	63.33
268	3.961	3.530	63.03	63.10
283	3.972	3.539	63.01	62.79
298	3.966	3.532	62.96	62.96



(a) (b)

Fig. S1 (a) Molecular stacking along the bending axis (a-axis) of 4-chlorobenzonitrile. (b) Schematic diagram of thermal expansion along the bending axis in 4-chlorobenzonitrile crystal structure.

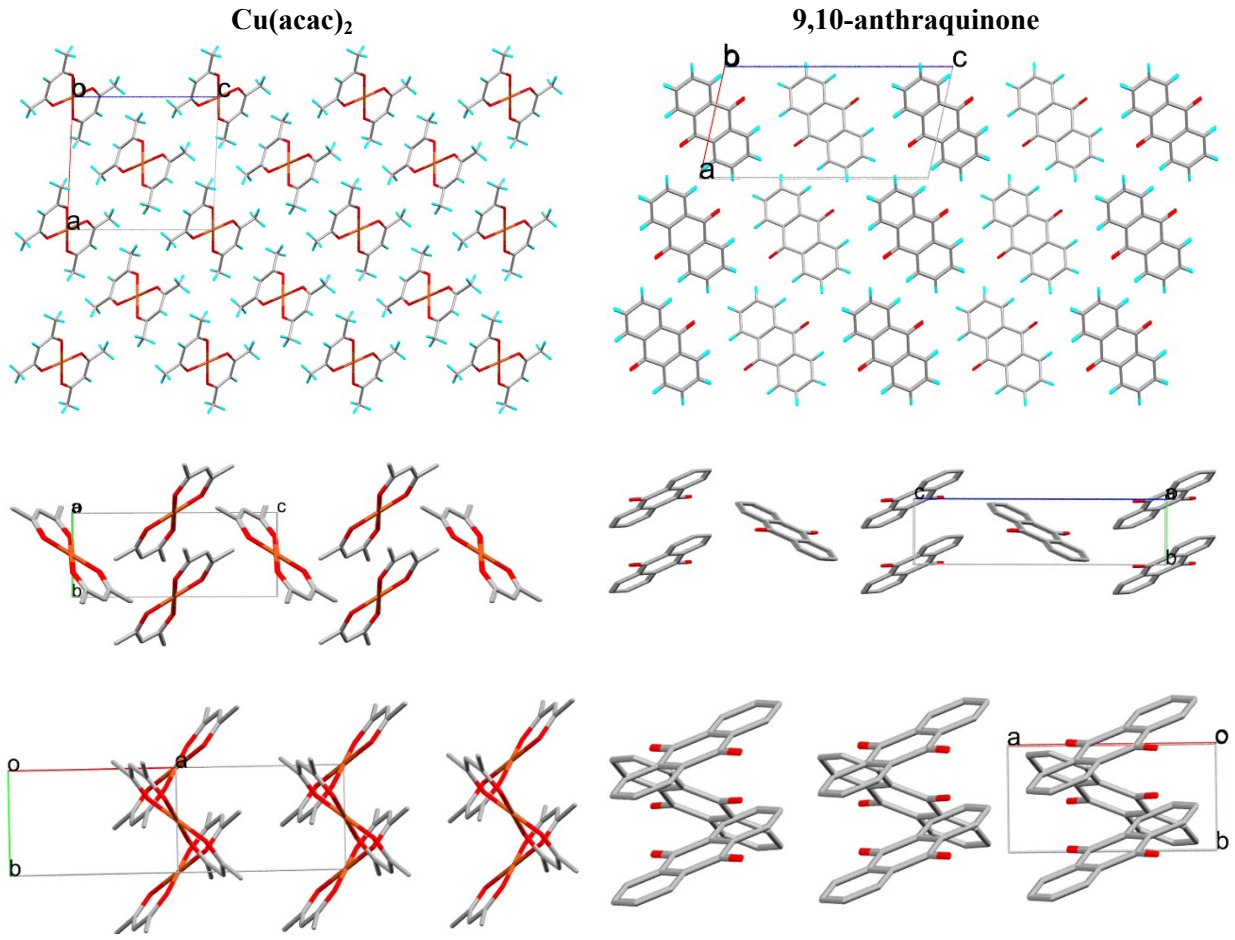


Fig. S2 Similarity in the molecular packing diagrams of $Cu(acac)_2$ and 9,10-anthraquinone.

References:

S1. *CrysAlisPro, Version 1.171.33.66*, Oxford Diffraction Ltd,Abingdon, UK, 2010.

S2. G.M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.

S3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.