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Deuterated γ–Malonic Acid: Its Neutron Crystal Structure in Relationship to Other Polymorphs of Aliphatic Dicarboxylic Acids

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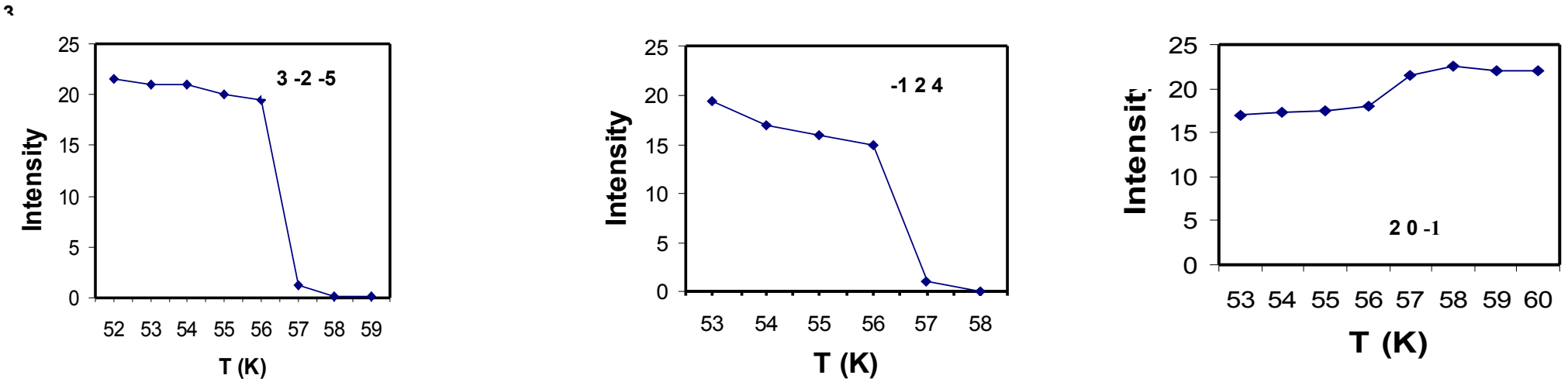

Fig. 1S Intensity *I vs* temperature *K* for super-lattice reflections 3 -2 -5 *(left),* -1 2 4 *(center)* and 2 0 -1 *(right)* near the temperature of the γ to β transition.

Table 1S. Nuclear positional (x10^5) and anisotropic displacement parameters (T_2: Å^2 x 10^4; T_3: x 10^7). The temperature factor is expressed as $T = T_2 (1+T_3)$, with $T_2 = \exp(-2\pi^2 \sum_i \sum_j h_i h_j a_i^{\cdot} a_j^{\cdot} U_{ij})$ and $T_3 = -\frac{4}{3}\pi^3 i \sum_j \sum_k \sum_l h_j h_k h_l c_{jkl})$

(a) β-malonic acid at 153K

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C0	60455(14)	12563(10)	24685(7)	309(5)	195(2)	123(2)	155(2)	34(2)	145(2)	43(2)
C1	57591(13)	30175(10)	36341(6)	247(4)	136(2)	114(2)	126(2)	25(2)	106(2)	43(2)
C2	55587(14)	28324(10)	13513(7)	255(4)	152(2)	136(2)	126(2)	17(2)	112(2)	35(2)
O11	55832(17)	54299(12)	37553(8)	362(6)	207(3)	115(2)	184(3)	35(2)	167(3)	47(2)
O12	57234(54)	16539(40)	44577(26)	531(8)	285(3)	131(3)	215(3)	55(2)	220(3)	70(2)
O21	80655(53)	41329(42)	18450(25)	463(7)	145(3)	379(4)	210(3)	19(3)	110(2)	171(3)
O22	21696(54)	26759(50)	-1903(29)	343(6)	172(3)	313(3)	154(3)	-51(3)	82(3)	94(3)
D12	53710(22)	28112(18)	51686(12)	552(8)	337(5)	204(4)	268(4)	55(3)	258(4)	76(3)
D21	19880(22)	38515(23)	-8380(13)	451(7)	239(4)	374(5)	211(4)	-13(3)	135(3)	123(3)
D01	87582(22)	5620(15)	33327(10)	742(10)	318(5)	314(4)	325(4)	177(3)	266(4)	188(3)
D02	39743(24)	-4627(14)	16512(10)	431(7)	410(5)	197(4)	285(4)	-66(3)	269(4)	-6(3)

	C_{111}	C_{222}	C_{333}	C_{112}	C_{122}	C_{113}	C_{133}	C_{223}	C_{233}	C_{123}
O21	**-55(56)**	-184(28)	-34(7)	-29(22)	-118(18)	-35(22)	-34(11)	-125(10)	-60(63)	-49(10)

(b) γ-malonic acid. Parameter values at 56K and 50K are listed on the first and second lines, resp.

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C0A	4205(7)	11896(9)	23879(6)	194(3)	125(2)	79(2)	92(2)	21(2)	92(2)	30(1
	3930(9)	11744(12)	23688(8)	148(2)	91(3)	58(2)	74(2)	15(2)	71(2)	16(2
C1A	3183(6)	29815(9)	35818(6)	138(2)	87(2)	71(2)	68(2)	9(1)	63(1)	23(1
	3043(8)	29771(12)	35716(8)	111(2)	67(2)	51(2)	57(2)	4(2)	53(2)	10(2
C2A	2027(6)	27620(9)	12820(6)	165(2)	97(2)	91(2)	77(2)	15(1)	72(2)	10(2
	1821(8)	27417(12)	12644(8)	122(2)	65(3)	67(2)	57(2)	10(2)	50(2)	13(2

O11A	3222(8)	54172(11)	37671(7)	188(3)	125(2)	73(2)	98(2)	14(2)	94(2)	27(2
	3285(10)	54168(14)	37702(9)	169(3)	96(3)	52(3)	77(3)	9(2)	72(3)	10(2
O12A	2349(8)	16217(11)	43784(8)	233(4)	161(2)	77(2)	109(2)	22(2)	118(2)	36(2
	2100(10)	16141(14)	43609(10)	218(4)	140(3)	57(3)	97(3)	16(2)	105(3)	21(2
O21A	15011(8)	36856(15)	16683(9)	406(7)	102(2)	290(3)	176(3)	58(2)	101(2)	166(2
	14782(10)	35536(17)	16073(11)	318(6)	76(3)	184(3)	120(3)	29(2)	72(3)	89(3
O22A	-15193(8)	30361(14)	-1291(8)	231(4)	96(2)	214(3)	106(2)	-4(2)	56(2)	86(2
	-15367(10)	31321(16)	-1041(10)	236(4)	72(3)	143(3)	87(3)	4(2)	51(3)	52(2
D12A	1138(10)	28128(14)	51244(9)	360(5)	244(4)	155(3)	181(3)	28(2)	183(3)	40(2
	1040(13)	28907(17)	51169(12)	334(6)	219(5)	134(4)	167(4)	19(3)	168(4)	20(3
D21A	-15632(10)	42136(16)	-7479(10)	391(6)	176(3)	271(4)	173(3)	31(2)	117(3)	128(3
	-15710(12)	43044(18)	-7171(12)	336(6)	157(4)	210(5)	156(5)	33(3)	109(4)	94(3
D01A	17582(11)	4376(16)	32382(10)	533(8)	233(4)	244(4)	224(4)	125(2)	187(3)	134(3
	17288(13)	4118(19)	32179(12)	487(7)	181(5)	207(5)	192(5)	105(3)	150(4)	108(3
D02A	-6682(11)	-5039(14)	15360(10)	295(6)	283(4)	152(3)	198(4)	-54(2)	186(3)	-7(2
	-7034(13)	-5104(17)	15137(12)	314(6)	222(5)	121(4)	175(5)	-53(3)	153(4)	-19(3
C0B	55955(7)	12864(9)	25266(6)	168(2)	113(2)	77(2)	82(2)	13(1)	81(2)	23(1
	55989(9)	12874(12)	25322(8)	142(2)	83(2)	61(2)	63(2)	14(2)	60(2)	15(2
C1B	54391(6)	30411(9)	36861(6)	154(2)	88(2)	79(2)	73(2)	15(1)	66(2)	30(1
	54465(8)	30473(12)	36932(8)	119(2)	65(2)	56(2)	57(2)	9(2)	51(2)	12(2
C2B	53307(6)	28594(9)	13935(6)	135(2)	85(2)	87(2)	66(2)	4(1)	60(2)	21(1
	53347(8)	28585(12)	13977(8)	113(2)	69(2)	63(2)	60(2)	5(2)	55(2)	10(2
O11B	52746(8)	54355(11)	37560(7)	228(3)	139(2)	80(2)	115(2)	26(2)	110(2)	39(2
	52689(10)	54377(14)	37533(9)	192(3)	102(3)	58(3)	87(3)	17(2)	80(3)	19(2
O12B	54962(8)	16994(11)	45802(8)	284(4)	171(2)	90(2)	130(2)	41(2)	134(2)	55(2
	55247(11)	17081(14)	46038(10)	239(4)	145(3)	67(3)	110(3)	33(2)	116(3)	36(2
O21B	65628(8)	43881(12)	19565(8)	169(3)	87(2)	150(2)	84(2)	-10(2)	55(2)	48(2
	65638(10)	44400(15)	19758(10)	213(3)	71(3)	128(3)	79(3)	-3(2)	48(2)	38(2
O22B	36412(8)	24381(12)	-2455(7)	148(2)	94(2)	133(2)	69(2)	-13(2)	49(2)	38(2
	36557(10)	23937(15)	-2523(10)	186(3)	76(3)	119(3)	70(3)	-13(2)	45(3)	27(2
D12B	52587(10)	28417(14)	52391(10)	413(7)	252(4)	171(3)	197(3)	52(2)	196(3)	63(2
	52762(12)	28434(17)	52534(12)	408(7)	211(5)	151(4)	167(4)	39(3)	165(4)	41(3
D21B	35296(10)	36400(10)	-8948(9)	308(5)	179(3)	217(4)	143(3)	8(2)	107(3)	79(2
	35396(12)	35973(18)	-9028(12)	331(6)	157(4)	201(5)	130(4)	6(3)	95(4)	70(3
D01B	69645(10)	6306(15)	34061(10)	454(7)	198(3)	233(4)	199(3)	98(2)	156(3)	111(2
	69712(13)	6327(18)	34140(12)	488(8)	181(5)	212(5)	187(5)	93(3)	146(4)	97(3
D02B	45652(11)	-4779(14)	17057(10)	272(4)	252(4)	144(3)	186(3)	-50(2)	166(3)	0(2
	45644(17)	-4789(17)	17098(12)	248(4)	229(5)	120(4)	173(5)	-46(3)	155(4)	-10(3

Table 2S. Malonic acid, phases β and γ: Selected intra- and intermolecular distances (Å). Successive rows are neutron values before and after correction for harmonic librational motion. The intermolecular O ··· D distances are uncorrected.

	50K		56K		153K
Molecule	**A**	**B**	**A**	**B**	
C0-C1	1.5129(9)	1.5121(8)	1.5126(7)	1.5132(7)	1.5113(8)
	1.5144(9)	1.5137(8)	1.5152(7)	1.5151(7)	1.5151(8)
-C2	1.5060(8)	1.5087(7)	1.5059(7)	1.5072(7)	1.5070(8)
	1.5072(8)	1.5101(7)	1.5069(7)	1.5086(7)	1.5089(8)
C0-D01	1.091(1)	1.090(1)	1.0921(9)	1.0927(9)	1.089(1)
-D02	1.088(1)	1.090(1)	1.0946(9)	1.0932(8)	1.088(1)
C1-O11	1.2226(9)	1.224(1)	1.2235(7)	1.2234(7)	1.2242(9)
	1.2241(9)	1.226(1)	1.2257(7)	1.2264(7)	1.2276(9)
-O12	1.311(1)	1.311(1)	1.3103(7)	1.3097(7)	1.306(1)
	1.312(1)	1.313(1)	1.3114(7)	1.3119(7)	1.308(1)
C2-O21	1.217(1)	1.224(1)	1.2159(8)	1.2196(7)	1.217(1)
	1.222(1)	1.226(1)	1.2238(8)	1.2218(7)	1.229(1)
-O22	1.315(1)	1.314(1)	1.3157(8)	1.3197(7)	1.308(1)
	1.321(1)	1.316(1)	1.3252(8)	1.3219(7)	1.322(1)
O12-D12	0.998(1)	1.000(1)	1.0012(9)	1.0026(9)	0.997(1)
O22-D21	0.993(1)	0.999(1)	0.998(1)	0.999(1)	0.995(1)

Table 3S. Malonic acid: Bond angles of phases β and γ (°)

	50K		56K		153K
Molecule	**A**	**B**	**A**	**B**	
D02-C0-D01	109.25(9)	108.86(9)	109.31(8)	108.90(7)	109.27(9)
D02-C0-C2	111.12(8)	111.74(8)	111.14(6)	111.68(6)	111.56(7)
D02-C0-C1	108.10(8)	108.09(8)	108.10(6)	108.17(6)	108.20(7)
D01-C0-C2	110.01(8)	109.92(8)	110.03(6)	109.98(6)	109.83(7)
D01-C0-C1	108.19(8)	108.16(8)	108.21(6)	108.07(6)	107.89(7)
C2-C0-C1	110.10(5)	109.97(5)	109.98(4)	109.94(4)	110.01(5)
O11-C1-O12	124.99(7)	124.91(7)	124.93(5)	124.88(5)	125.08(6)
O11-C1-C0	122.92(7)	122.90(7)	112.17(5)	112.28(4)	122.58(5)
O12-C1-C0	112.09(6)	112.19(6)	112.17(5)	112.28(4)	112.33(5)
O12-C1-C0	112.09(6)	112.19(6)	112.17(5)	112.28(4)	112.33(5)
O21-C2-O22	123.66(8)	123.62(8)	123.71(6)	123.82(6)	123.63(7)
O21-C2-C0	122.92(7)	122.85(7)	122.84(5)	122.77(5)	122.84(6)
O22-C2-C0	113.43(7)	113.51(7)	113.46(5)	113.41(5)	113.52(6)
D12-O12-C1	111.59(9)	111.13(8)	111.58(7)	111.16(7)	111.70(7)
D21-O22-C2	109.55(9)	109.68(9)	109.52(7)	109.50(7)	109.76(9)

Table 4S. Mean-square displacement amplitude difference, Δ^{A-B} , between intramolecular atom pairs along the direction A-B ($Å^2$ X 10^4; e.s.d.$^{A-B}$ =0.0007 $Å^2$) : γ phase at 50K

Molecule A

A \ B	0(11)	C(1)	0(12)	D(12)	D(O1)	C(0)	D(02)	0(21)	C(2)	0(22)	D(2
D(21)	109	90	81	14	-12	63	-53	96	66	55	
0(22)	58	81	27	-37	-65	7	-112	13	11	-	
C(2)	-5	6	8	-60	-77	2	-62	-8	-		
0(21)	65	35	20	-32	-111	-5	-50	-			
D(02)	62	66	97	45	-19	26	-				
C(0)	-3	-1	7	-49	-62	-					
D(O1)	91	84	95	49	-						
D(12)	76	68	81	-							
0(12)	-11	2	-								
C(1)	-4	-									
0(11)	-										

Molecule B

A \ B	0(11)	C(1)	0(12).	D(12)	D(01)	C(O)	D(02)	0(21)	C(2)	0(22)	D(
D(21)	99	80	71	14	-30	63	-44	88	60	40	
0(22)	39	34	25	-32	-79	19	-88	2	4	-	
C(2)	-12	-4	5	-64	-84	3	-58	-15	-		
0(21)	53	34	36	-26	-103	8	-34	-			
D(02)	70	69	83	8	21	28	-				
C(0)	-3	-4	7	-52	-70	-					
D(01)	94	89	108	52	-						
D(12)	78	60	55	-							
0(12)	-6	-6	-								
C(1)	-1	-									
0(11)	-										