Polymorphism in *N*-(5-methylisoxazol-3-yl)malonamide: Understanding the Supramolecular Structure and the Crystallization Mechanism

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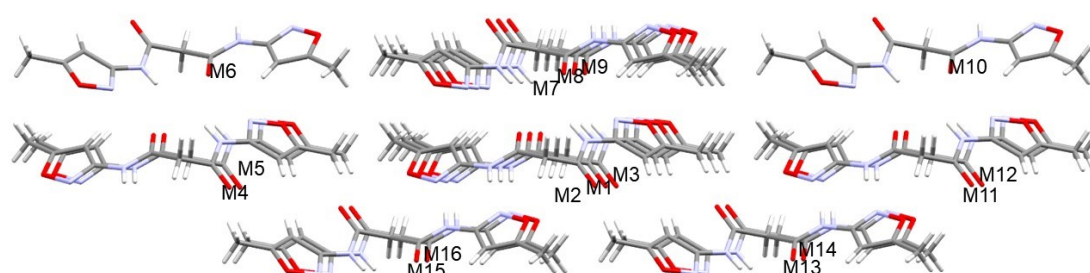*E-mail of the corresponding author: marcos.nuquimhe@gmail.com

Fig. S1. Supramolecular cluster of the compound **1I**.

Table S1. Topological and energetic data of each dimer from the supramolecular cluster of compound **1I**.

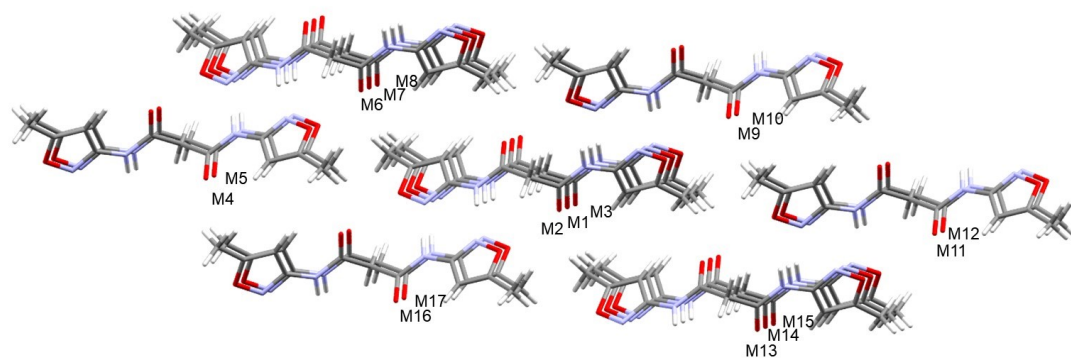| Dimer	Symmetry code	$C_{M1\cdots MN}$ (Å^2)	$G_{M1\cdots MN}$ (kcal mol^{-1})	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1	x,y,z				
M1···M2	1+x,y,z	44.33	−9.88	2.03	1.98
M1···M3	−1+x,y,z	44.33	−9.88	2.03	1.98
M1···M4	1+x,1+y,−1+z	9.36	−0.99	0.43	0.20
M1···M5	x,1+y,−1+z	8.7	0.02	0.40	0.00
M1···M6	1−x,2−y,−z	3.55	−0.12	0.16	0.02
M1···M7	2−x,1−y,1−z	5.03	−1.37	0.23	0.28
M1···M8	1−x,1−y,1−z	48.03	−13.72	2.20	2.75
M1···M9	−x,1−y,1−z	36.92	−3.16	1.69	0.63
M1···M10	−x,−y,2−z	2.15	−0.41	0.10	0.08
M1···M11	x,−1+y,1+z	8.7	0.02	0.40	0.00
M1···M12	−1+x,−1+y,1+z	9.36	−0.99	0.43	0.20
M1···M13	1−x,1−y,2−z	23.14	−4.44	1.06	0.89
M1···M14	−x,1−y,2−z	23.22	−5.29	1.07	1.06
M1···M15	2−x,2−y,1−z	21.23	−15.43	0.97	3.10
M1···M16	1−x,2−y,1−z	38.9	−9.10	1.78	1.83
Total		326.95	−74.75	15.00	15.00

Fig. S2. Supramolecular cluster of the compound **1II**.

Table S2. Topological and energetic data of each dimer from the supramolecular cluster of compound **1II**.

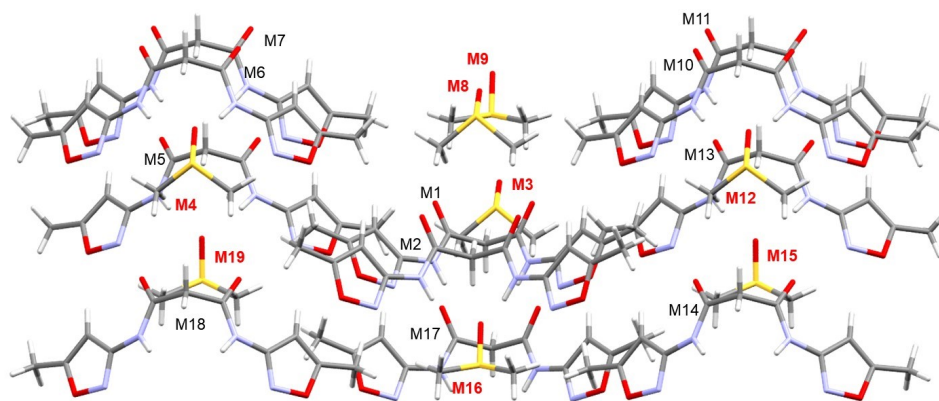| Dimer	Symmetry code	$C_{M1\cdots MN}$ (Å^2)	$G_{M1\cdots MN}$ (kcal mol^{-1})	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1	x,y,z				
M1···M2	x,−1+y,z	52.38	−11.96	2.51	2.43
M1···M3	x,1+y,z	52.38	−11.96	2.51	2.43
M1···M4	−2−x,1−y,1−z	11.28	−2.28	0.54	0.46
M1···M5	−1,5+x,2−y,−1/2+z	9.07	−0.29	0.44	0.06
M1···M6	−1+x,−1+y,z	8.3	−1.45	0.40	0.30
M1···M7	−1+x,y,z	27.49	−4.79	1.32	0.97
M1···M8	−1+x,1+y,z	8.3	−1.45	0.40	0.30
M1···M9	−x,−y,2−z	21.7	−14.48	1.04	2.95
M1···M10	−x,1−y,2−z	28.27	−2.63	1.36	0.53
M1···M11	1−x,1−y,2−z	11.28	−2.28	0.54	0.46
M1···M12	1−x,2−y,2−z	9.07	−0.29	0.44	0.06
M1···M13	1+x,−1+y,z	8.3	−1.45	0.40	0.30
M1···M14	1+x,y,z	27.49	−4.79	1.32	0.97
M1···M15	1+x,1+y,z	8.3	−1.45	0.40	0.30
M1···M16	−1−x,−y,1−z	21.7	−14.48	1.04	2.95
M1···M17	−1−x,1−y,1−z	28.27	−2.63	1.36	0.53
Total		334.00	−79.00	16.00	16.00

Fig. S3 Supramolecular cluster of the compound **1III**.

Table S3. Topological and energetic data of each dimer from the supramolecular cluster of compound **1III**.

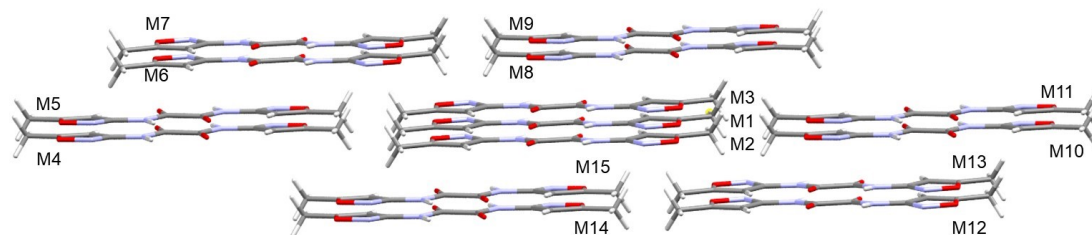| Dimer	Symmetry code	$C_{M1\cdots MN}$ (Å^2)	$G_{M1\cdots MN}$ (kcal mol^{-1})	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1	x,y,z				
M1···M2	x,y,z	52.63	−9.94	2.89	2.25
M1···M3	x,1+y,z	10.85	−0.11	0.60	0.03
M1···M4	1,5−x,1−y,1/2+z	10.79	−0.24	0.59	0.05
M1···M5	1/2+x,1−y,−1/2+z	22.12	−3.48	1.21	0.79
M1···M6	1,5−x,−y,−1/2+z	9.63	−1.83	0.53	0.41
M1···M7	1,5−x,1−y,−1/2+z	15.41	−4.31	0.85	0.98
M1···M8	x,y,z	21.74	−3.55	1.19	0.80
M1···M9	x,y,z	15.92	−4.43	0.87	1.00
M1···M10	1/2−x,−y,−1/2+z	9.63	−1.83	0.53	0.41
M1···M11	1/2−x,1−y,−1/2+z	15.41	−4.31	0.85	0.98
M1···M12	1/2−x,1−y,1/2+z	10.79	−0.24	0.59	0.05
M1···M13	−1/2+x,1−y,−1/2+z	22.12	−3.48	1.21	0.79
M1···M14	−1/2+x,1−y,1/2+z	15.41	−4.31	0.85	0.98
M1···M15	1/2−x,1−y,1/2+z	6.98	−1.14	0.38	0.26
M1···M16	x,y,1+z	25.41	−20.23	1.39	4.57
M1···M17	x,1+y,z	40.8	−10.73	2.24	2.43
M1···M18	1,5−x,1−y,1/2+z	15.41	−4.31	0.85	0.98
M1···M19	1,5−x,1−y,1/2+z	6.98	−1.14	0.38	0.26
Total		328.03	−79.61	18.00	18.00

Fig. S4. Supramolecular cluster of the compound **2**.

Table S4. Topological and energetic data of each dimer from the supramolecular cluster of compound **2**.

Dimer	Symmetry code	$C_{M1\cdots MN}$ (Å²)	$G_{M1\cdots MN}$ (kcal mol⁻¹)	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1	x,y,z				
M1···M2	1−x,−y,−z	35.7	−9.25	1.63	2.02
M1···M3	x,1+y,z	35.7	−9.25	1.63	2.02
M1···M4	−1+x,1/2−y,−1,5+z	12.02	−0.83	0.55	0.18
M1···M5	−1+x,1,5−y,−1,5+z	12.02	−0.83	0.55	0.18
M1···M6	−1+x,−1+y,−1+z	0.11	−0.38	0.01	0.08
M1···M7	−1+x,y,−1+z	21.18	−4.22	0.97	0.92
M1···M8	1−x,−1/2+y,1/2−z	36.06	−8.27	1.65	1.81
M1···M9	x,1,5−y,1/2+z	36.06	−8.27	1.65	1.81
M1···M10	2−x,−1/2+y,1,5−z	12.02	−0.83	0.55	0.18
M1···M11	2−x,1/2+y,1,5−z	12.02	−0.83	0.55	0.18
M1···M12	2−x,1−y,1−z	21.18	−4.22	0.97	0.92
M1···M13	2−x,2−y,1−z	0.11	−0.38	0.01	0.08
M1···M14	x,1/2−y,−1/2+z	36.06	−8.28	1.65	1,81
M1···M15	x,1,5−y,−1/2+z	36.06	−8.28	1.65	1.81
Total		306.30	−64.14	14.00	14.00

Table S5. QTAIM analysis and intramolecular interactions data for compounds **1** and **2**.

1I

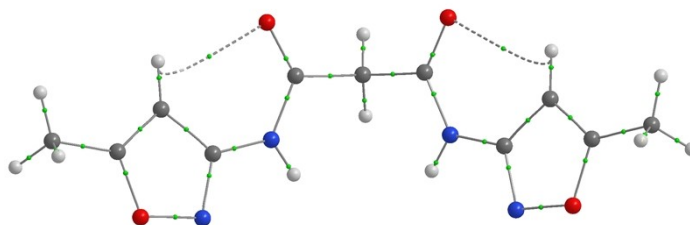| Atoms	ρ_{int} (a.u.)	$\nabla^2\rho$	ε	K	V	G	BPL	$G_{AI(X\cdots Y)}$ (kcal mol⁻¹)
O3···H12	0.010626	0.04485	1.097157	-0.00182	-0.00756	0.009388	5.467346	-1.76
O1···H25	0.012281	0.050695	0.607466	-0.00178	-0.00911	0.01089	5.101537	-2.03

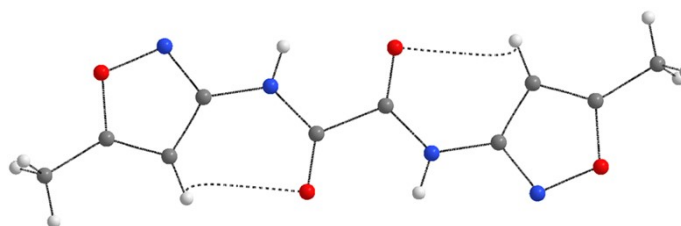| Atoms	ρ_{int} (a.u.)	$\nabla^2\rho$	ε	K	V	G	BPL	$G_{AI(X\cdots Y)}$ (kcal mol^{-1})
O1⋯H9	0.01722	0.06115	0.19791	0.00071	-0.01387	0.014579	4.344413	-2.86
Total	0.040127							-6.65

1II
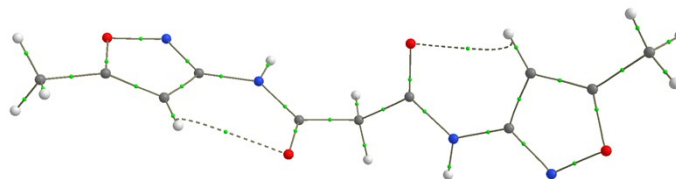
Atoms	ρ_{int} (a.u.)	$\nabla^2\rho$	ε	K	V	G	BPL	$G_{AI(X\cdots Y)}$ (kcal mol^{-1})
O17⋯H27	0.012146	0.050156	0.680682	0.00179	-0.00895	0.010746	5.149239	-2.01
O1⋯H11	0.012147	0.050156	0.680365	0.00179	-0.00895	0.010747	5.148992	-2.01
Total	0.024293							-4.02

1III

Atoms	ρ_{int} (a.u.)	$\nabla^2\rho$	ε	K	V	G	BPL	$G_{AI(X\cdots Y)}$ (kcal mol^{-1})
O1⋯H11	0.011681	0.048214	0.769936	0.00178	-0.0085	0.010275	5.232394	-1.93
O18⋯H28	0.011681	0.048214	0.769936	0.00178	-0.0085	0.010275	5.232394	-1.93
Total	0.023362							-3.86

2

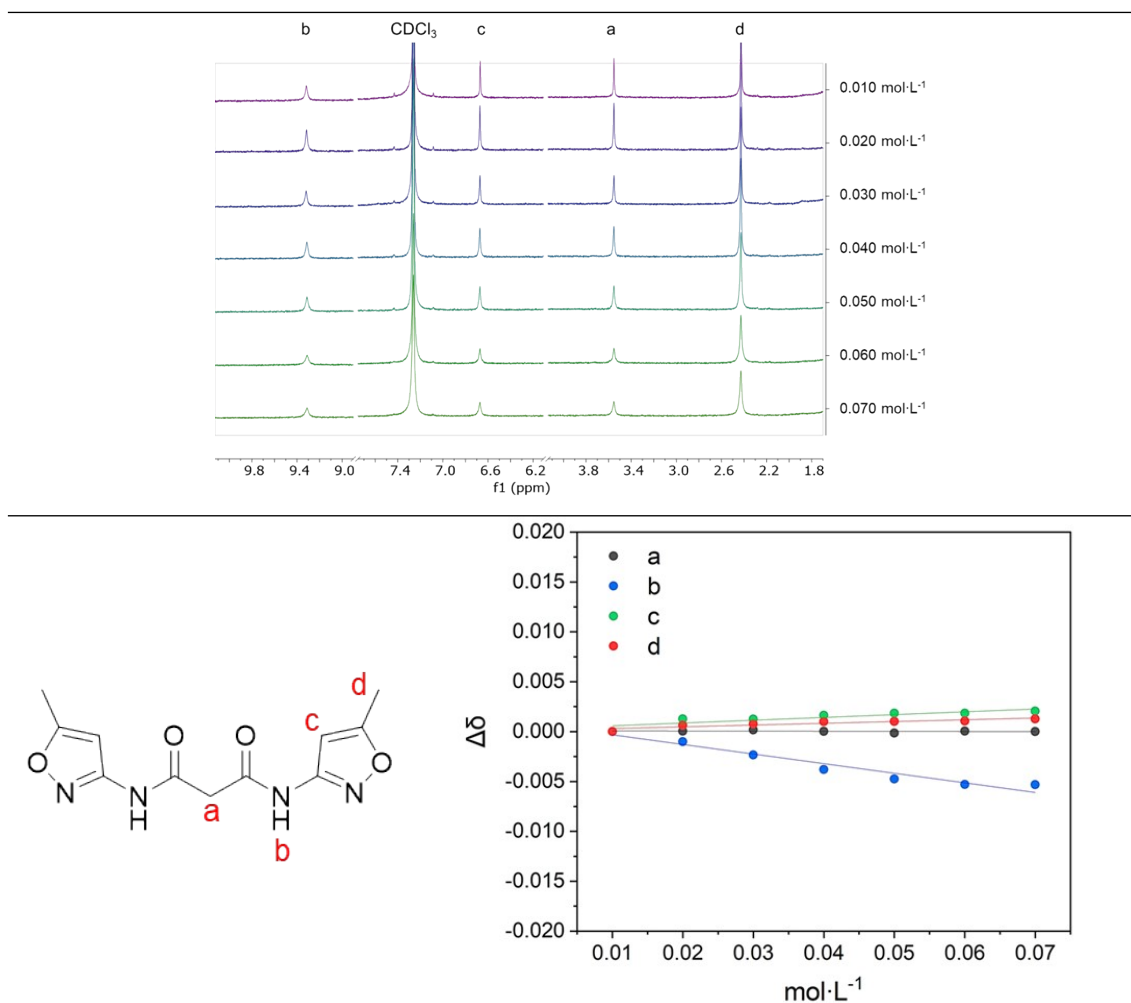| Atoms	ρ_{int} (a.u.)	$\nabla^2\rho$	ε	K	V	G	BPL	$G_{AI(X\cdots Y)}$ (kcal mol^{-1})
H4⋯O71	0.012261	0.04999	0.484268	-0.001694	-0.009109	0.010803	4.98478	-2.03
H4⋯O71	0.012261	0.04999	0.484268	-0.001694	-0.009109	0.010803	4.98478	-2.03
Total	0.024522							-4.06

Fig. S5. Concentration-dependent ^{1}H NMR experiments performed in CDCl$_3$ at 298 K (top) and correlation between concentration and $\Delta\delta$ for **1** (down).

Table S6. Linear equations based on the graphics of $\Delta\delta$ as a function of concentration for the ^{1}H NMR signals of compound **1**.

Hydrogen	Linear Equation	R^2
NH(b)	y = -0.09624x – 0.00063	0.9452
CH(a)	y = -0.00010x + 0.00007	0.0622
CH(c)	y = 0.01769x – 0.00012	0.8305
CH(d)	y = 0.02805x + 0.00029	0.7714

Table S7. Energies obtained from the fragmentation via QTAIM ($G_{AI(X\cdots Y)}$), sum of the cluster contribution ($\Sigma G_{AI(X\cdots Y)}$), number of contacts, normalized G_{AI}, and the average value of G_{AI}.

Form **1I**

Interaction	NH···O=C	O···π	CH···O	N···π	CH···N	CH···HC	N···O	O···O	π···π	CH···π	NH···N
	-3.24	-0.93	-1.13	-1.25	-2.03	-0.76	-1.15	-1.55	-0.59	-0.95	-7.72
	-3.24	-0.93	-1.13	-1.25	-2.03	0.02	-1.15		-2.21	-0.95	-7.72
			-2.42	-2.12		-0.12	-1.84				
			-2.42	-2.12		-1.37	-1.84				
			-0.23	-1.69		-0.67					
			-0.45	-1.69		-0.67					
$G_{AI(X\cdots Y)}$			-0.45			-0.41					
			-0.45			-0.76					
			-0.45			0.02					
			-0.23			-0.59					
			-0.86								
			-0.86								
			-1.07								
			-1.07								
			-1.40								
			-1.40								
			-1.60								
			-1.60								
$\Sigma G_{AI(X\cdots Y)}$	-6.49	-1.87	-19.22	-10.12	-4.06	-5.31	-5.98	-1.55	-2.80	-1.90	-15.43
Contacts	2	2	18	6	2	10	4	1	2	2	2
$NG_{AI(X\cdots Y)}$	4.43	1.27	13.12	6.91	2.77	3.63	4.08	1.06	1.91	1.30	10.53
$G_{AI(X\cdots Y)_{av}}$	-3.24	-0.93	-1.07	-1.69	-2.03	-0.53	-1.50	-1.55	-1.40	-0.95	-7.72

Form **1II**

Interaction	O···π	CH···O	N···π	CH···HC	O···O	NH···N	N···N
	-2.25	-1.74	-1.99	-0.50	-0.38	-7.24	-0.59
	-2.25	-1.74	-1.99	-0.29	-0.38	-7.24	-0.59
	-2.25	-1.74	-1.99	-0.50	-0.38	-7.24	
	-2.25	-1.74	-1.99	-0.29	-0.38	-7.24	
	-0.36	-0.89		-0.64			
	-0.36	-0.89		-0.64			
	-0.36	-0.89		-0.86			
	-0.36	-0.89		-0.64			
		-1.45		-0.64			
		-1.45		-0.86			
$G_{AI(X\cdots Y)}$		-1.32					
		-1.32					
		-1.32					
		-1.32					
		-1.45					
		-1.45					
		-0.28					
		-0.28					
		-0.28					
		-0.28					
$\Sigma G_{AI(X\cdots Y)}$	-10.45	-22.73	-7.94	-5.89	-1.52	-28.96	-1.18
Contacts	8	20	4	10	4	4	2
$NG_{AI(X\cdots Y)}$	6.91	15.03	5.25	3.89	1.00	19.15	0.78
$G_{AI(X\cdots Y)_{av}}$	-1.31	-1.14	-1.99	-0.59	-0.38	-7.24	-0.59

Form **1III** (M1···MN)

Interaction	NH···O=S	O···π	CH···O	N···π	CH···N	CH···HC	CH···π
Energy Gai	-7.50	-0.98	-1.62	-1.77	-1.11	-0.24	-1.12
	-7.50	-0.98	-0.75	-1.77	-1.11	-0.53	-1.12
		-1.86	-0.25	-1.04	-1.68	-0.55	
		-1.86	-0.64	-1.04	-1.68	-0.53	
			-1.74		-1.68	-0.55	
			-1.78		-1.45	-0.24	
			-1.78		-1.45	-1.14	
			-2.22		-0.81	-1.14	
			-2.22		-0.81		
$G_{AI(X···Y)}$			-0.75		-1.68		
			-0.25				
			-0.64				
			-1.74				
			-1.62				
			-0.25				
			-0.64				
			-1.74				
			-2.32				
			-1.52				
			-1.52				
			-2.00				
			-2.00				
			-0.25				
			-0.64				
			-1.74				
$\Sigma G_{AI(X···Y)}$	-15.00	-5.68	-32.59	-5.61	-13.46	-4.93	-2.23
Contacts	2	4	25	4	10	8	2
$NG_{AI(X···Y)}$	10.36	3.92	22.52	3.87	9.30	3.40	1.54
$G_{AI(X···Y)_{av}}$	-7.50	-1.42	-1.30	-1.40	-1.35	-0.62	-1.12

Form **1III** (M1···S)

Interaction	NH···O=S	CH···O	CH···N	CH···HC
		-7.50	-1.78	-1.45	-0.24
	-7.50	-1.78	-1.45	-0.24
$G_{AI(X···Y)}$		-2.22		-1.14
		-2.22		-1.14
		-2.32		
$\Sigma G_{AI(X···Y)}$	-15.00	-10.30	-2.91	-2.76
Contacts	2	5	2	4
$NG_{AI(X···Y)}$	6.30	4.32	1.22	1.16
$G_{AI(X···Y)_{av}}$	-7.50	-2.06	-1.45	-0.69