

Electronic Supplementary Information

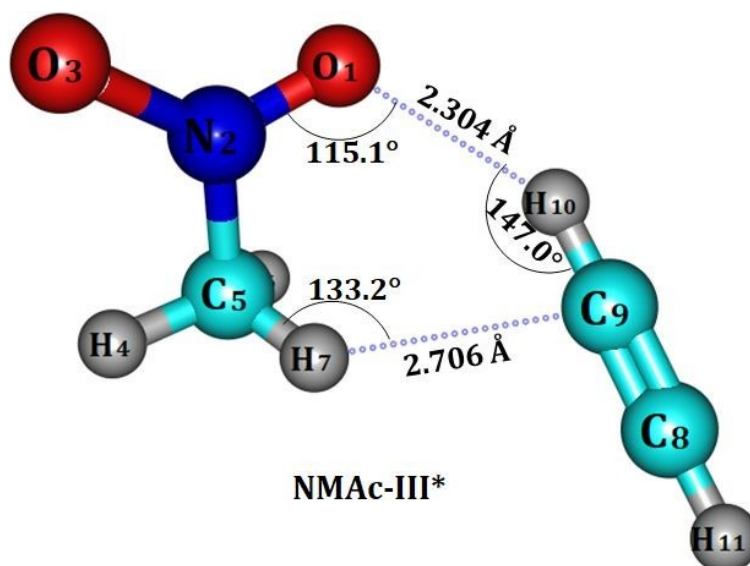
Interplay of unique $N\cdots\pi$ pnicoen and $H\cdots\pi/H\cdots O$ hydrogen bonding interaction in the heterodimers of nitromethane with acetylene and benzene as π -electron donors: Experimental characterization at low temperatures under isolated conditions with computational corroboration

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SerialNo.	Subject
Fig.S1	NMAcIII* optimized at B2PLYP/aug-cc-pVDZ with empirical dispersion GD3.
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Table S1	Relevant bond distances and bond angles in all the heterodimers of NMAc and NMBz.
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Table S4	<p>Co-ordinates of all the heterodimers in different levels of theory.</p> <ul style="list-style-type: none"> ❖ MP2/aug-cc-pVTZ ❖ MP2/aug-cc-pVDZ ❖ B2PLYP-GD3/aug-cc-pVDZ



FigureS1. NMAcIII* optimized at B2PLYP/aug-cc-pVDZ with empirical dispersion GD3.

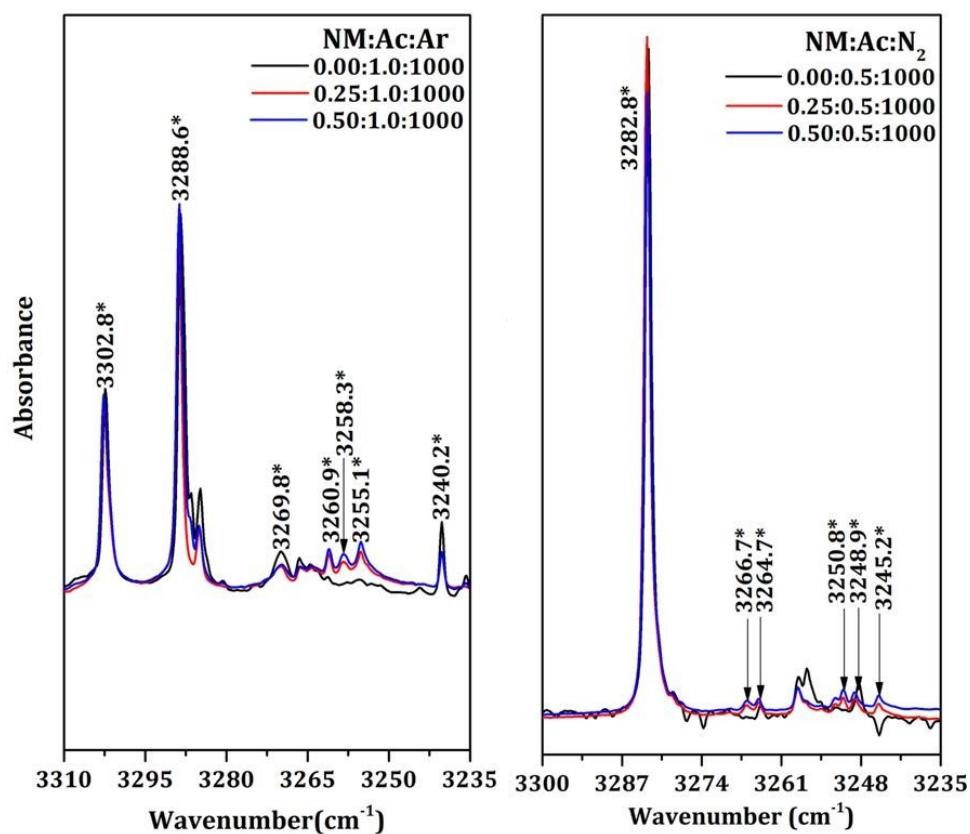


Figure S2. C-H stretching region of acetylene in the infrared spectra recorded after annealing N_2 and Ar matrixes containing greater concentrations of acetylene, in acetylene/nitromethane depositions.

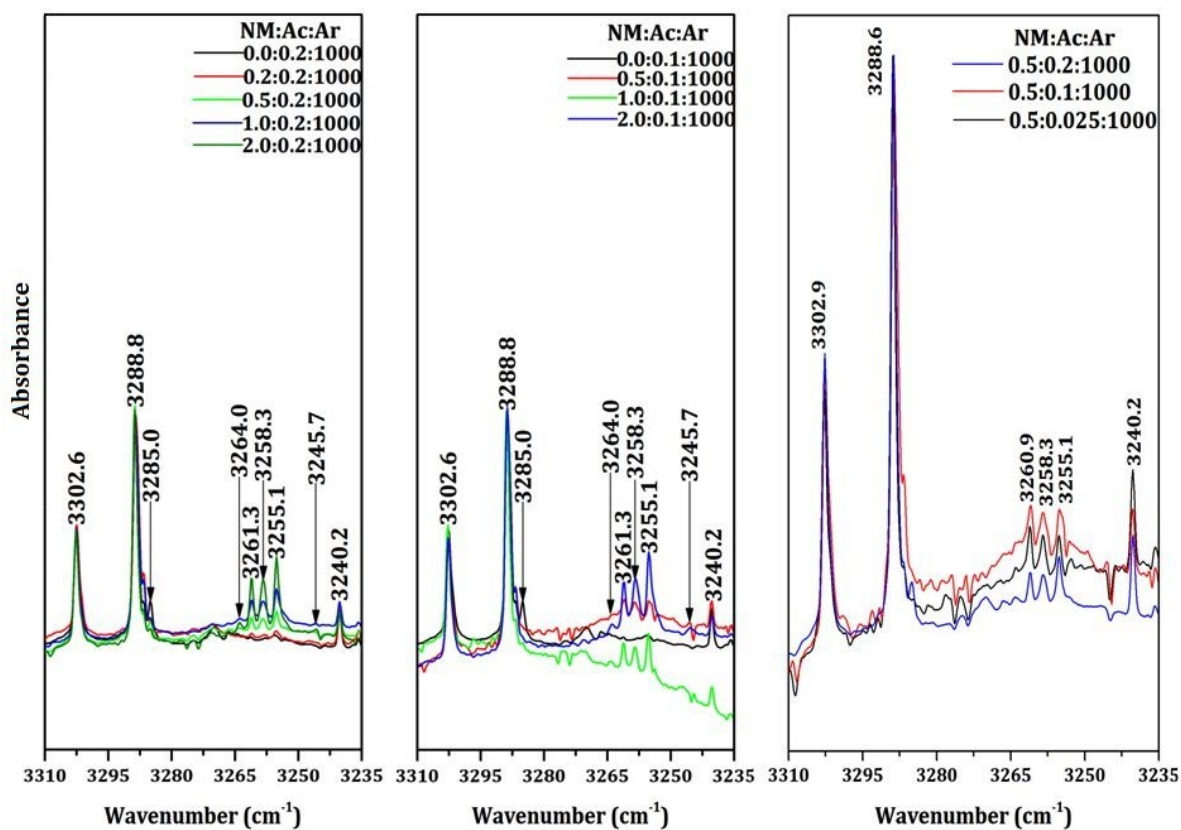
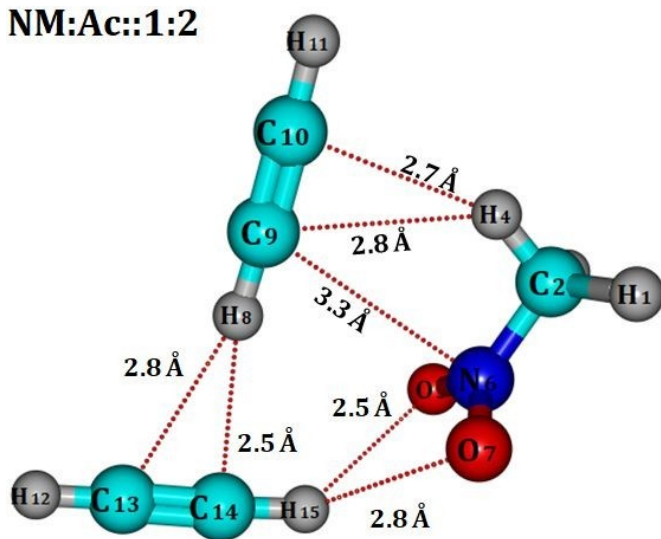


Figure S3. C-H stretching region of acetylene in the infrared spectra recorded after annealing Ar matrixes containing greater concentrations of acetylene, in acetylene/ nitromethane depositions.

NM:Ac::1:2



NM:Ac::2:1

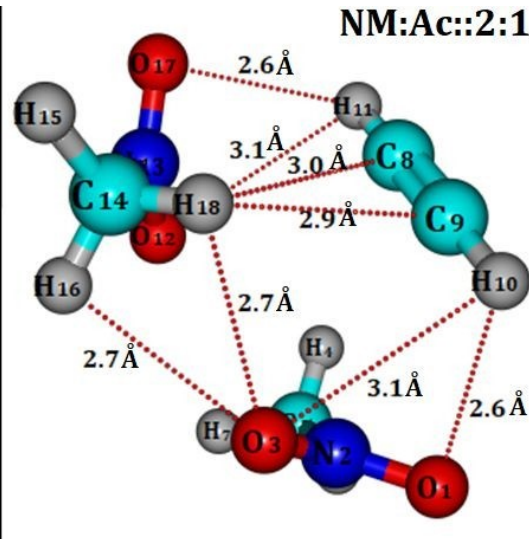


Figure S4. Geometry of NM:Ac::1:2 and NM:Ac::2:1 heterotrimers corresponding to the global minima on the respective PESs at MP2/aug-cc-pVDZ level.

Table S1. Relevant bond distances and bond angles in all the heterodimers of NMAc and NMBz.

Heterodimers	Bond lengths (Å)	Bond angles (degree)
NMAc-I	C8---H4: 3.082	\angle C5-H4-C8= 140.5°
	C9---N2: 2.949	\angle C9-N2-O1= 84.8°
NMAc-II	H10---O1: 2.304	\angle O1-H10-C9= 147.0°
	C9---H6: 2.706	\angle C5-H6-C9= 133.2°
NMAc-III	C9---N2: 3.155	\angle C8-N2-O3= 81.9°
	C8---N2: 3.221	\angle C9-N2-O1= 81.7°
NMBz-I	H14---C3: 2.768	\angle C3-H4-C15= 121.1°
	N17---C3: 3.029	\angle C3-N17-O19= 92.2°
NMBz-II	H11---O19: 2.552	\angle C10-H11-O19= 124.7°
	H9---O19: 2.608	\angle C7-H9-O19= 119.5°

Table S2. Comparison of experimental shifts associated with the perturbed modes of submolecules within NMAc and NMBz dimers, with those predicted by harmonic frequency calculations at B2PLYP/aug-cc-pVDZ level of theory with empirical dispersion GD3.

Computed wavenumber(cm ⁻¹)		Experimental wavenumber(cm ⁻¹)		Experimental wavenumber(cm ⁻¹)		Mode assignment
		Ar Matrix		N ₂ Matrix		
ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	
C-H stretching region						
3431.6 (94.7)	-	3288.6/3302.9	-	3282.8/3311.0	-	Fermi diad of ν_3 & $\nu_2+\nu_4+\nu_5$ of C ₂ H ₂ monomer
3418.1(106.4)	-13.5	-- ^b	-	3266.7	-16.1	1:1NMAc-I heterodimer
3408.2(112)	-23.8	3264.0	-24.6	-- ^b	-	2:1::NM:Ac trimer
3406.6 (203)	-25.0	3260.9/3258.3	-29.0	3264.7	-18.1	1:2::NM:Ac trimer (proton accepting acetylene)
3393.2 (229)	-38.4	3255.1	-33.5	3251.1/3250.8	-31.9	1:1NMAc-IIheterodimer
3390.6 (225)	-41.0	3240.2	-48.4	3248.9/3245.3	-35.7	1:2::NM:Ac trimer(proton donating acetylene)

C-H bending region						
683.5 (114)	-	675.0	-	678.3	-	v ₄ out-of-plane bending of C ₆ H ₆
690.2(118)	6.7	681.2	6.2	687.5/686.1	8.5	1:1 NMBz-I heterodimer
691.4(105)	7.9	-- ^b		-- ^b		1:1 NMBz-II heterodimer
O=N=O stretching region						
1616.6(257)	-	1570.0	-	1572.7	-	v ₃ Mode of NM monomer
1611.5(223)	-4.9	-- ^b	-	1570.8	-1.9	1:1 NMAc-I heterodimer
1612.4(296)	-6.8	1568.4	-1.6			1:1 NMAc-II heterodimer
1608.1(205)	-8.5	-- ^b	-	-- ^b	-	1:2::NM:Ac trimer
1608.2(162)	-8.4	-- ^b	-	-- ^b	-	2:1::NM:Ac trimer
1606.0(300)	-10.6	-- ^b	-	-- ^b	-	2:1::NM:Ac trimer
1611.2(190)	-5.4	1568.1	-1.9	1570.2	-2.5	1:1NMBz-I heterodimer
1614.1(288)	-2.5	-- ^b		-- ^b		1:1NMBz-II heterodimer

^bfeatures were not discerned.

Table S3. NBO delocalization and associated second order perturbation energies, in NMAc and NMBz heterodimers.

Heterodimers	NBO	Donor-acceptor delocalization interaction	E ₂ (Kcal/mol)
NMBz I	Bz to NM	$\pi(\text{C1-C3})$ to $\sigma^*(\text{C15-H16})$	0.77
		$\pi(\text{C2-C6})$ to $\sigma^*(\text{C15-H16})$	0.54
		$\pi(\text{C7-C10})$ to $\sigma^*(\text{C15-H16})$	0.29
		$\pi(\text{C7-C10})$ to $\pi^*(\text{N17-O18})$	0.13
	NM to Bz	$\pi^*(\text{N17-O18})$ to $\pi^*(\text{C7-C10})$	0.36
		nO19 to $\pi^*(\text{C7-C10})$	0.17
		nO19 to $\pi^*(\text{C2-C6})$	0.15
NMBz II	NM to Bz	nO19 to $\pi^*(\text{C10-H11})$	0.70
		nO19 to $\pi^*(\text{C7-H9})$	0.69
NMAc I	NM to Ac	$\pi(\text{O1-N2})$ to $\pi^*(\text{C8-C9})$	0.45
		nO3 to $\sigma^*(\text{C9-H10})$	0.26
	Ac to NM	$\pi(\text{C8-C9})$ to $\pi^*(\text{O1-N2})$	0.14
		$\pi(\text{C8-C9})$ to $\sigma^*(\text{C4-H5})$	0.96
NMAc II	NM to Ac	n ¹ O1 to $\sigma^*(\text{C8-H11})$	4.12
NMAc III	NM to Ac	$\pi(\text{C8-C9})$ to $\pi^*(\text{O1-N2})$	0.18
		$\pi(\text{C8-C9})$ to $\sigma^*(\text{C4-H5})$	0.15
	Ac to NM	$\pi(\text{O1-N2})$ to $\pi^*(\text{C8-C9})$	0.37

Table S4: Co-ordinates of all the heterodimers in different levels of theory

MP2/aug-cc-pVTZ

NMBz-I

6	1.042082000	-1.203223000	-0.796882000
6	1.930516000	-1.211936000	0.278946000
6	0.604937000	0.009048000	-1.330681000
1	2.270491000	-2.152757000	0.692318000
1	-0.095196000	0.015558000	-2.155992000
6	2.379808000	-0.008021000	0.822733000
6	1.050012000	1.212817000	-0.784335000
1	3.070408000	-0.014540000	1.656212000
1	0.699125000	2.151736000	-1.192033000
6	1.938390000	1.204416000	0.291539000
1	2.284713000	2.138576000	0.714640000
1	0.684239000	-2.135466000	-1.213767000
1	-1.653244000	0.892030000	2.038531000
1	-1.649858000	-0.914274000	2.026882000
6	-1.363636000	-0.007206000	1.507554000
1	-0.295101000	-0.003791000	1.298351000
7	-2.043784000	0.000077000	0.192086000
8	-2.282135000	-1.089077000	-0.327187000
8	-2.280583000	1.094954000	-0.315686000

NMBz-II

6	3.647500000	0.757566000	0.009740000
6	3.706499000	-0.635470000	0.024468000
6	2.410976000	1.401826000	-0.016515000
1	4.666014000	-1.135927000	0.044773000
1	2.365947000	2.483379000	-0.028115000
6	2.529314000	-1.383133000	0.012955000
6	1.234429000	0.653506000	-0.027882000
1	2.576017000	-2.464470000	0.024297000
1	0.271028000	1.145082000	-0.048169000
6	1.292505000	-0.739758000	-0.013162000
1	0.375187000	-1.312870000	-0.022234000
1	4.561005000	1.338077000	0.018593000
1	-3.425152000	1.719710000	-0.848510000
1	-4.845805000	1.100076000	0.062564000
6	-3.767831000	1.196178000	0.038206000
1	-3.382009000	1.685445000	0.926781000
7	-3.180368000	-0.167017000	-0.002285000
8	-3.949108000	-1.126095000	-0.001115000
8	-1.953394000	-0.235615000	-0.033989000

NMAc-I

8	1.028707000	-0.639749000	1.121442000
7	1.043945000	-0.117417000	0.008398000
8	1.029267000	-0.725761000	-1.060456000
1	-0.041631000	1.634028000	-0.070604000
6	1.011129000	1.362275000	-0.050691000
1	1.491083000	1.744723000	0.842049000
1	1.505838000	1.672737000	-0.963145000
6	-2.686113000	0.394068000	0.015111000
6	-1.997338000	-0.604123000	-0.022392000
1	-1.386870000	-1.474793000	-0.056048000
1	-3.305887000	1.255982000	0.048912000

NMAc-II

8	0.744295000	-1.129480000	0.038552000
7	1.391296000	-0.083429000	0.001235000
8	2.615789000	-0.010975000	-0.064863000
1	1.320739000	2.005953000	-0.009645000
6	0.618441000	1.183835000	0.041605000
1	-0.066244000	1.174716000	-0.800584000
1	0.050719000	1.187592000	0.966816000
6	-3.486150000	0.199181000	-0.033636000
6	-2.462761000	-0.451824000	0.004521000
1	-1.554269000	-1.007336000	0.037090000
1	-4.387877000	0.759564000	-0.066762000

NMAc-III

6	-1.175272000	-0.000680000	1.254395000
1	-1.719241000	-0.903145000	1.506784000
1	-0.191974000	-0.000969000	1.717644000
1	-1.719163000	0.901567000	1.507730000
7	-0.939630000	0.000076000	-0.208480000
8	-0.825214000	-1.092042000	-0.760343000
8	-0.825344000	1.092767000	-0.759238000
6	2.176506000	-0.606746000	0.099177000
6	2.176318000	0.606787000	0.099636000
1	2.173859000	-1.669086000	0.081859000
1	2.173079000	1.669132000	0.082739000

MP2/aug-cc-pVDZ

NMBz-I

6	1.015304000	-1.208975000	-0.815231000
6	1.920127000	-1.229112000	0.264759000
6	0.575917000	0.020745000	-1.343211000
1	2.261044000	-2.184325000	0.675258000
1	-0.137027000	0.036094000	-2.172569000
6	2.383287000	-0.019024000	0.818743000
6	1.035500000	1.230631000	-0.787336000
1	3.084942000	-0.034457000	1.658058000
1	0.681950000	2.184096000	-1.189884000
6	1.940216000	1.211015000	0.292840000
1	2.296644000	2.150786000	0.725200000
1	0.646023000	-2.146938000	-1.239457000
1	-1.593459000	-0.950089000	2.026704000
1	-0.254863000	0.020777000	1.297381000
6	-1.330301000	-0.016109000	1.519732000
1	-1.643520000	0.874615000	2.074340000
7	-2.028493000	0.000119000	0.204055000
8	-2.271066000	1.106510000	-0.297913000
8	-2.276758000	-1.092312000	-0.325237000

NMBz-II

6	3.662920000	0.765234000	0.006114000
6	3.722896000	-0.641515000	0.020871000
6	2.414039000	1.415657000	-0.015447000
1	4.693274000	-1.147174000	0.037570000
1	2.368322000	2.509117000	-0.027045000
6	2.534384000	-1.396977000	0.014071000
6	1.226121000	0.659416000	-0.022123000
1	2.582034000	-2.490167000	0.025414000
1	0.252458000	1.156346000	-0.038960000
6	1.285150000	-0.747435000	-0.007462000
1	0.358535000	-1.327427000	-0.013016000
1	4.586455000	1.352305000	0.011307000
1	-3.418366000	1.734943000	-0.856328000
1	-4.862648000	1.108907000	0.053322000
6	-3.773212000	1.205697000	0.036422000
1	-3.387480000	1.695243000	0.939020000
7	-3.186439000	-0.167327000	-0.003760000
8	-3.962210000	-1.132477000	-0.005187000
8	-1.950453000	-0.240182000	-0.032267000

NMAc-I

8	1.044541000	-0.642475000	1.128970000
7	1.055213000	-0.110491000	0.010163000
8	1.055371000	-0.719990000	-1.068631000
1	-0.071226000	1.628833000	-0.142807000
6	0.993861000	1.377347000	-0.047136000
1	1.408410000	1.768190000	0.887564000
1	1.550938000	1.702119000	-0.932269000
6	-2.733314000	0.369113000	0.015592000
6	-1.985591000	-0.609700000	-0.027870000
1	-1.338097000	-1.469529000	-0.063315000
1	-3.385548000	1.222982000	0.053463000

NMAc-II

8	-0.911464000	-1.144267000	-0.673501000
7	-0.940617000	-0.010479000	-0.176575000
8	-0.936911000	1.050831000	-0.812493000
1	-2.055798000	0.301974000	1.565764000
6	-1.008947000	0.091934000	1.309799000
1	-0.681683000	-0.864366000	1.728878000
1	-0.364462000	0.923594000	1.612163000
6	2.215652000	0.607954000	-0.003990000
6	2.145897000	-0.620833000	0.060871000
1	2.080467000	-1.693791000	0.096427000
1	2.277177000	1.679096000	-0.079336000

NMAc-III

8	0.741187000	1.135097000	-0.028325000
7	1.401487000	0.085929000	-0.002123000
8	2.636542000	0.025372000	0.044875000
1	1.356578000	-2.017720000	-0.020080000
6	0.634646000	-1.195960000	-0.027495000
1	-0.014239000	-1.205887000	0.856819000
1	0.018650000	-1.190895000	-0.934829000
6	-3.540772000	-0.174435000	0.021323000
6	-2.460246000	0.418376000	-0.000559000
1	-1.503666000	0.917651000	-0.019203000
1	-4.491330000	-0.676296000	0.040143000

B2PLYP/aug-cc-pVDZ

NMBz-I

6	1.053827000	-1.176792000	-0.838255000
6	1.938272000	-1.246572000	0.248159000
6	0.650728000	0.070759000	-1.335399000
1	2.250978000	-2.216928000	0.635283000
1	-0.050620000	0.124570000	-2.167807000
6	2.418253000	-0.068210000	0.838830000
6	1.128274000	1.248877000	-0.743699000
1	3.105806000	-0.122248000	1.683568000
1	0.802873000	2.217633000	-1.122819000
6	2.012941000	1.179821000	0.342709000
1	2.384075000	2.096165000	0.802937000
1	0.669498000	-2.091217000	-1.289902000
1	-1.699400000	-0.948725000	2.014414000
1	-0.348431000	0.012512000	1.310693000
6	-1.423942000	-0.018536000	1.514106000
1	-1.741544000	0.872225000	2.059545000
7	-2.097870000	-0.000134000	0.181255000
8	-2.336097000	1.101630000	-0.317715000
8	-2.333686000	-1.086522000	-0.351461000

NMBz-II

6	3.662920000	0.765234000	0.006114000
6	3.722896000	-0.641515000	0.020871000
6	2.414039000	1.415657000	-0.015447000
1	4.693274000	-1.147174000	0.037570000
1	2.368322000	2.509117000	-0.027045000
6	2.534384000	-1.396977000	0.014071000
6	1.226121000	0.659416000	-0.022123000
1	2.582034000	-2.490167000	0.025414000
1	0.252458000	1.156346000	-0.038960000
6	1.285150000	-0.747435000	-0.007462000
1	0.358535000	-1.327427000	-0.013016000
1	4.586455000	1.352305000	0.011307000
1	-3.418366000	1.734943000	-0.856328000
1	-4.862648000	1.108907000	0.053322000
6	-3.773212000	1.205697000	0.036422000
1	-3.387480000	1.695243000	0.939020000
7	-3.186439000	-0.167327000	-0.003760000
8	-3.962210000	-1.132477000	-0.005187000
8	-1.950453000	-0.240182000	-0.032267000

NMAc-I

8	1.097214000	-0.626051000	1.125826000
7	1.074152000	-0.111126000	0.006445000
8	1.051229000	-0.731445000	-1.059233000
1	-0.073037000	1.614408000	-0.068677000
6	0.997134000	1.378526000	-0.065210000
1	1.484269000	1.783930000	0.823802000
1	1.468796000	1.694906000	-0.997747000
6	-2.775299000	0.354184000	0.028699000
6	-2.019445000	-0.599837000	-0.020615000
1	-1.341300000	-1.429834000	-0.066411000
1	-3.459685000	1.177194000	0.073928000

NMAc-II

8	0.739364000	-1.131361000	0.028327000
7	1.399787000	-0.087271000	0.001859000
8	2.627374000	-0.029412000	-0.044386000
1	1.351661000	2.018139000	0.017132000
6	0.632889000	1.197853000	0.027108000
1	-0.017150000	1.202960000	-0.852752000
1	0.019226000	1.190626000	0.932467000
6	-3.528464000	0.167346000	-0.021051000
6	-2.455600000	-0.410462000	0.000518000
1	-1.503720000	-0.910626000	0.019258000
1	-4.475383000	0.667559000	-0.040097000

NMAc-III*

8	-0.765061000	-1.111648000	0.394478000
7	-1.341712000	-0.087688000	0.012904000
8	-2.392183000	-0.064547000	-0.626283000
1	-1.338162000	2.018632000	-0.010479000
6	-0.698992000	1.217572000	0.363284000
1	-0.595721000	1.240102000	1.451881000
1	0.292350000	1.222921000	-0.100816000
6	3.378810000	0.209330000	-0.273401000
6	2.405867000	-0.461754000	0.022915000
1	1.534639000	-1.035875000	0.280469000
1	4.242712000	0.786706000	-0.533736000