Supporting Information for

Butadiene and Heterodienes Revisited

Kenneth B. Wiberg*, Paul R. Rablen* and Joshua H. Baraban*

Table S1 MP2/aug-cc-pVZ optimized coordinates for trans forms, starting point for scans

butadiene #1 trans C2h E = -155.638454

0 1

C	0.60516500	1.74300200	0.00000000
C	0.60516500	0.40181900	0.00000000
H	1.52714600	2.30629600	0.00000000
H	-0.32404700	2.29848600	0.00000000
H	1.54957000	-0.13308300	0.00000000
C	-0.60516500	-0.40181900	0.00000000
C	-0.60516500	-1.74300200	0.00000000
H	-1.54957000	0.13308300	0.00000000
H	-1.52714600	-2.30629600	0.00000000
H	0.32404700	-2.29848600	0.00000000

diene2 (2-azabutadiene) Cs E = -171.671355 μ= 1.5807

0 1

C	1.11338500	1.39270100	0.00000000
C	0.00000000	0.65378200	0.00000000
H	1.06075500	2.47100300	0.00000000
H	2.08045900	0.91091500	0.00000000
H	-0.98802200	1.11600900	0.00000000
C	-1.04653500	-1.37125700	0.00000000
H	-1.04452100	-2.45487400	0.00000000
H	-2.01184400	-0.85606300	0.00000000
N	0.07172500	-0.74833500	0.00000000

acrolein #3 trans Cs E= -191.555490 μ = 3.8178

0 1

C	1.22108700	1.27147200	0.00000000
C	0.00000000	0.72324500	0.00000000
H	1.36972300	2.34147000	0.00000000
H	2.10255000	0.64190300	0.00000000
C	-0.15073500	-0.73823900	0.00000000
H	-0.90518000	1.31616800	0.00000000
H	0.80010000	-1.30381200	0.00000000
O	-1.22366300	-1.31682500	0.00000000

diene #4 (nitrosoethylene) Cs E = -207.517929 μ = 3.0425

0 1

C	1.21048700	1.21442200	0.00000000
C	0.00000000	0.64674600	0.00000000
H	1.33230900	2.28704600	0.00000000
H	2.08866200	0.58389500	0.00000000
H	-0.94846500	1.17208400	0.00000000
N	-0.03676700	-0.77449700	0.00000000
O	-1.18475700	-1.22356800	0.00000000

diene #5 (E-1-azabutadiene) trans s E = -171.683939 μ = 2..386

0 1

C	-0.64002700	0.35188200	0.00000000
H	-0.51495000	1.43916500	0.00000000
C	1.79714900	0.14602300	0.00000000
H	2.70540100	-0.43871900	0.00000000
H	1.89368500	1.22448100	0.00000000
C	0.58886200	-0.43246800	0.00000000
H	0.47331900	-1.50919600	0.00000000
N	-1.78632000	-0.22595800	0.00000000
H	-2.52911200	0.47335100	0.00000000

Z-1-azabutadiene #6 Cs E = -171.681525 μ = 2.6404

0 1

C	-0.64633500	0.39334800	0.09765200
H	-0.50509200	1.46894800	0.20660900
C	0.57004200	-0.42057100	0.10687300
C	1.78308100	0.11591000	-0.07759900
H	0.44942900	-1.49598500	0.18593600
H	2.67119200	-0.49664100	-0.13297800
H	1.90291900	1.18718500	-0.17730300
N	-1.84492500	-0.02208800	-0.09339400
H	-1.84470500	-1.04100700	-0.19006100

diene #7 Z-(HN=CH-CH=O)) Cs E = -207.593094 μ1.2631

0 1

O	-0.97152800	1.46524800	0.00000000
C	0.00000000	0.73715100	0.00000000
H	1.03299400	1.13667200	0.00000000
C	-0.08750400	-0.75271000	0.00000000
H	-1.08461300	-1.18479200	0.00000000
N	0.93669600	-1.51834300	0.00000000
H	1.79199400	-0.95211000	0.00000000

diene #8 (E-HN=CH-CH=O)) Cs E= -207.595138 μ = 2.6060

0 1

O	-1.10094100	-1.37885600	0.00000000
C	-0.05294700	-0.76148500	0.00000000
H	0.93232500	-1.25417800	0.00000000
C	0.00000000	0.72797000	0.00000000
H	-0.95860000	1.24831900	0.00000000
N	1.15447200	1.27756900	0.00000000
H	1.07018500	2.29480400	0.00000000

E-C-nitrosomethanimine (#9) Cs E= -223.556426 μ = 2.9694

0 1

C	0.54416100	0.34615000	0.00000000
H	0.32093000	1.41615500	0.00000000
N	1.66950200	-0.23769200	0.00000000
H	2.42302200	0.45022100	0.00000000
N	-0.63374500	-0.51296400	0.00000000
O	-1.65740200	0.16391400	0.00000000

Z-C-nitrosomethanimine (#10) Cs E = -223.558655 μ= 0.2507

0 1

C	0.00000000	0.68599300	0.00000000
H	-0.99249900	1.13261800	0.00000000
N	1.07496800	1.35854000	0.00000000
H	1.86924200	0.71040500	0.00000000
N	0.04026700	-0.77290300	0.00000000
O	-1.08542300	-1.25730500	0.00000000

glyoxal #11 C2h E = -227.460954 μ = 0.0

0 1

C	-0.32952600	0.68170200	0.00000000
H	-1.43074000	0.67187500	0.00000000
C	0.32952600	-0.68170200	0.00000000
H	1.43074000	-0.67187500	0.00000000
O	-0.32952600	-1.70192600	0.00000000
O	0.32952600	1.70192600	0.00000000

Nitrosoformaldehyde # 12 Cs E = -243.426793 μ= 1.8886

0 1

C	0.00000000	0.68411000	0.00000000
H	-1.06329400	0.98306100	0.00000000
O	-0.95945800	-1.32148000	0.00000000
O	0.95784700	1.40025000	0.00000000
N	0.15374000	-0.81684000	0.00000000

Z,Z-1,4-Diazabutadiene (#13) C2h E= -187.722999 μ = 0.0
0 1

C	-0.31274400	0.66929400	0.00000000
H	-1.40335800	0.69114600	0.00000000
C	0.31274400	-0.66929400	0.00000000
H	1.40335800	-0.69114600	0.00000000
N	-0.31274400	-1.78545100	0.00000000
H	-1.32301900	-1.61654100	0.00000000
N	0.31274400	1.78545100	0.00000000
H	1.32301900	1.61654100	0.00000000

E,Z-1,4-Diazabutadiene (#14) Cs E= - 187.724395 μ = 2.6229
0 1

C	-0.03289500	-0.76174400	0.00000000
H	-1.02209600	-1.21290500	0.00000000
C	0.00000000	0.71194700	0.00000000
H	0.99367200	1.17131100	0.00000000
N	-1.09902200	1.36784700	0.00000000
H	-0.91619900	2.37171300	0.00000000
N	0.99798300	-1.52199500	0.00000000
H	1.84927000	-0.95230300	0.00000000

E,E-1,4-Diazabutadiene (#15) C2h E = -187.715209 μ = 0.0

C	0.74381000	0.49952600	0.00000000
H	1.20457700	1.49030200	0.00000000
C	-0.74381000	0.49952600	0.00000000
H	-1.20457700	1.49030200	0.00000000
N	-1.41633000	-0.58787000	0.00000000
H	-2.41388400	-0.37237100	0.00000000
N	1.41633000	-0.58787000	0.00000000
H	2.41388400	-0.37237100	0.00000000

diene16 (CH2=N-CH=O)) Cs E== -207.592968 μ = 4.3764
0 1

C	0.84322800	1.41112900	0.00000000
H	0.78700700	2.49309200	0.00000000
H	1.83615200	0.94879700	0.00000000
N	-0.23781100	0.72819200	0.00000000
O	-0.88624000	-1.49414800	0.00000000
C	0.00000000	-0.68093200	0.00000000
H	1.07207300	-0.96722900	0.00000000

diene17 (2,3-diazabutadiene) C2h E = -187.689848 μ = 0.0

0 1

C	0.38348600	-1.62236000	0.00000000
H	-0.08507000	-2.59730600	0.00000000
H	1.46652700	-1.52626100	0.00000000
C	-0.38348600	1.62236000	0.00000000
H	0.08507000	2.59730600	0.00000000
H	-1.46652700	1.52626100	0.00000000
N	0.38348600	0.59685100	0.00000000
N	-0.38348600	-0.59685100	0.00000000

diene18 (CH2=N-N=O)) Cs E=-223.547602 μ = 3.3528

0 1

C	1.06189000	1.20116800	0.00000000
H	1.20314300	2.27411800	0.00000000
H	1.92475300	0.53601300	0.00000000
N	-0.13477500	0.74196500	0.00000000
N	0.00000000	-0.73101400	0.00000000
O	-1.06947600	-1.26172400	0.00000000

Table S2. Butadiene rotational profile, CCSD(T)/ANO1 and MP2/aug-cc-pVTZ

CCSDT)/ANO1		MP2/aug=cc=pVTZ	
Erel	tors	E	Erel
0	-180	0.638454	0.000
0.048	-175	0.63838	0.046
0.190	-170	0.638158	0.186
0.425	-165	0.637787	0.419
0.749	-160	0.637269	0.744
1.157	-155	0.63661	1.157
1.639	-150	0.635823	1.651
2.185	-145	0.634923	2.216
2.781	-140	0.633935	2.836
3.405	-135	0.632888	3.493
4.033	-130	0.631823	4.161
4.633	-125	0.630793	4.807
5.168	-120	0.629859	5.393
5.602	-115	0.629089	5.877
5.905	-110	0.62854	6.221
6.065	-105	0.628248	6.404
6.084	-100	0.628214	6.426
5.981	-95	0.628408	6.304
5.778	-90	0.628788	6.066
5.500	-85	0.629306	5.740
5.169	-80	0.629916	5.358
4.806	-75	0.630579	4.942
4.431	-70	0.631258	4.516
4.064	-65	0.631917	4.102
3.722	-60	0.632526	3.720
3.422	-55	0.633053	3.389
3.177	-50	0.633473	3.126
2.999	-45	0.633767	2.941
2.893	-40	0.633924	2.843
2.860	-35	0.633944	2.830
2.892	-30	0.63384	2.895
2.976	-25	0.633638	3.022
3.094	-20	0.633372	3.189
3.223	-15	0.633085	3.369
3.338	-10	0.632822	3.534
3.418	5	0.632626	3.657
3.447	0	0.632545	3.708

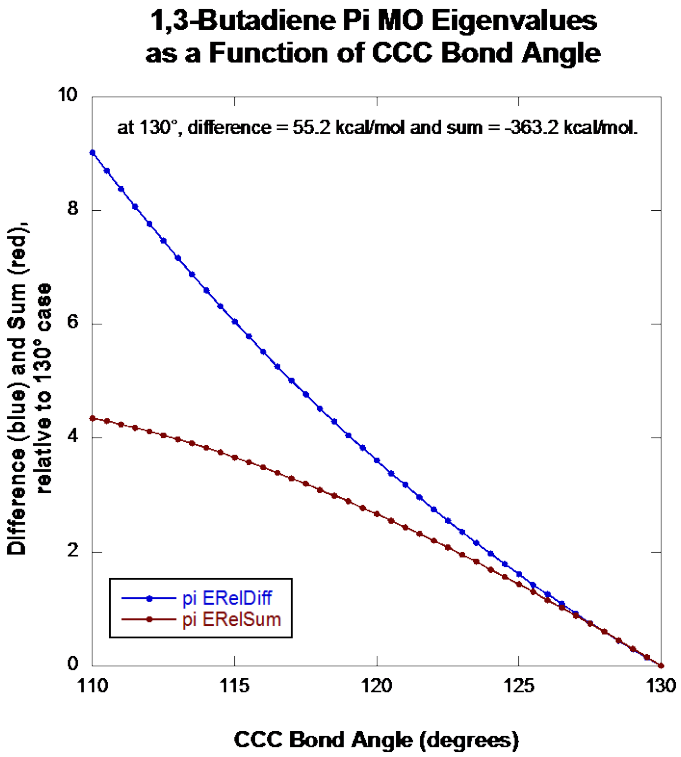


Figure S1. Variation of butadiene π MO (HOMO and HOMO–1) eigenvalues (computed at B3LYP/aug-cc-pVTZ) as a function of CCC bond angle, for a rigid compression starting with the *s-cis* geometry, but with the CCC angle expanded to 130°. The value of π_2–π_1 is shown in blue, while that of π_1+π_2 is shown in red, in both cases relative to the value at 130°. As expected, both quantities increase as the bond angle decreases, and therefore as the C1…C4 (repulsive) π interaction goes stronger.

Figure S2 MP2/aug-cc-pVTZ rotational profiles

(a) Butadiene

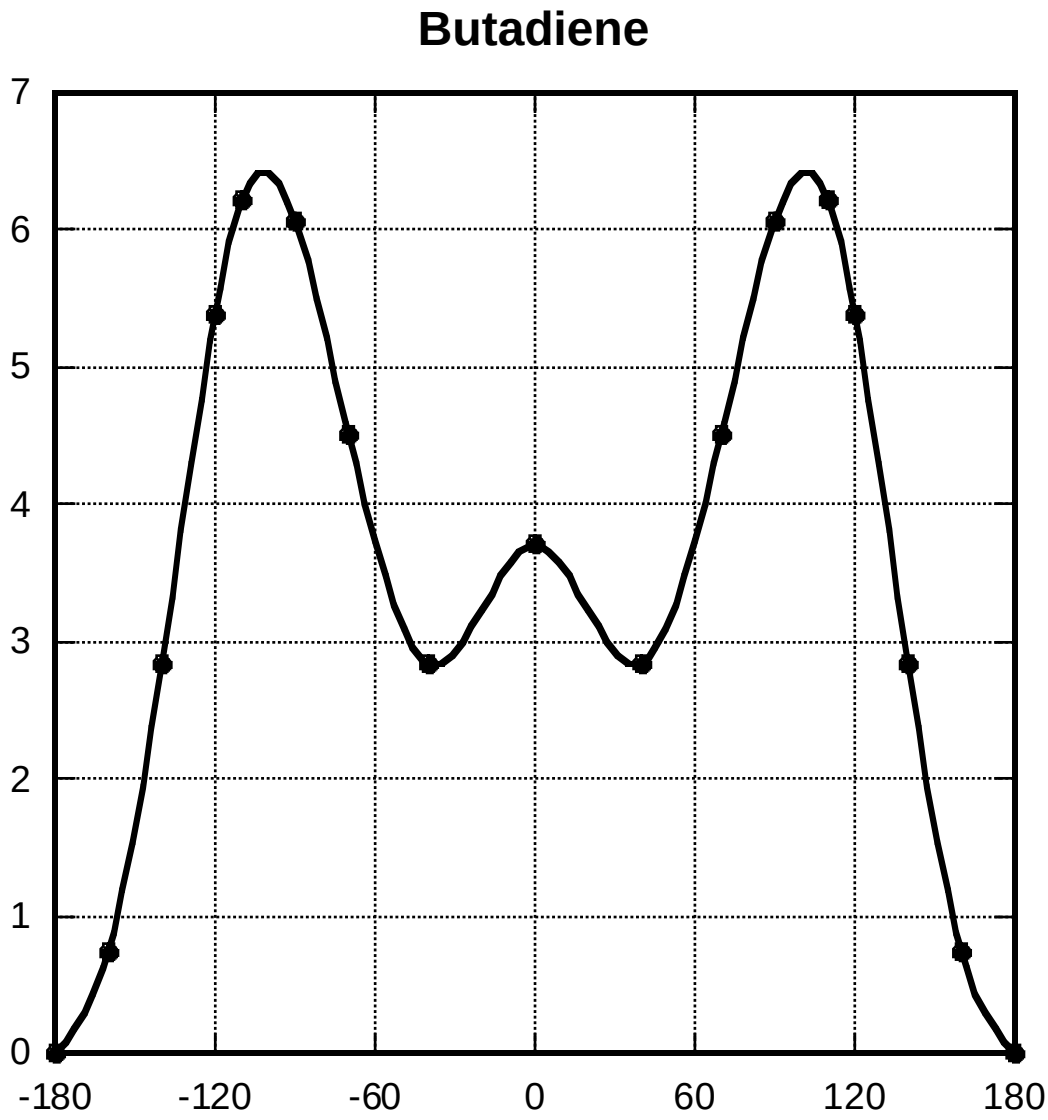


Fig S2b 2-Azabutadiene

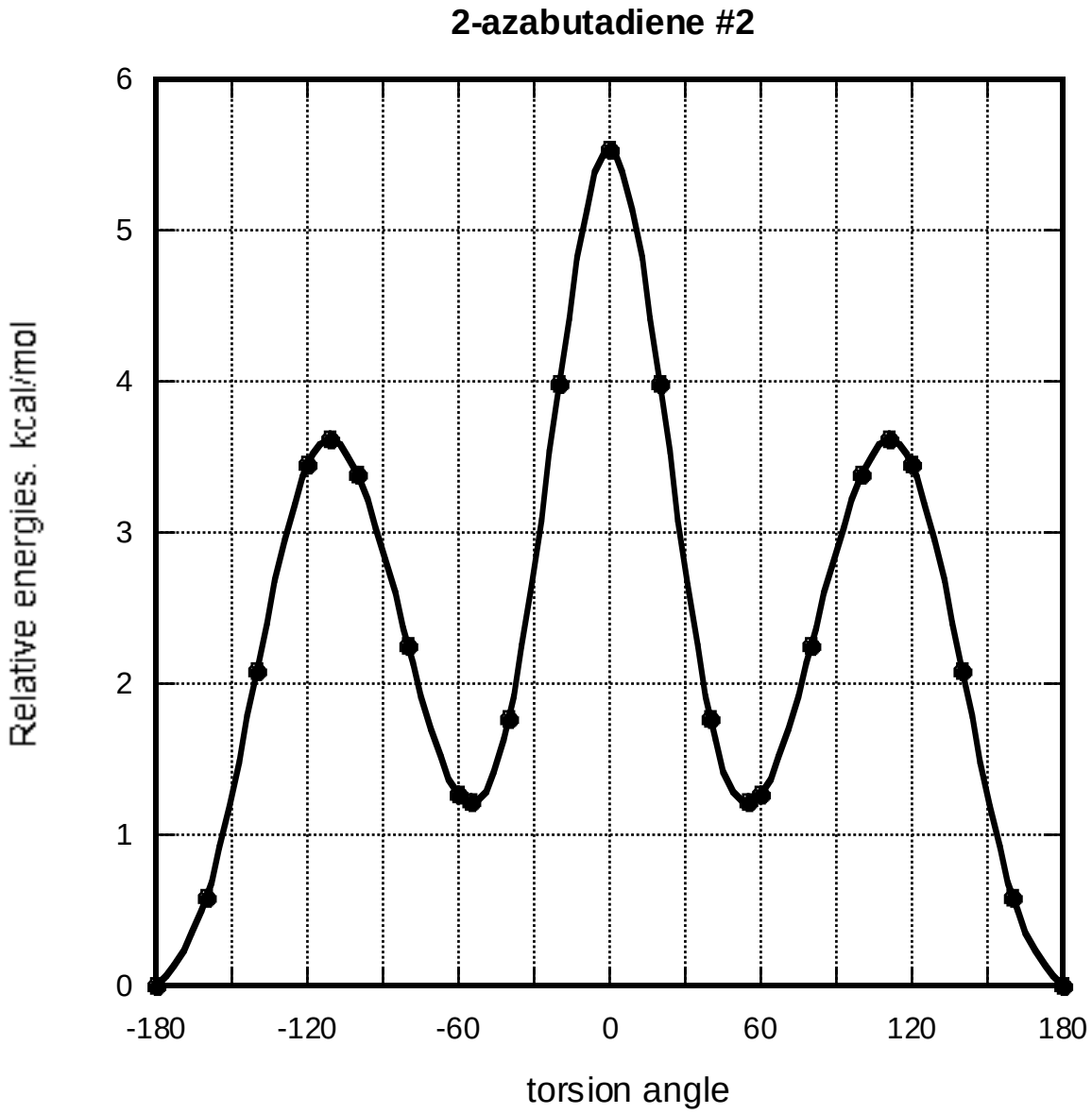


Figure S2c Acrolein

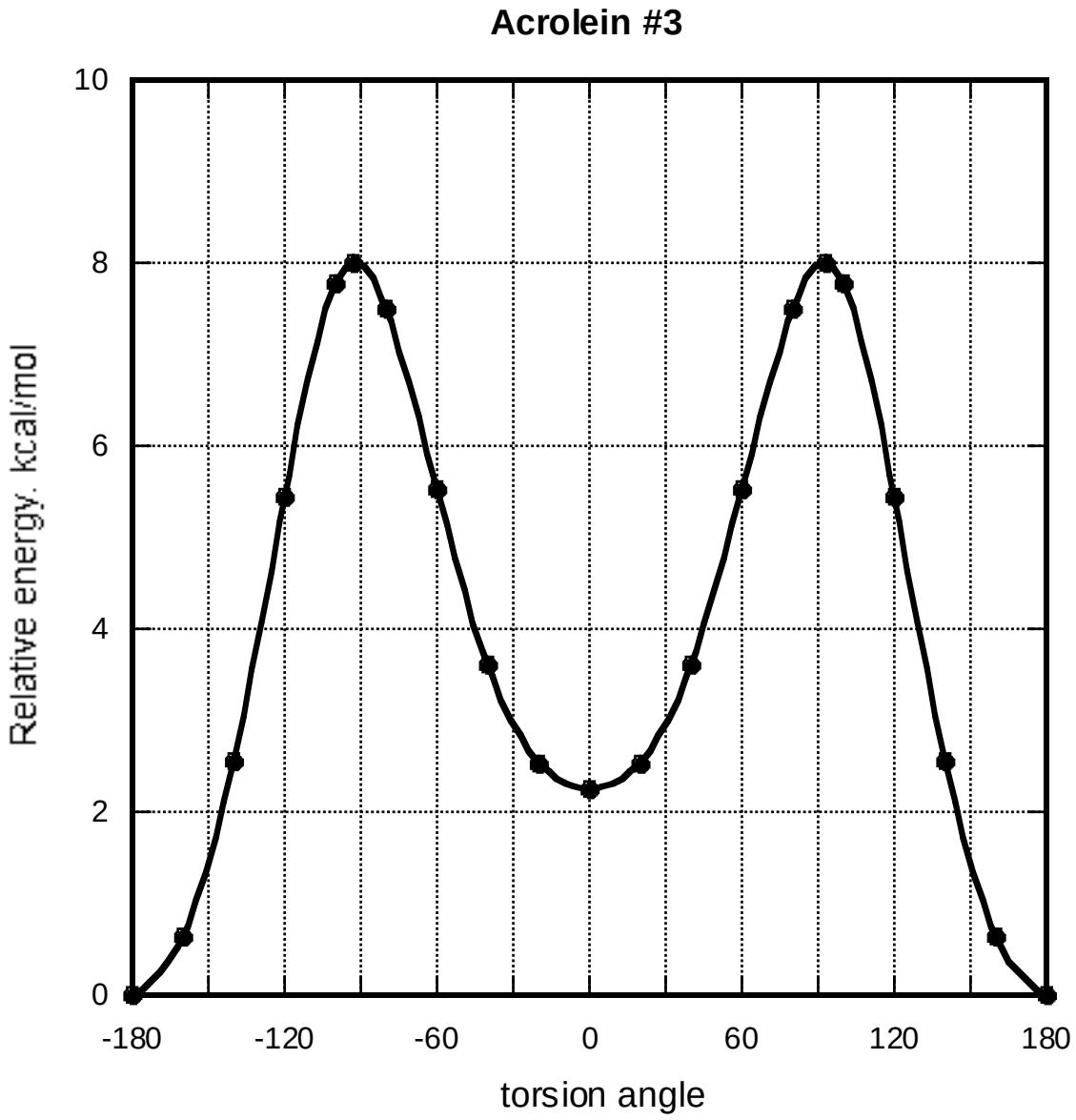


Figure S2d Nitrosoethylene

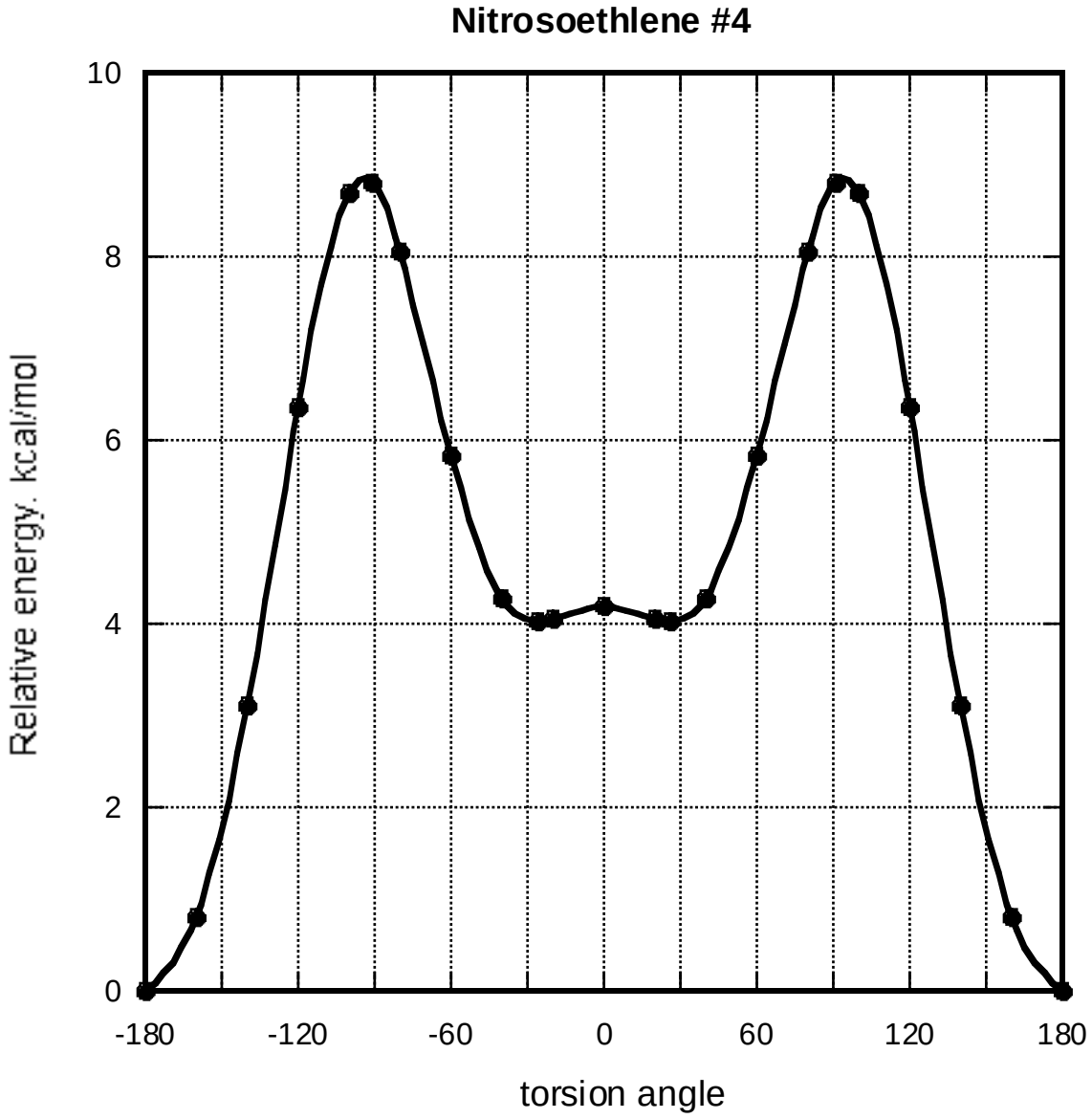


Figure S2e E-1-Azabutadiene

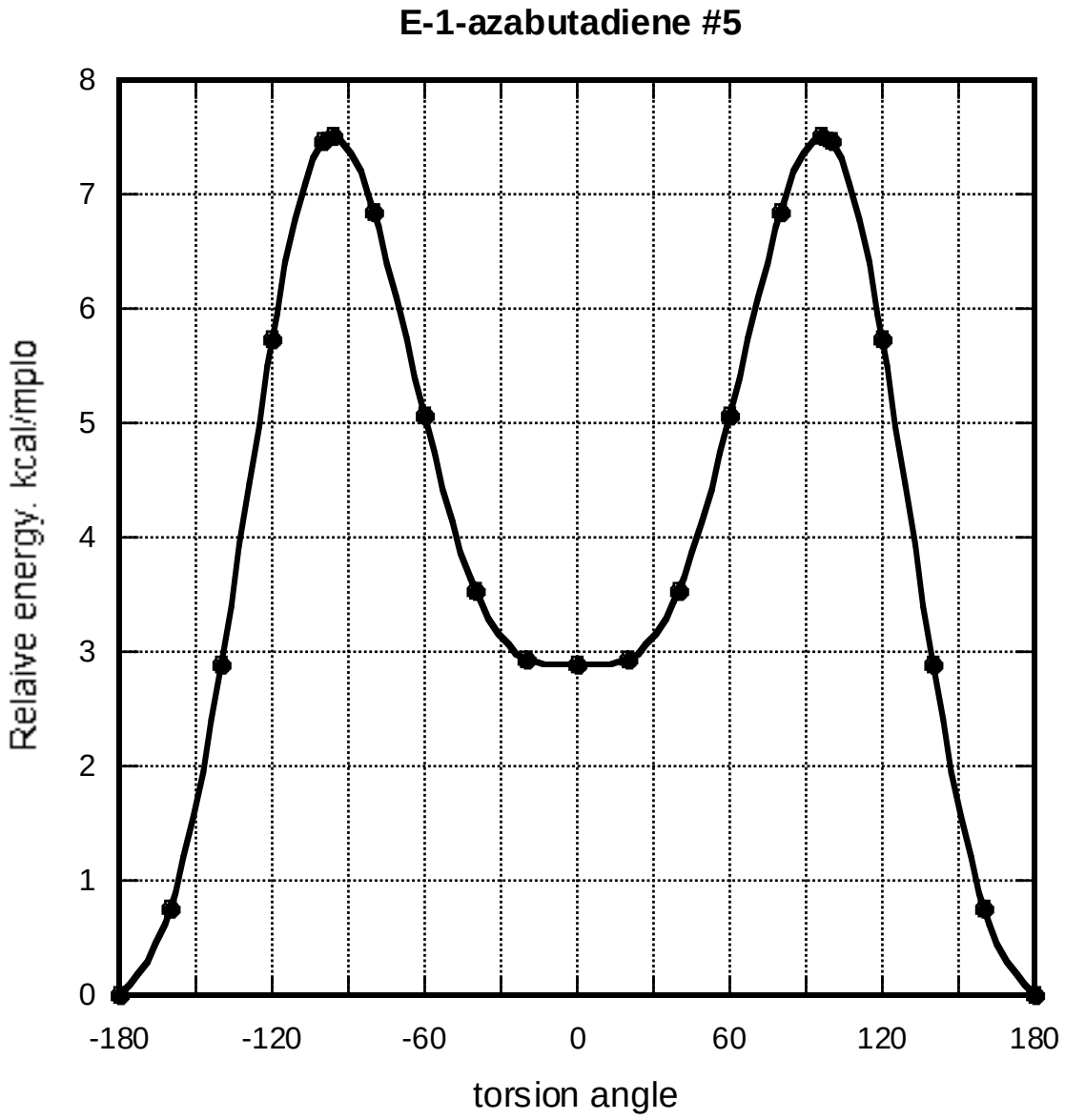


Figure S2f Z-1-azabutadiene

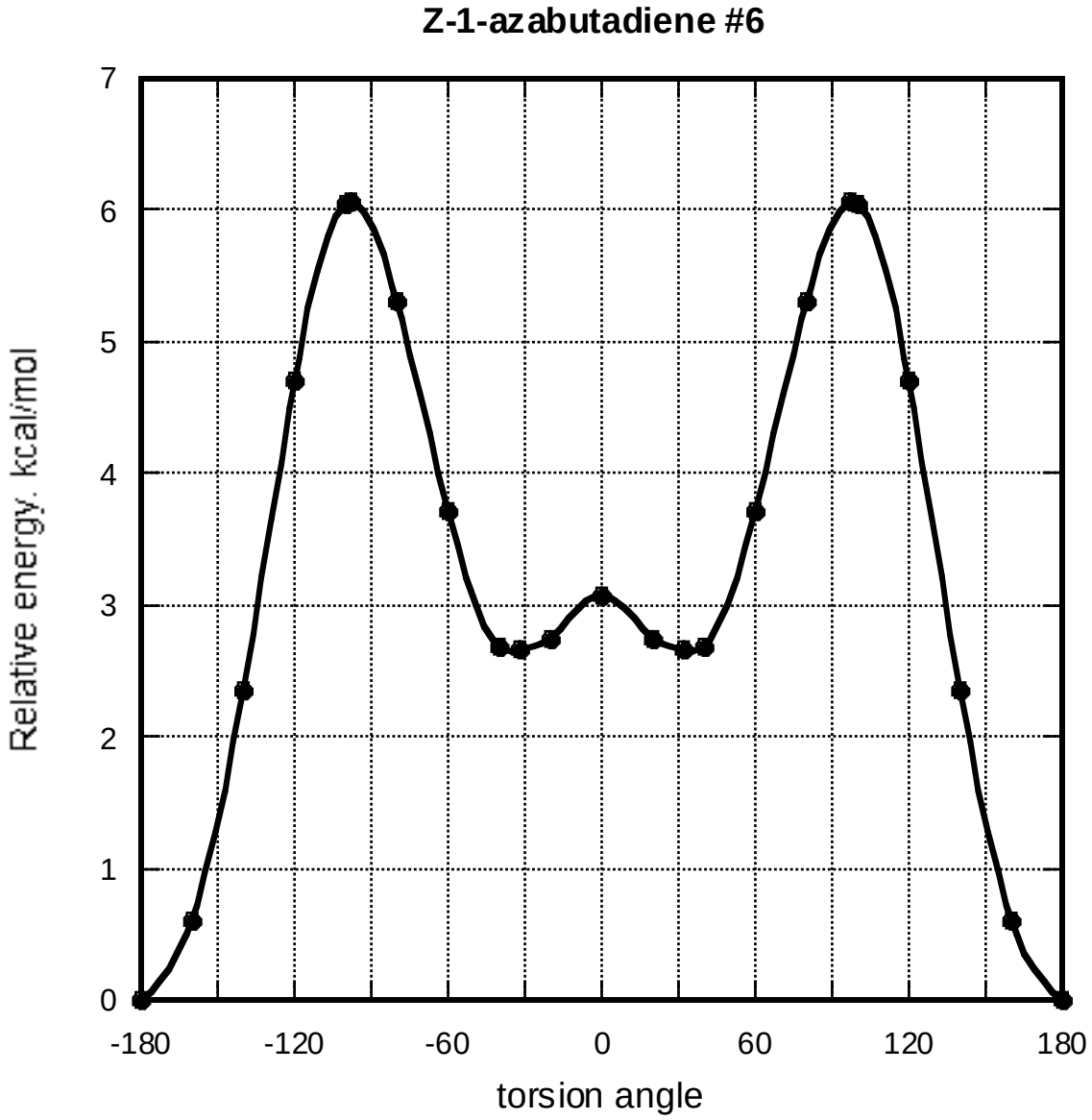
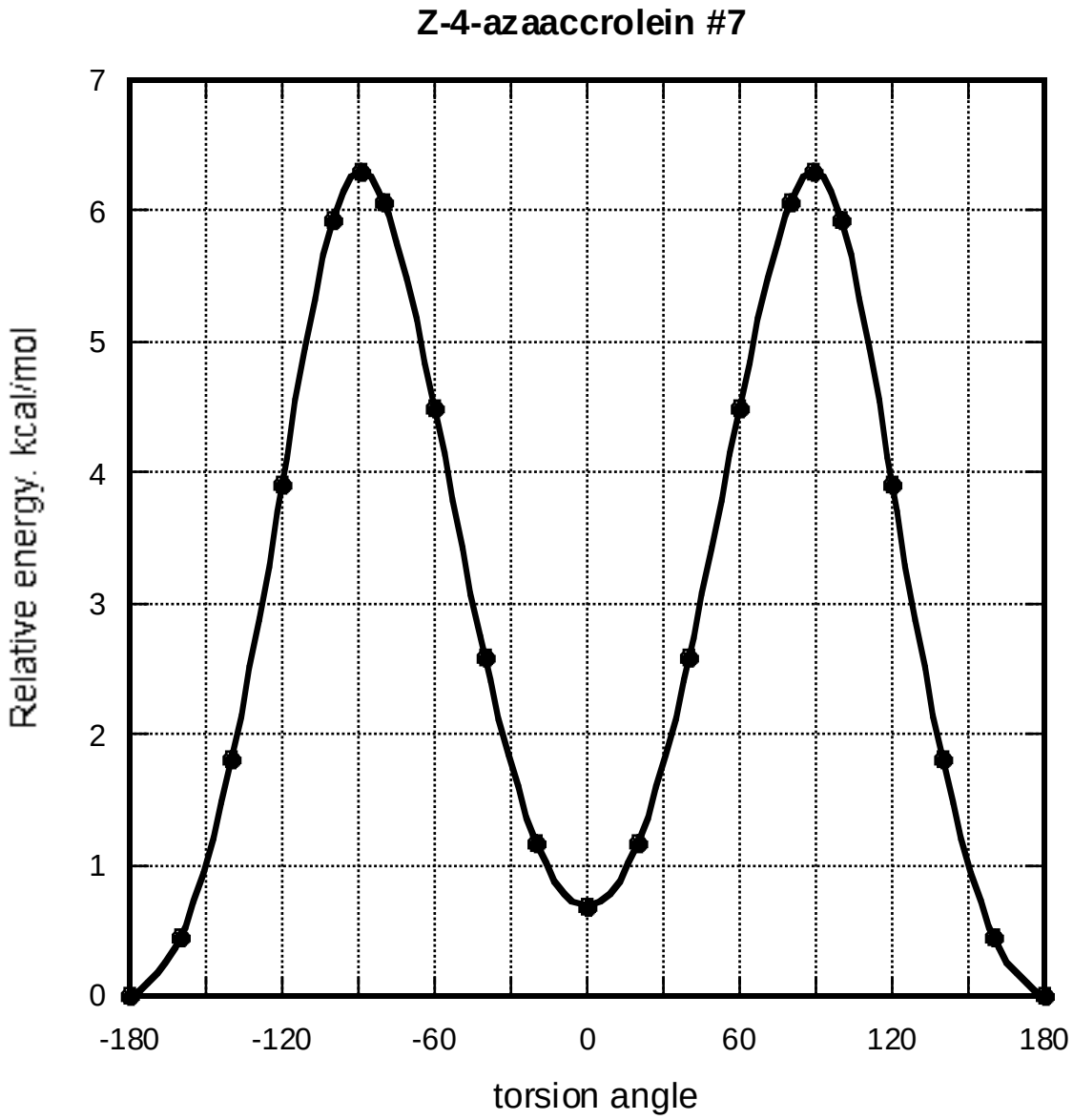


Figure S2g Z-4-azaacrolein



Fgure S2 h E-4-azaacrolein

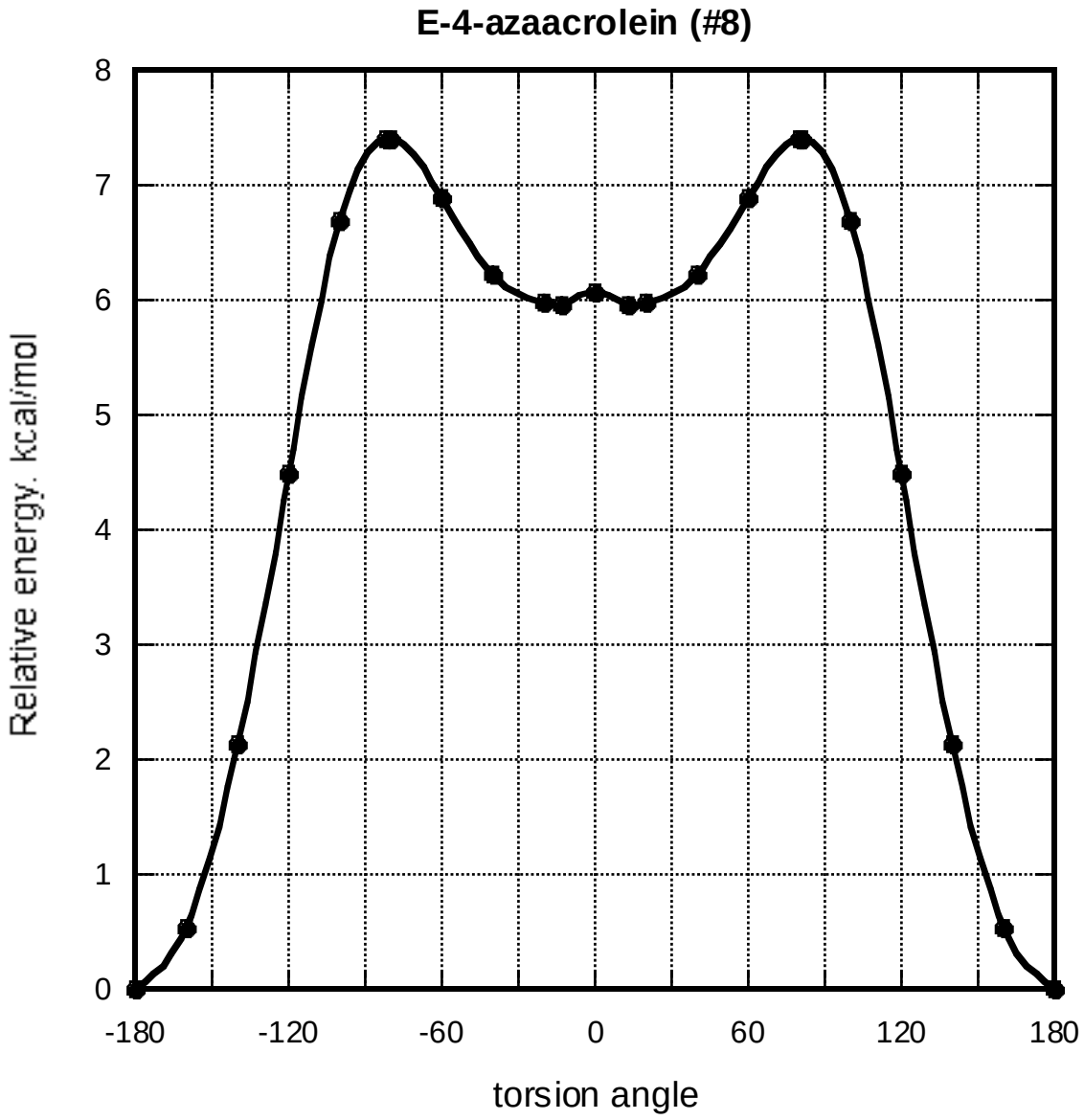


Figure S2i E-C-Nitrosomethanimine

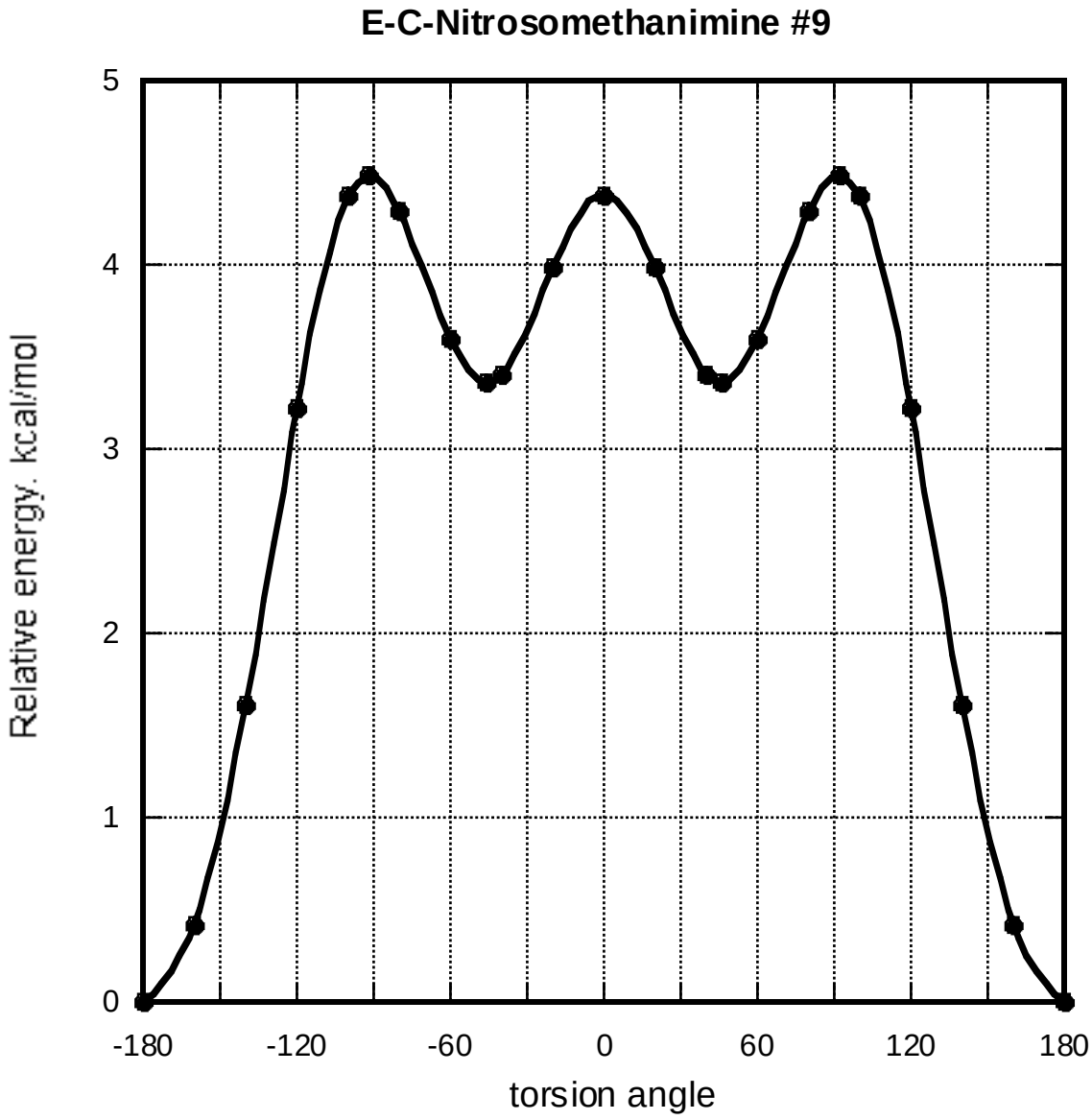


Figure S2j Z-C-Nitrosomethanimine

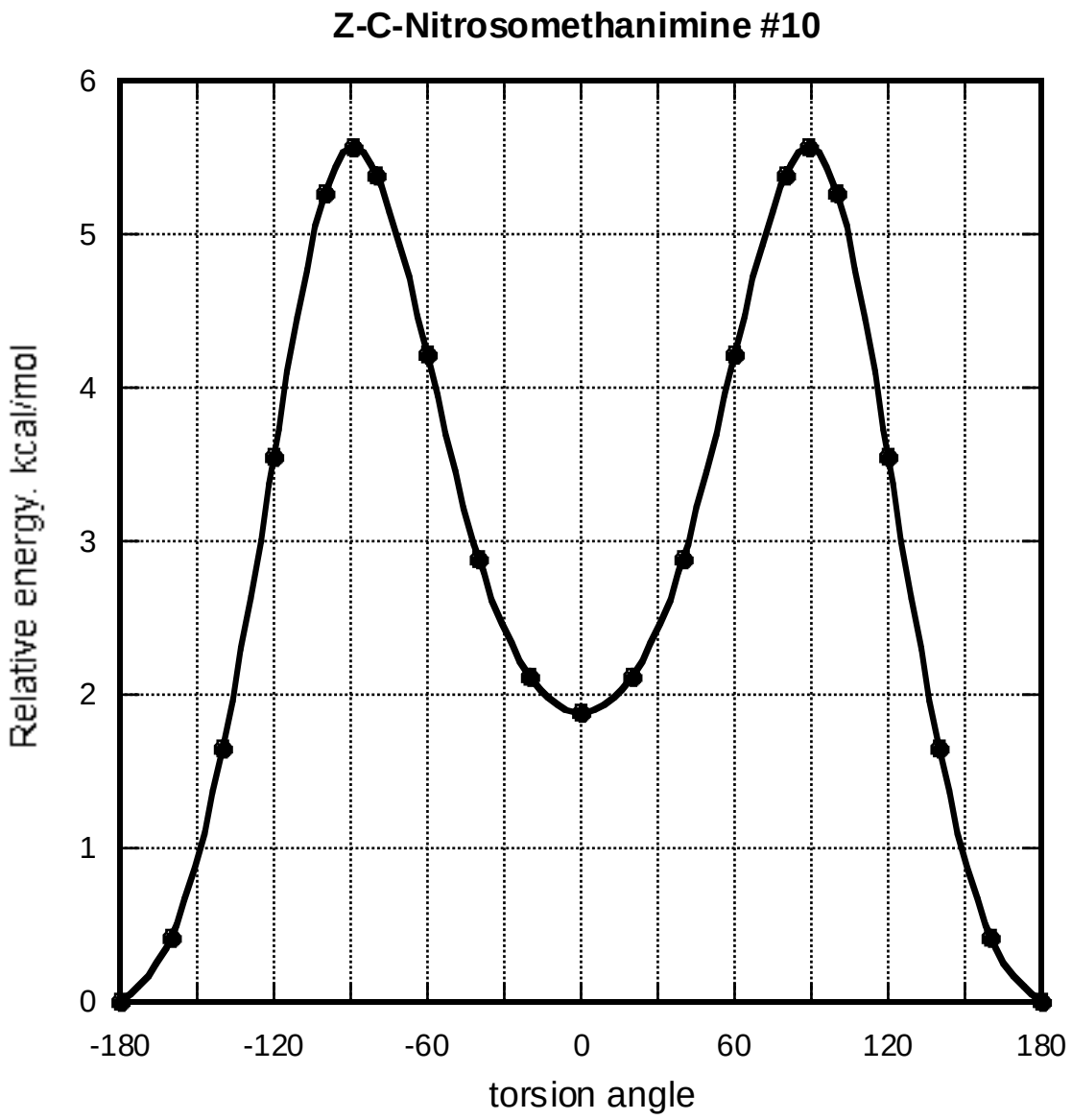


Figure S2k Glyoxal

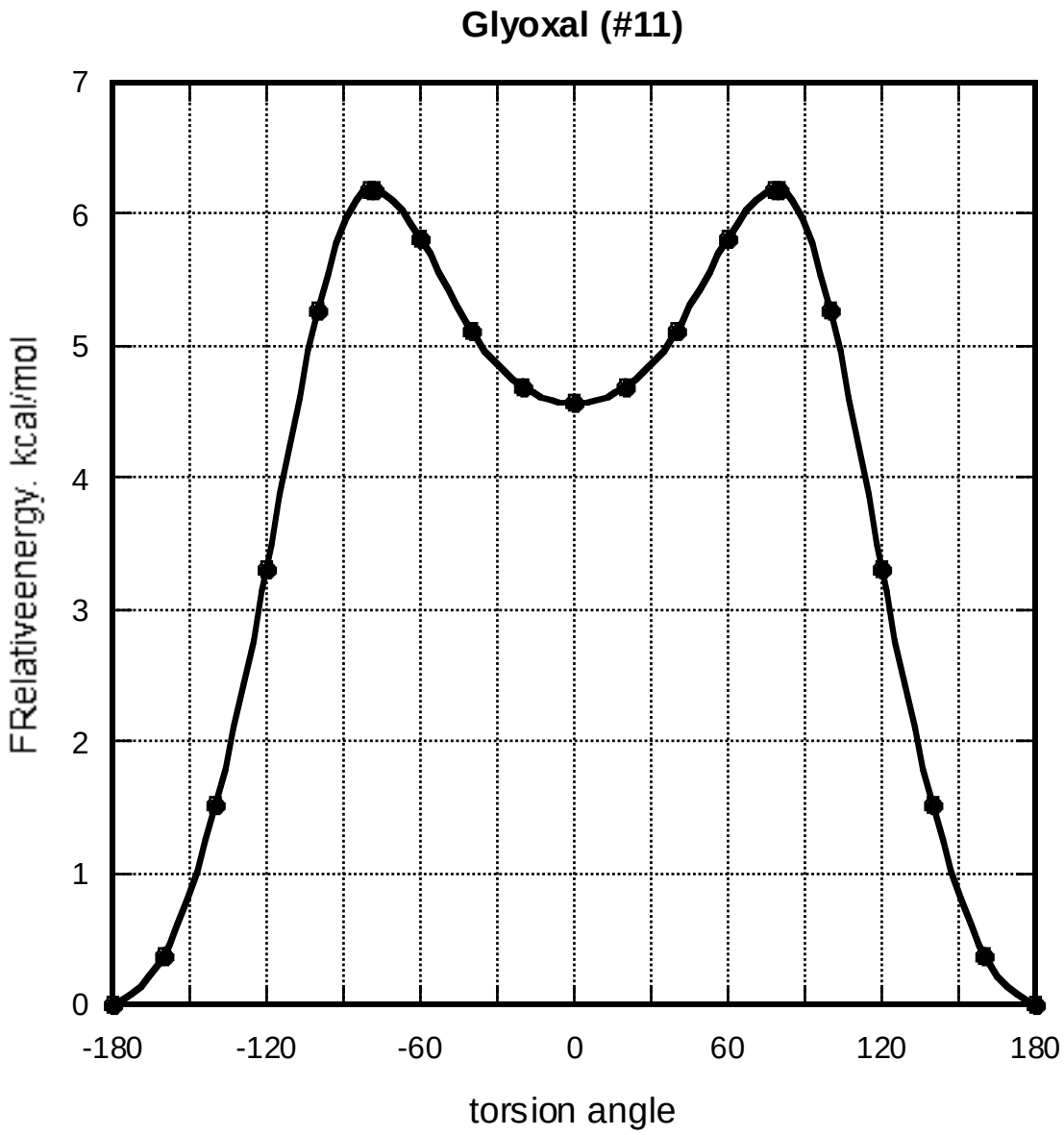


Figure S2l Nitrosoformaldehyde

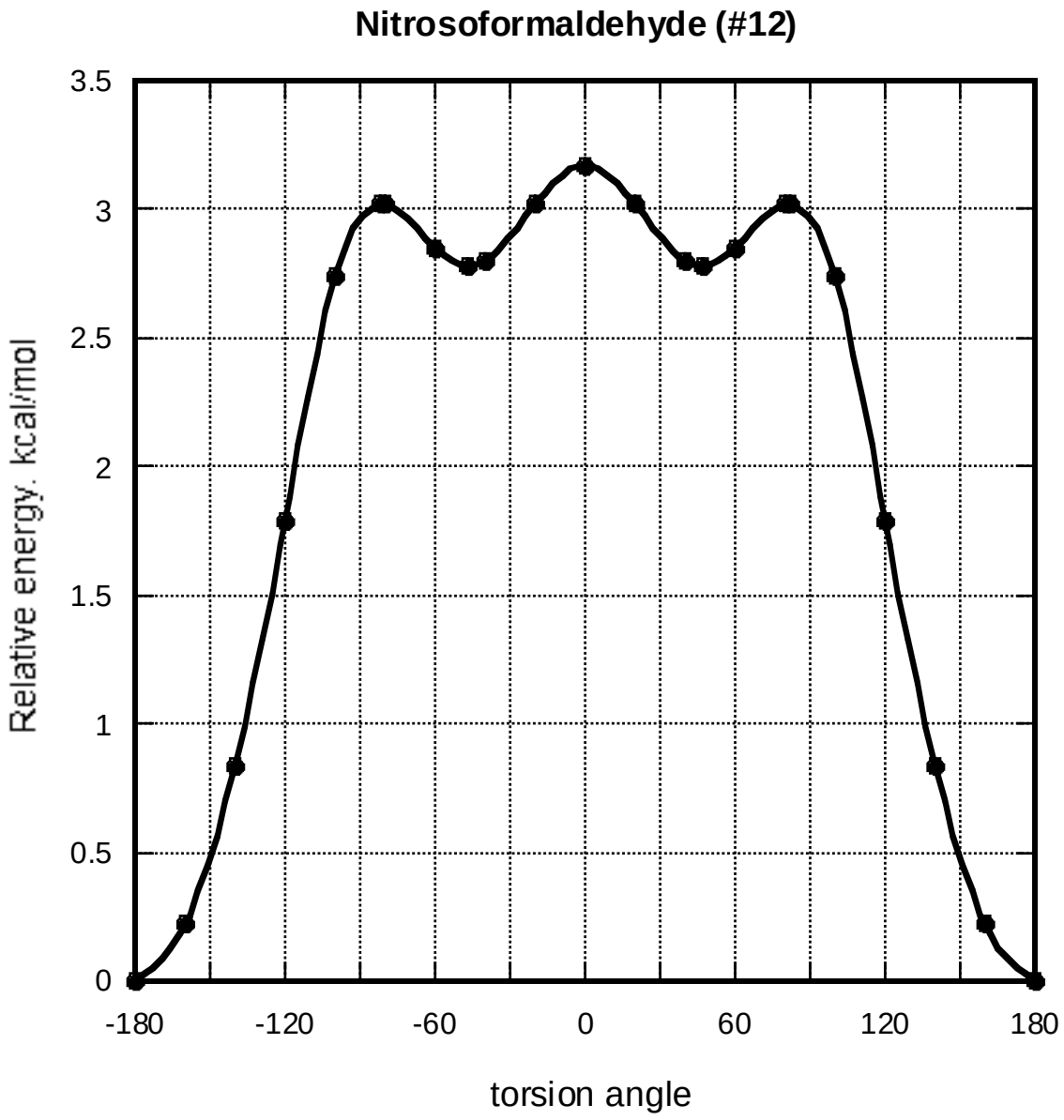


Figure S2m Z,Z-1,4-diazabutadiene

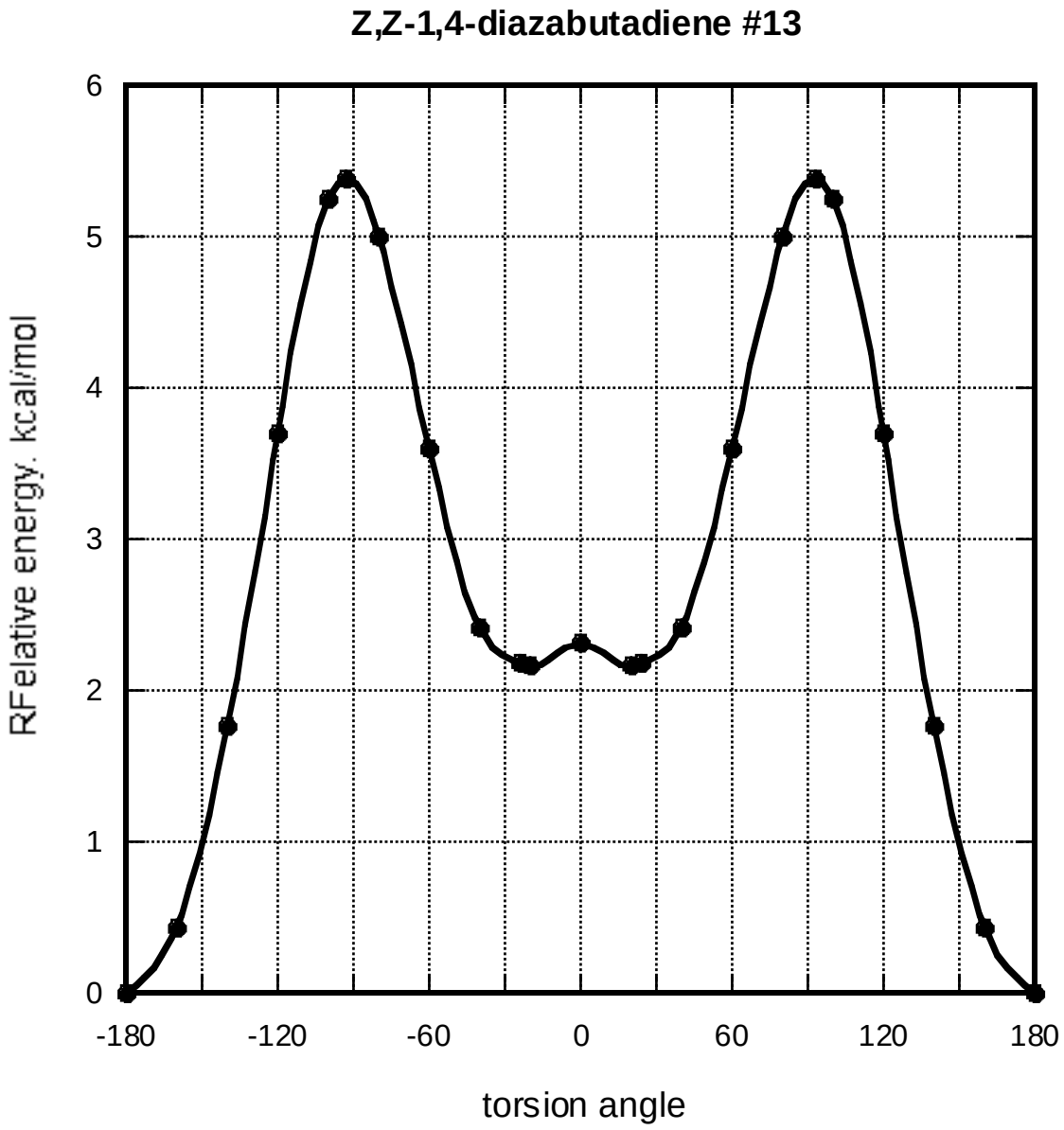


Figure S2n E,Z-1,4-diazabutadiene

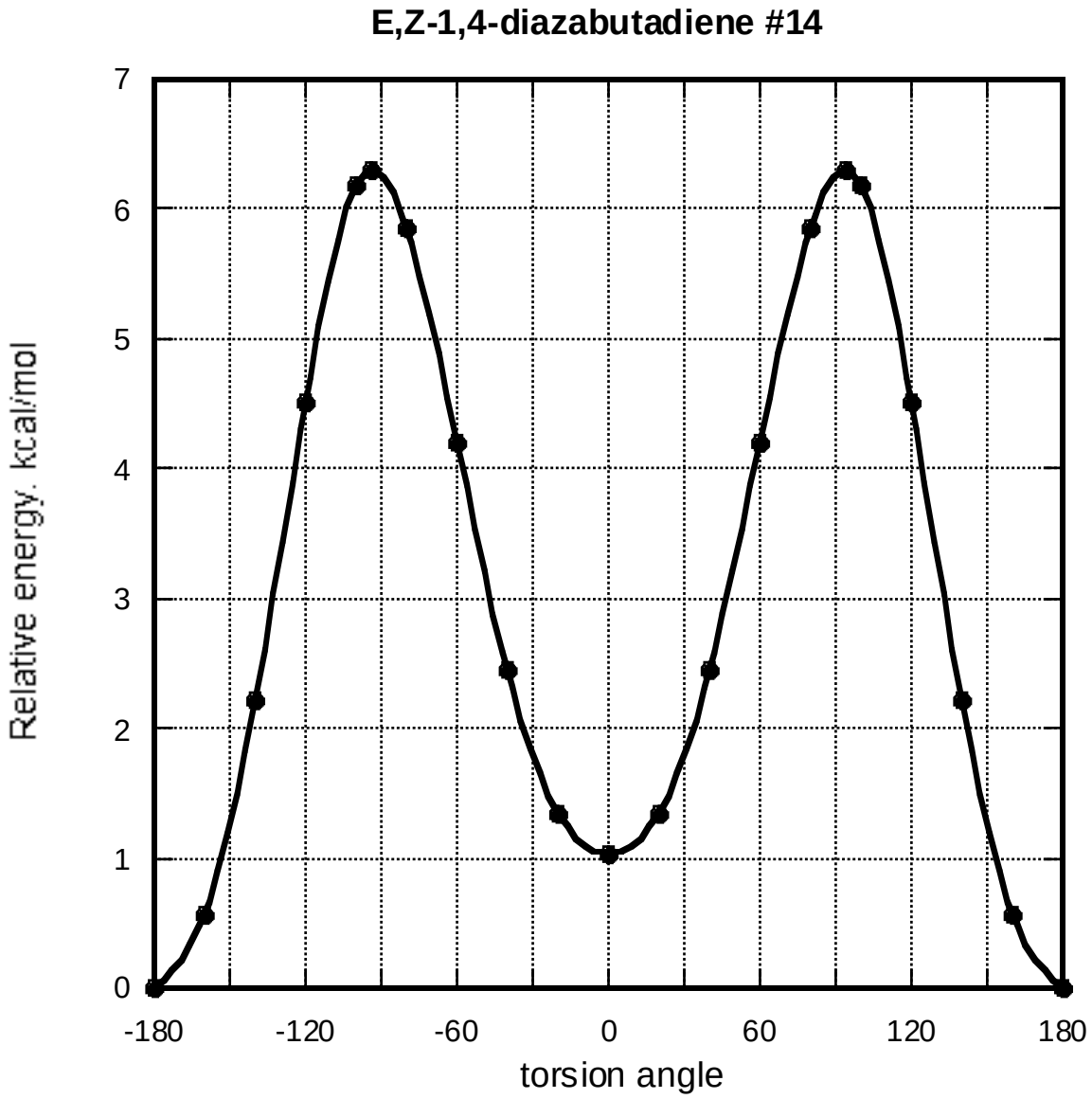


Figure S2o E,E-1,4-diazabutadiene

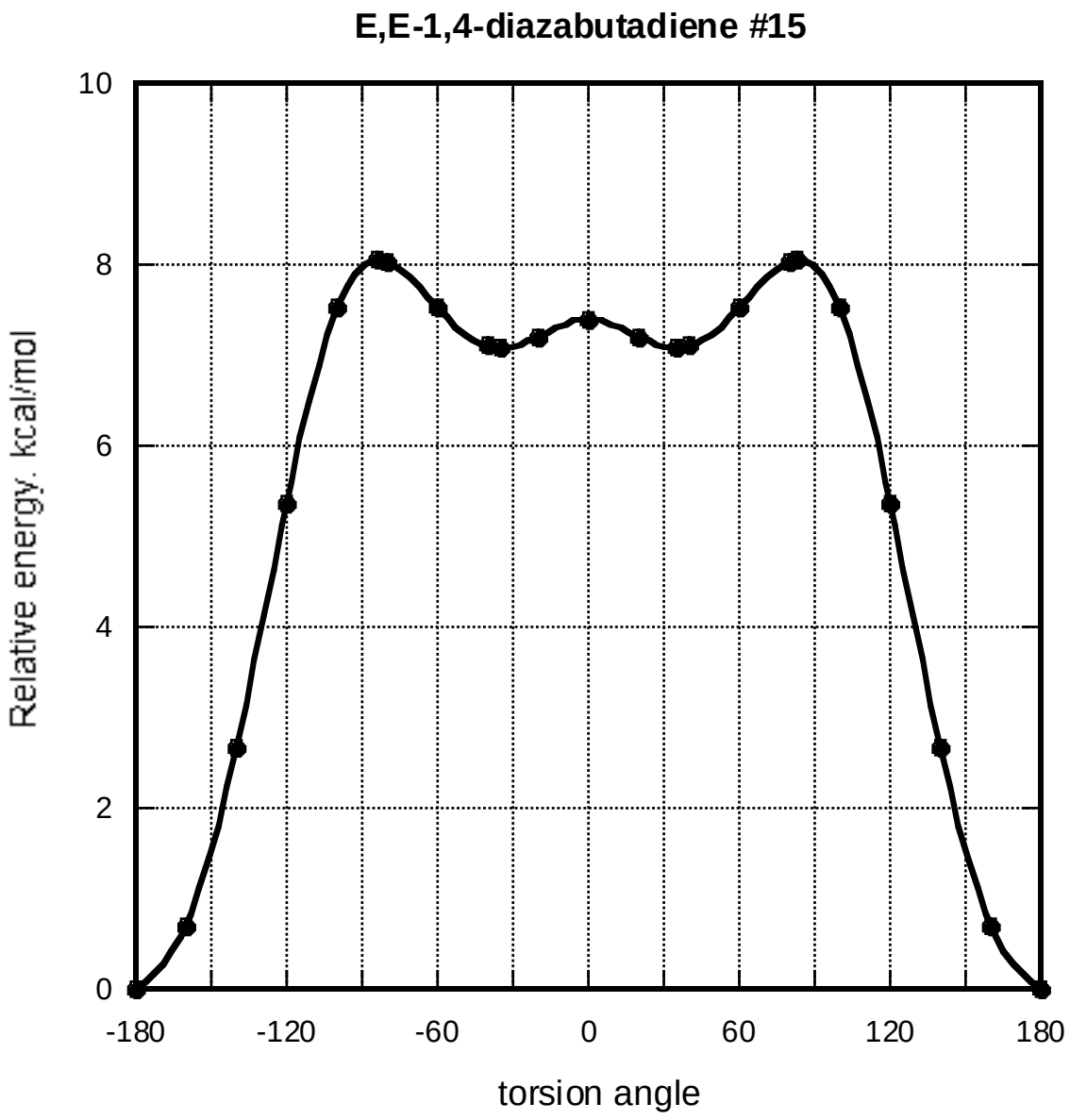


Figure S2p Methyleneformamide

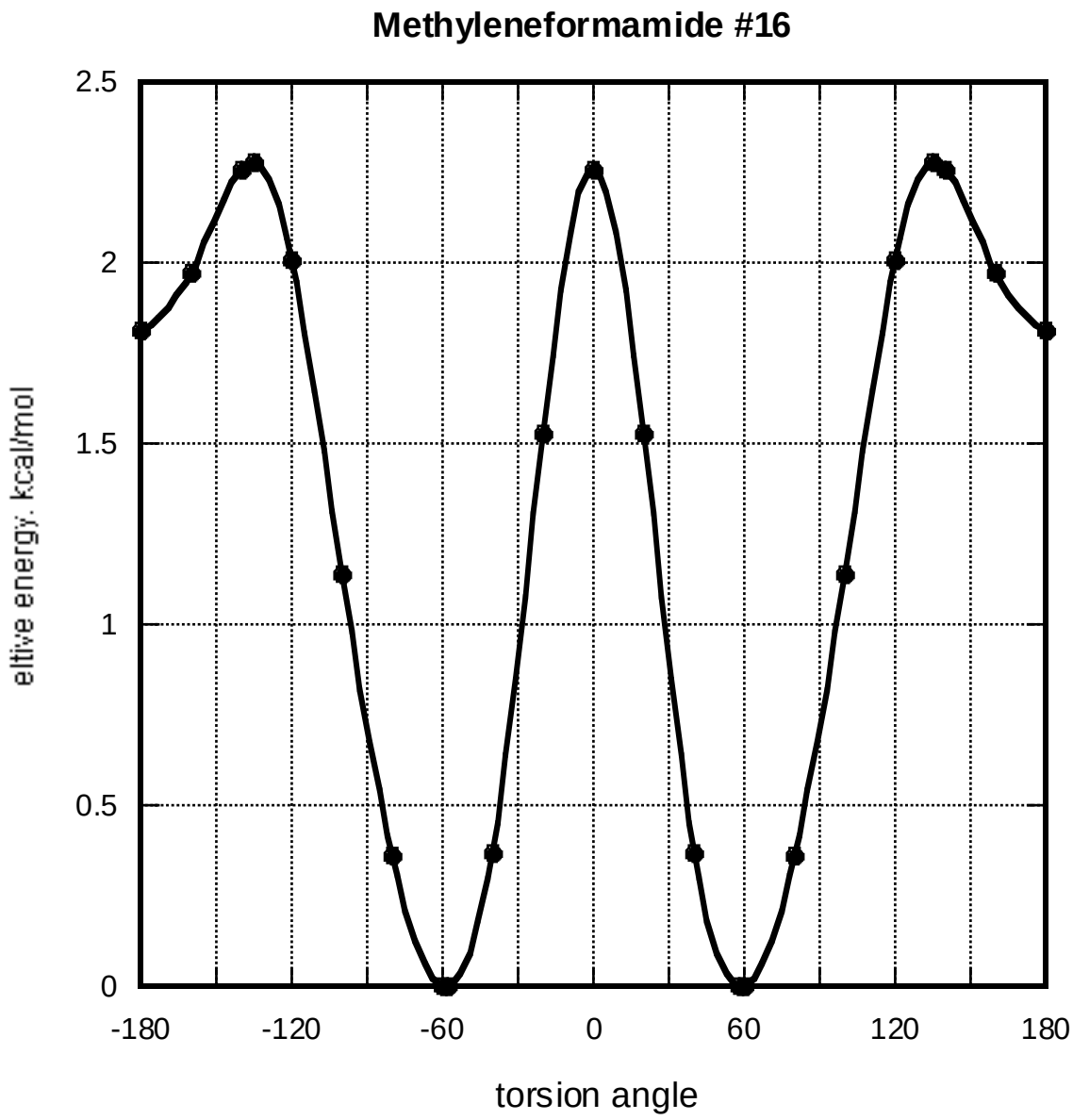


Figure S2q 2,3-diazabutadiene

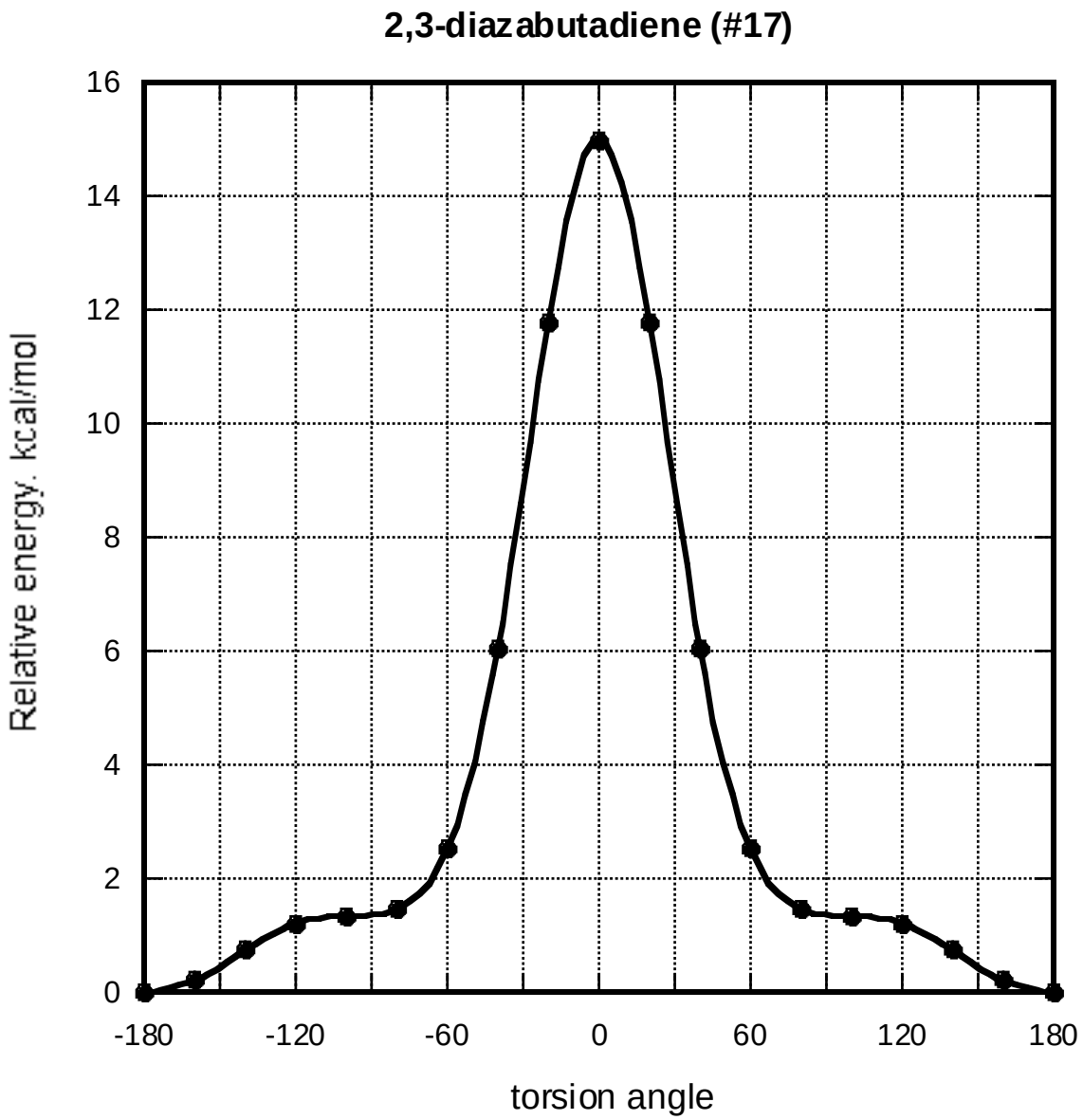


Figure S2r Nitrosomethanimine

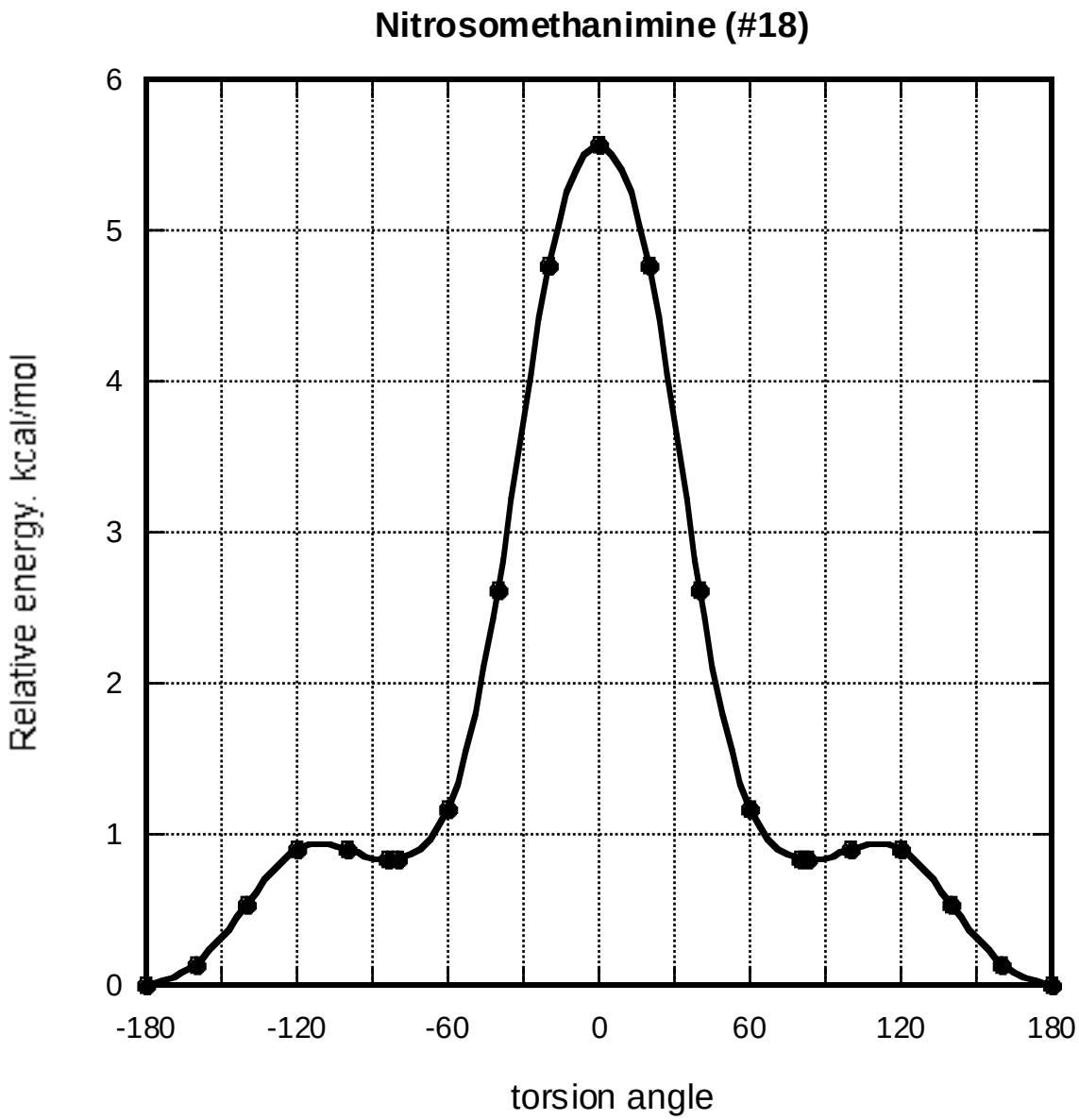


Figure S3 Components of the three-fold terms for rotational profiles
Figure S3a

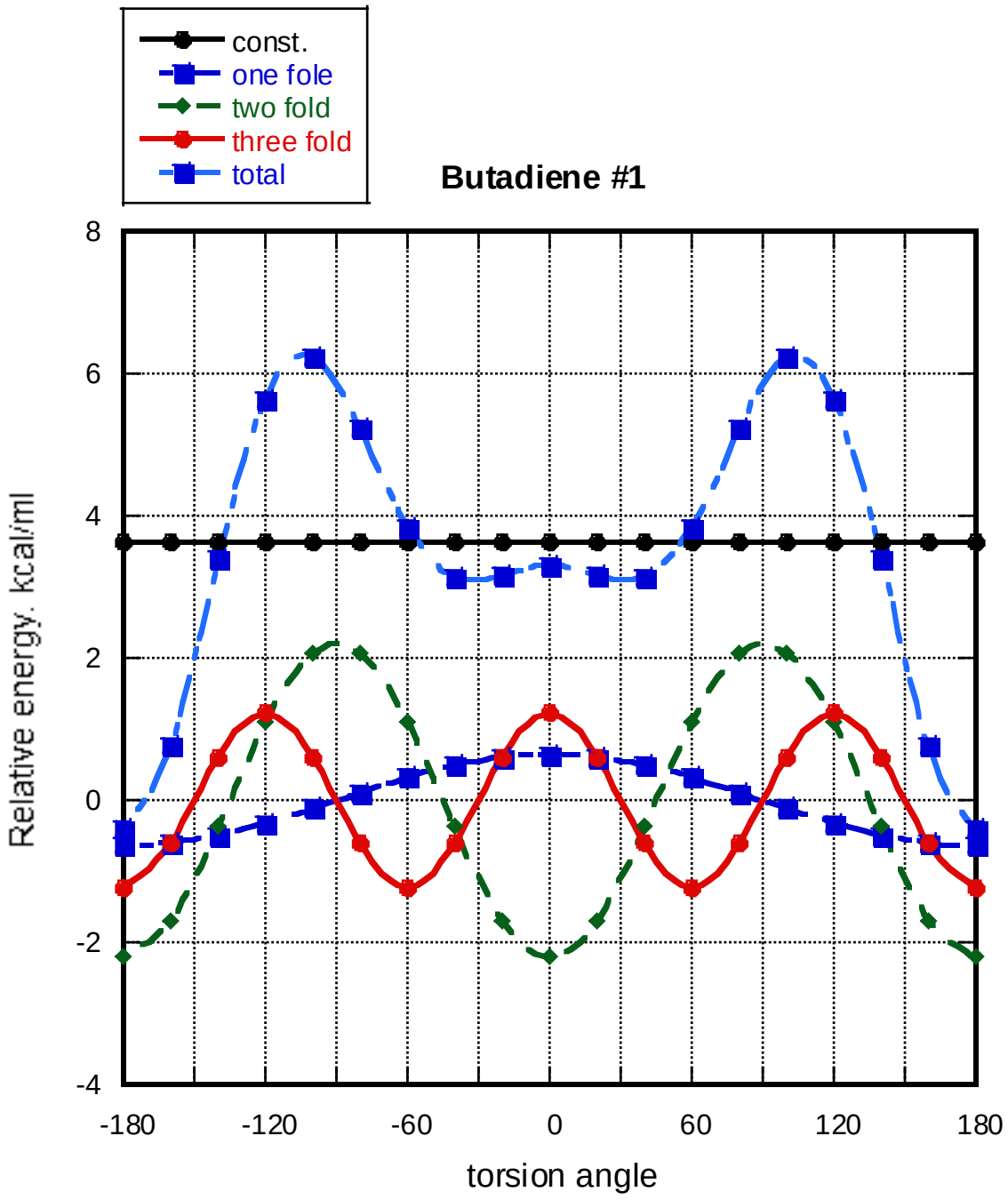


Figure S3b 2-Azabutadiene

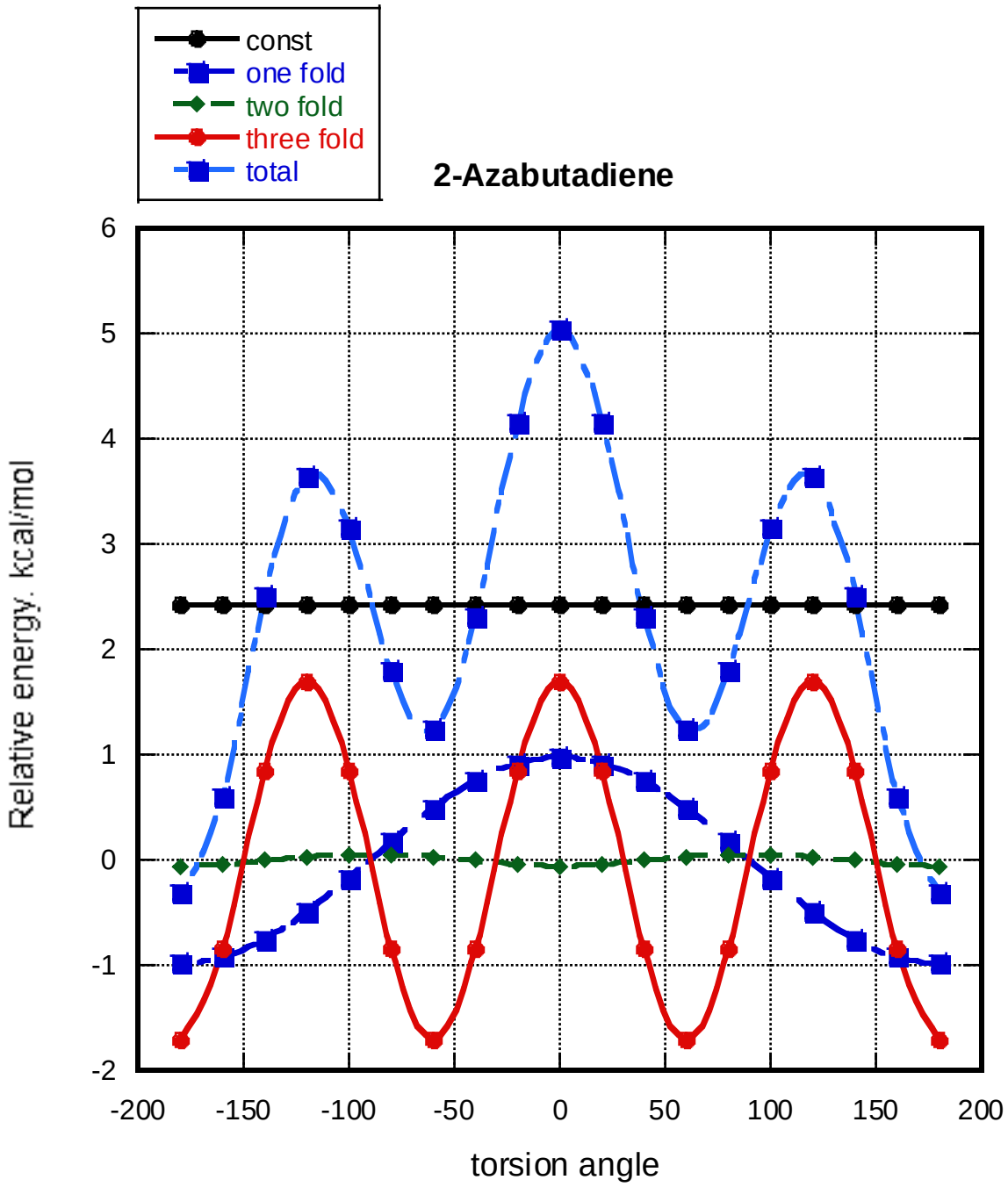


Figure S3c acrolein

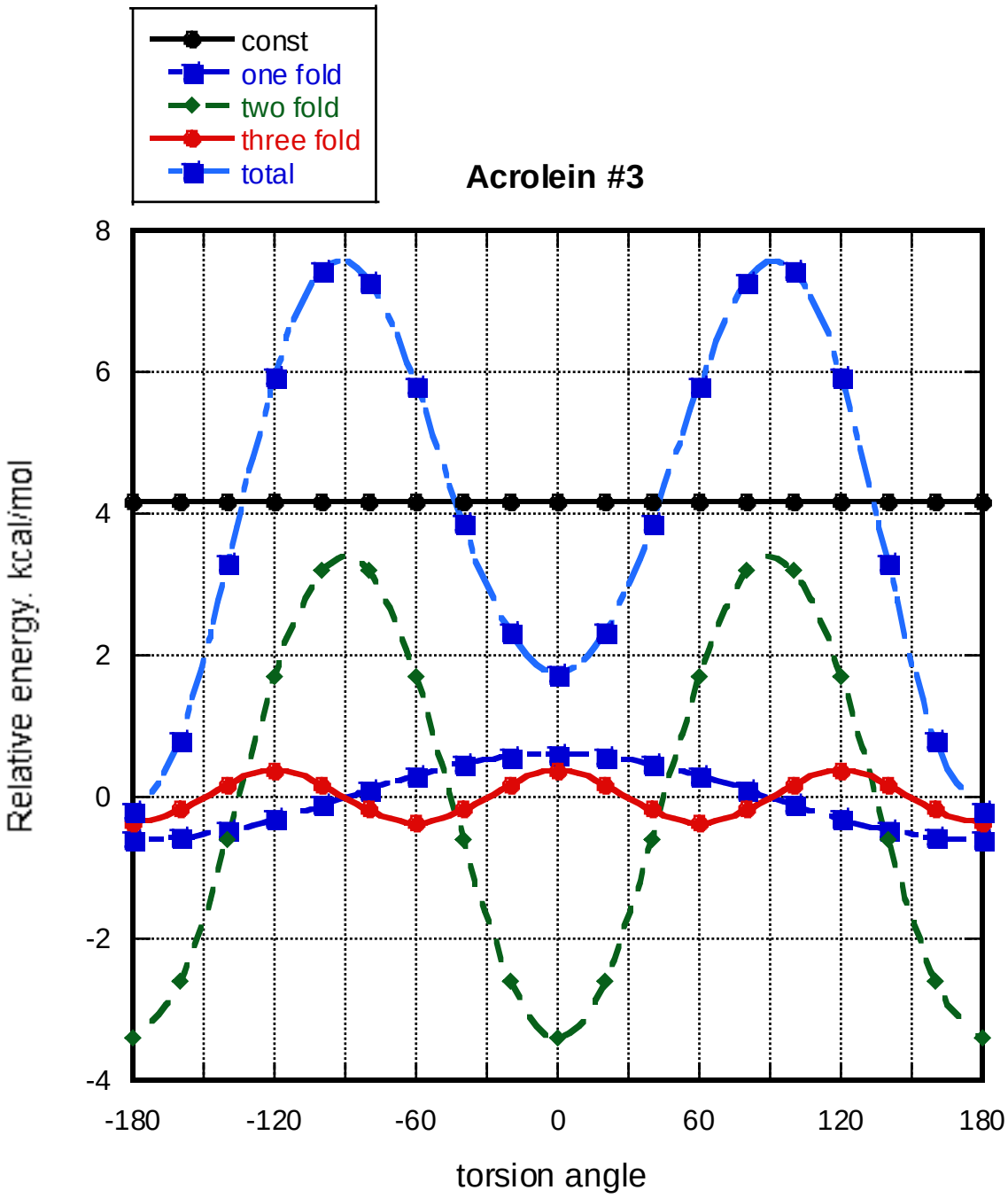


Figure S3d nitrosoethylene

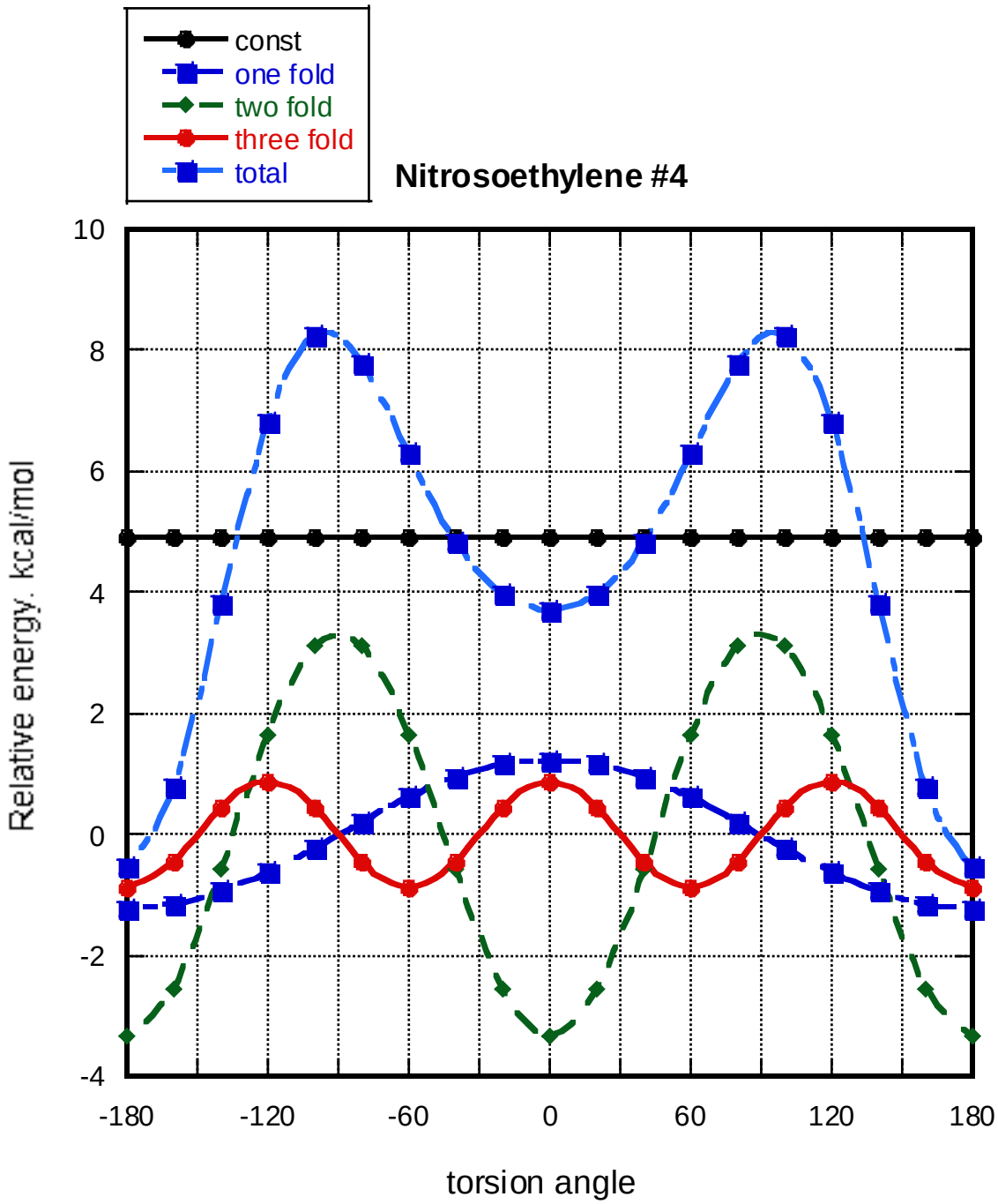


Figure S3e E-1-azabutadiene

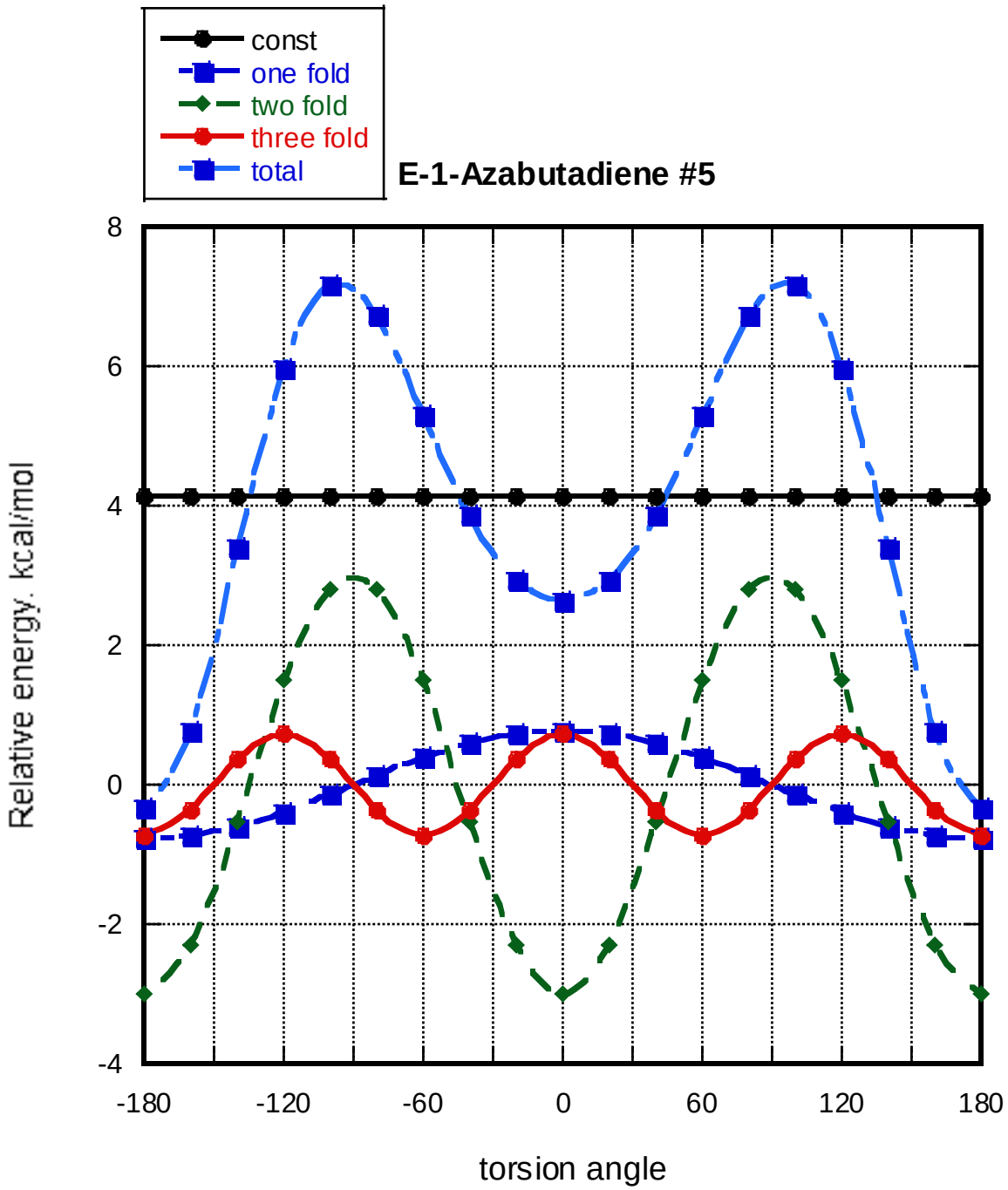


Figure S3f Z-1-azabutadiene

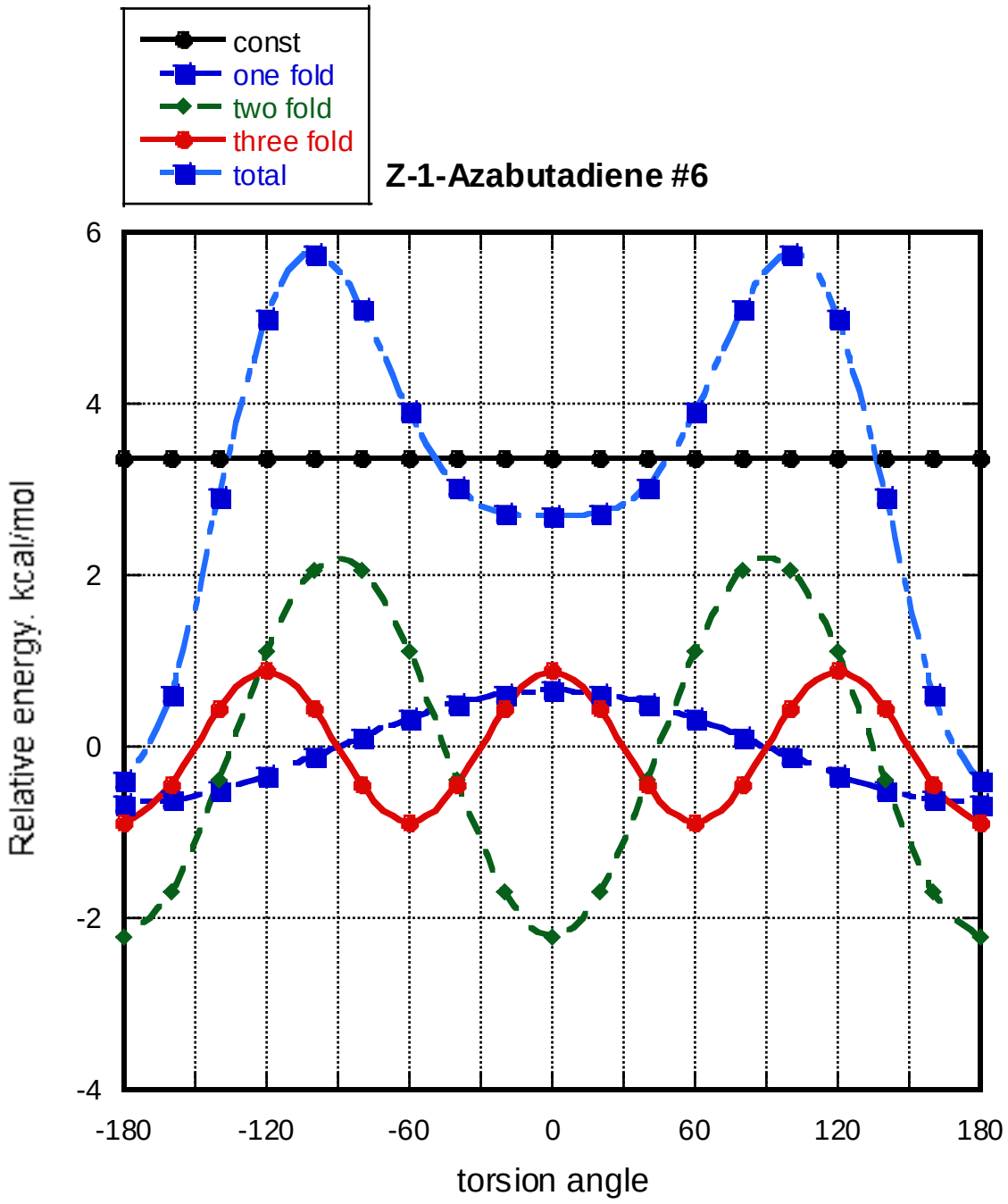


Figure S3g Z-4-azaacrolein

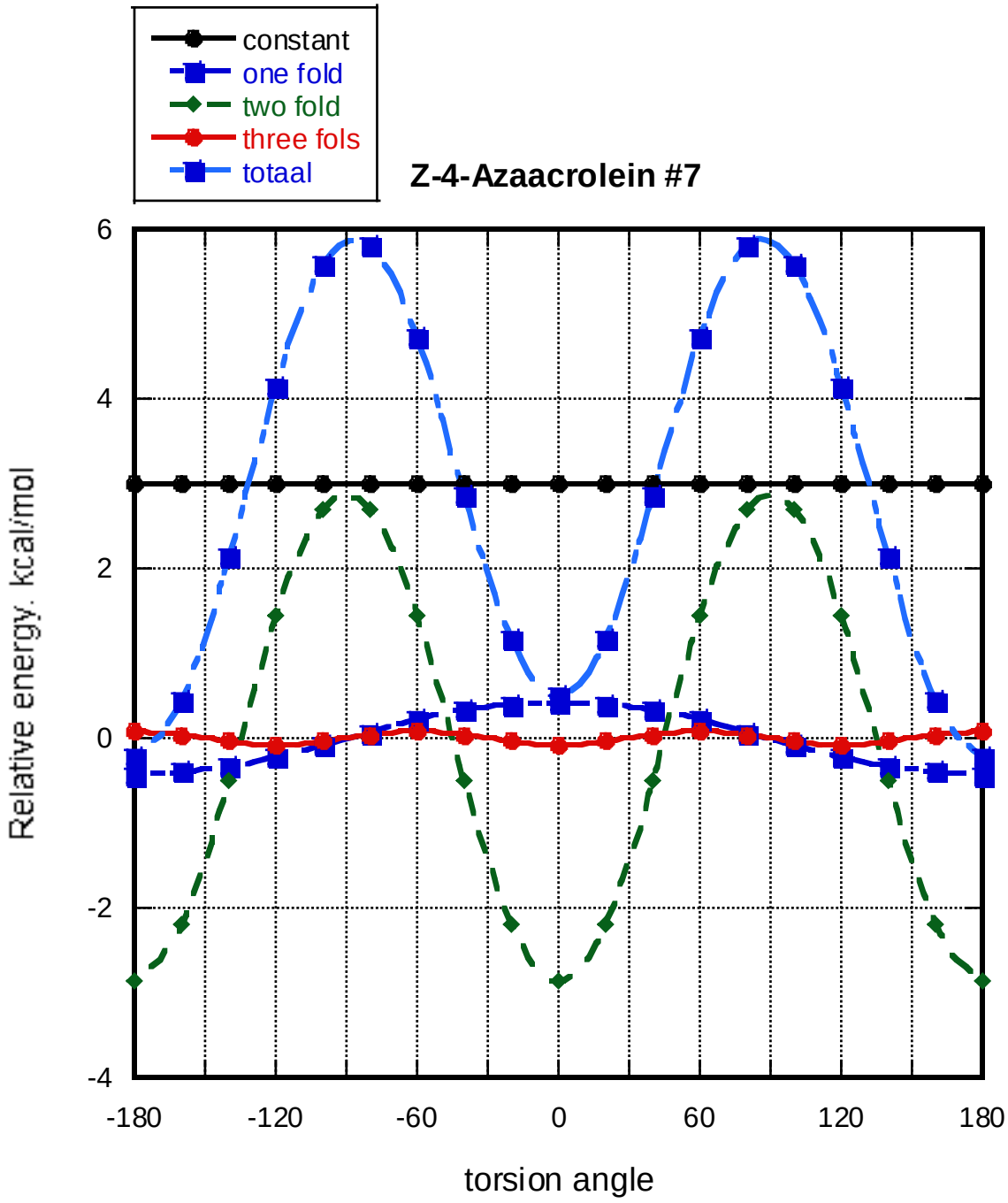


Figure S3h E-4-azaacrolein

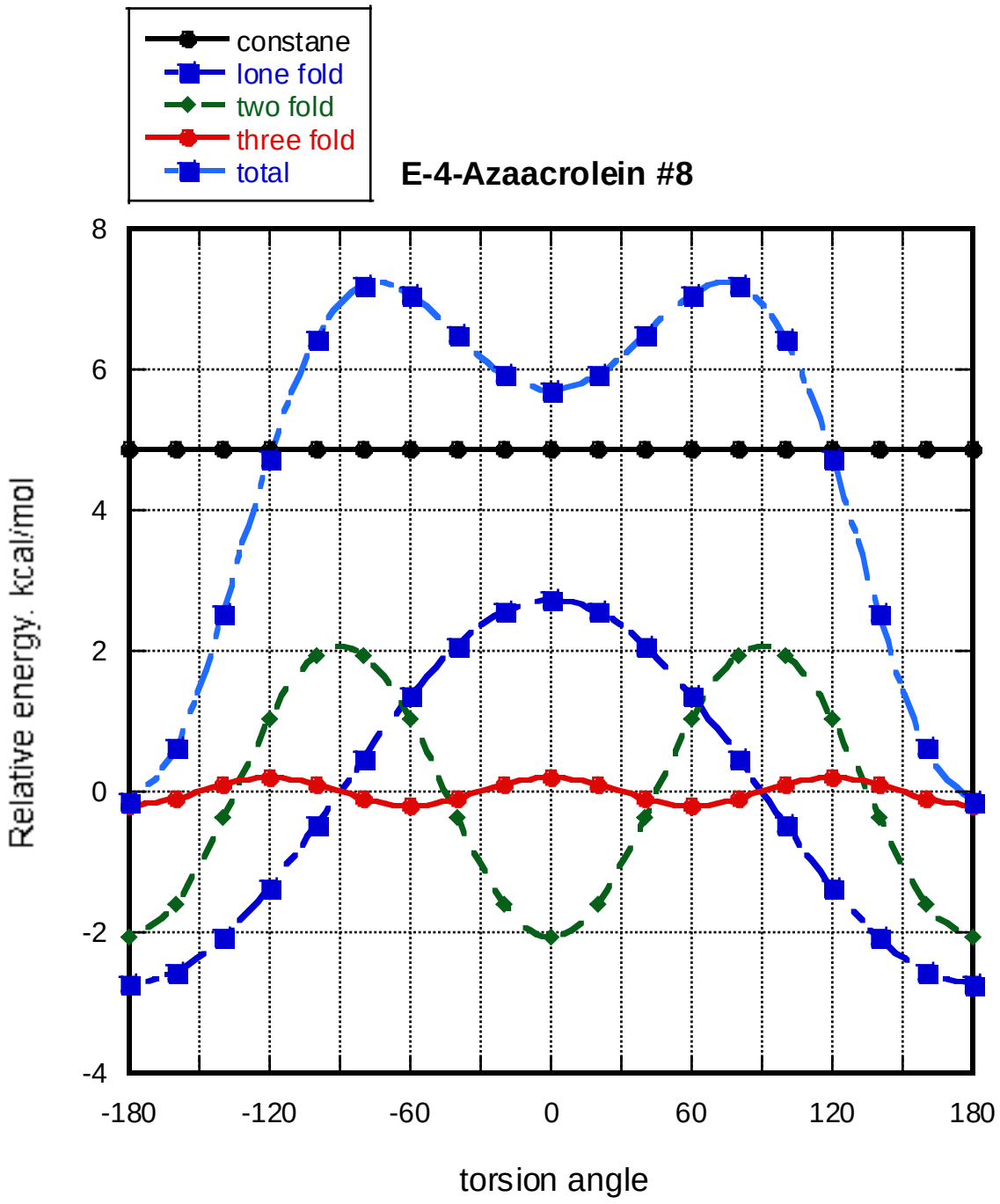


Figure S3i E-C-nitrosomethanimine

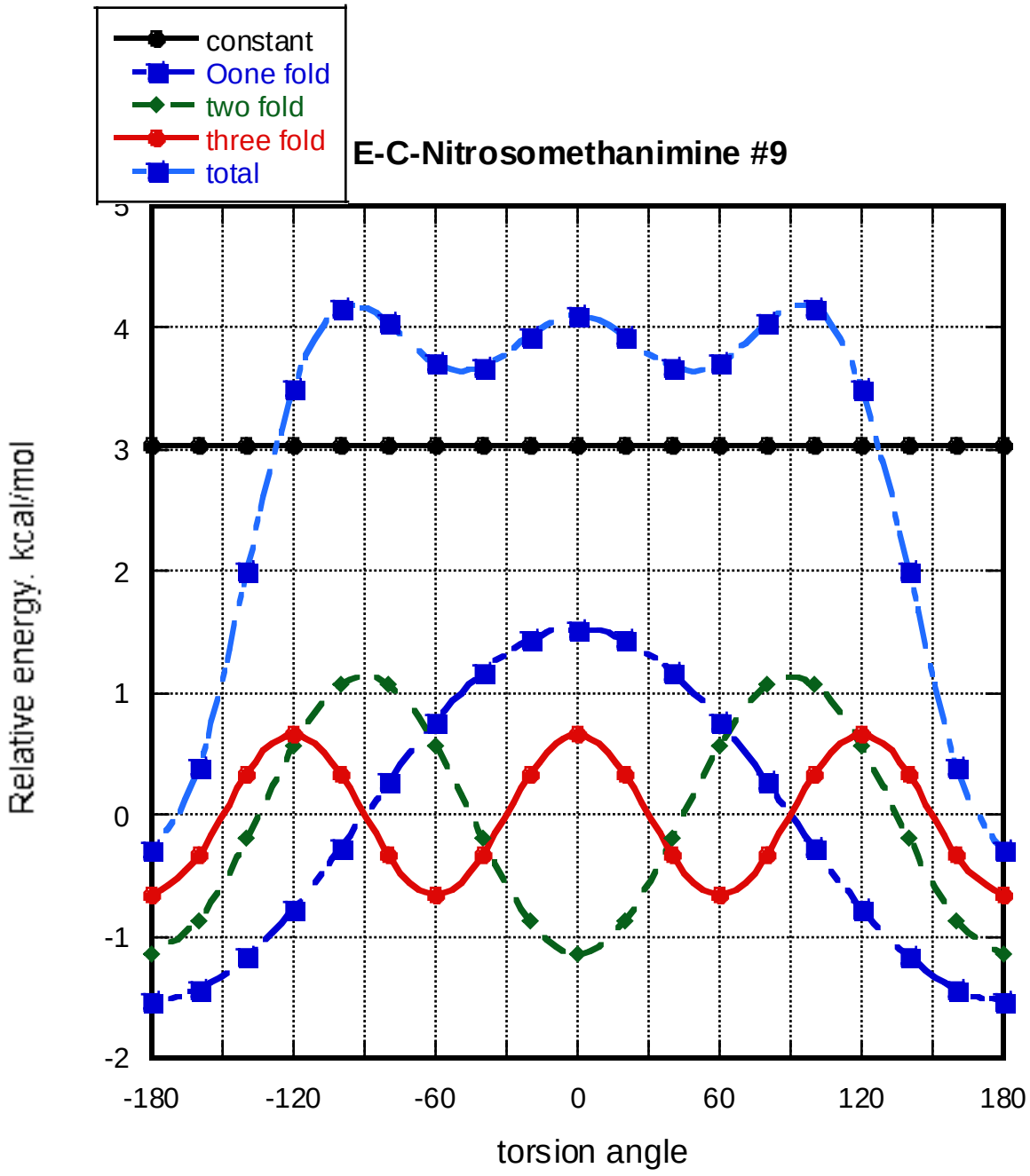


Figure S3j Z-C-nitrosomethanimine

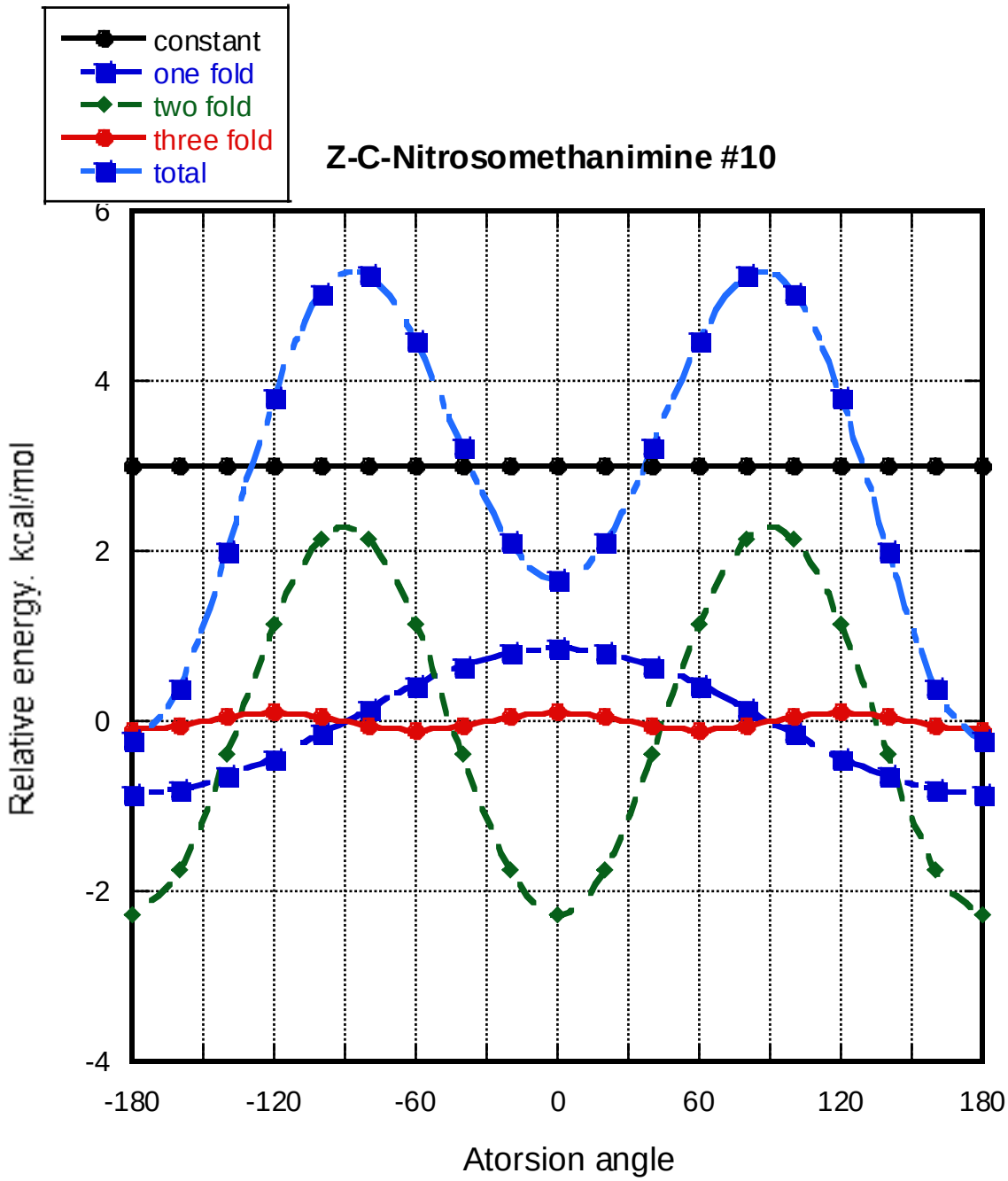


Figure S3k Glyoxal

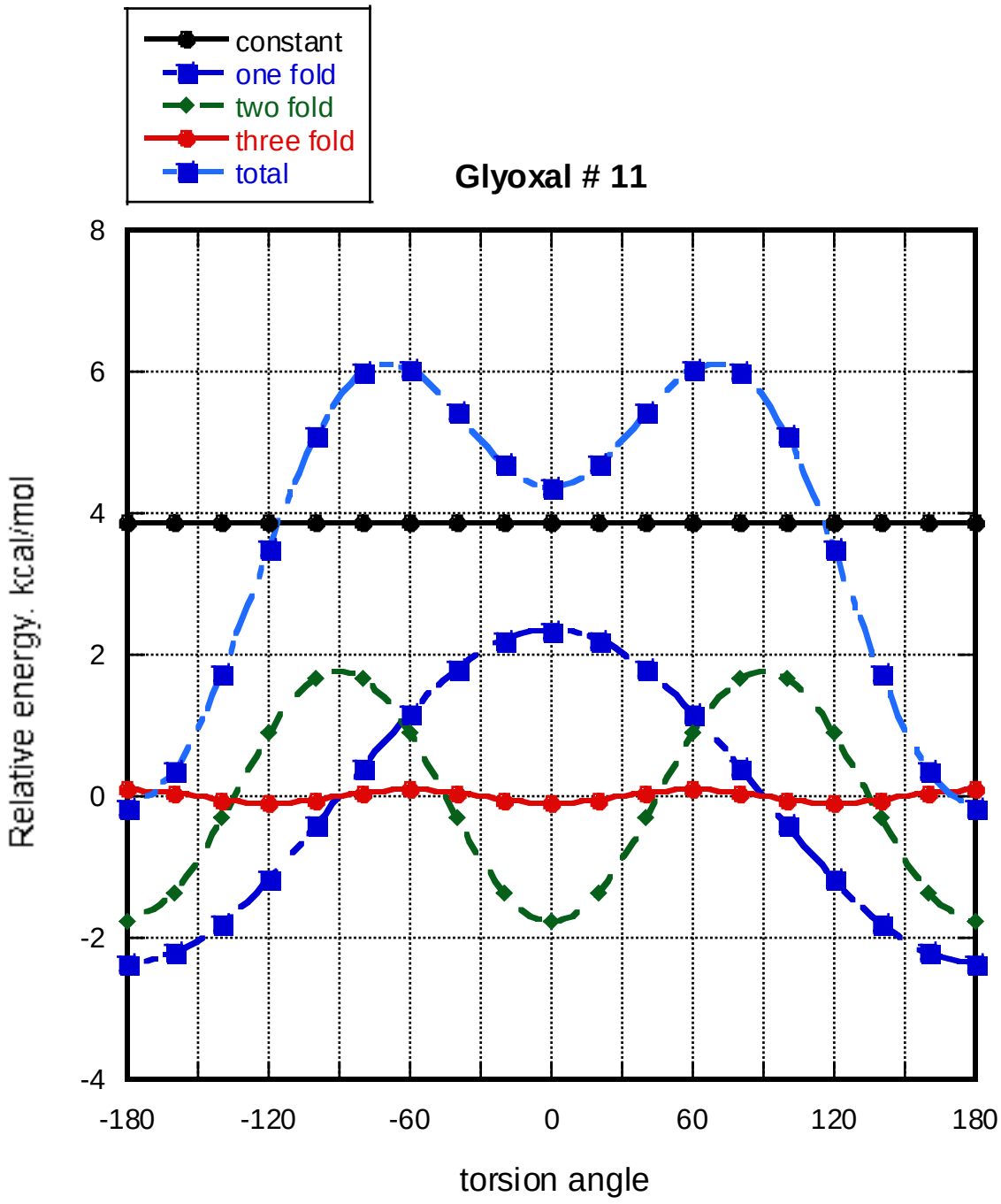


Figure S3l nitrosoformaldehyde

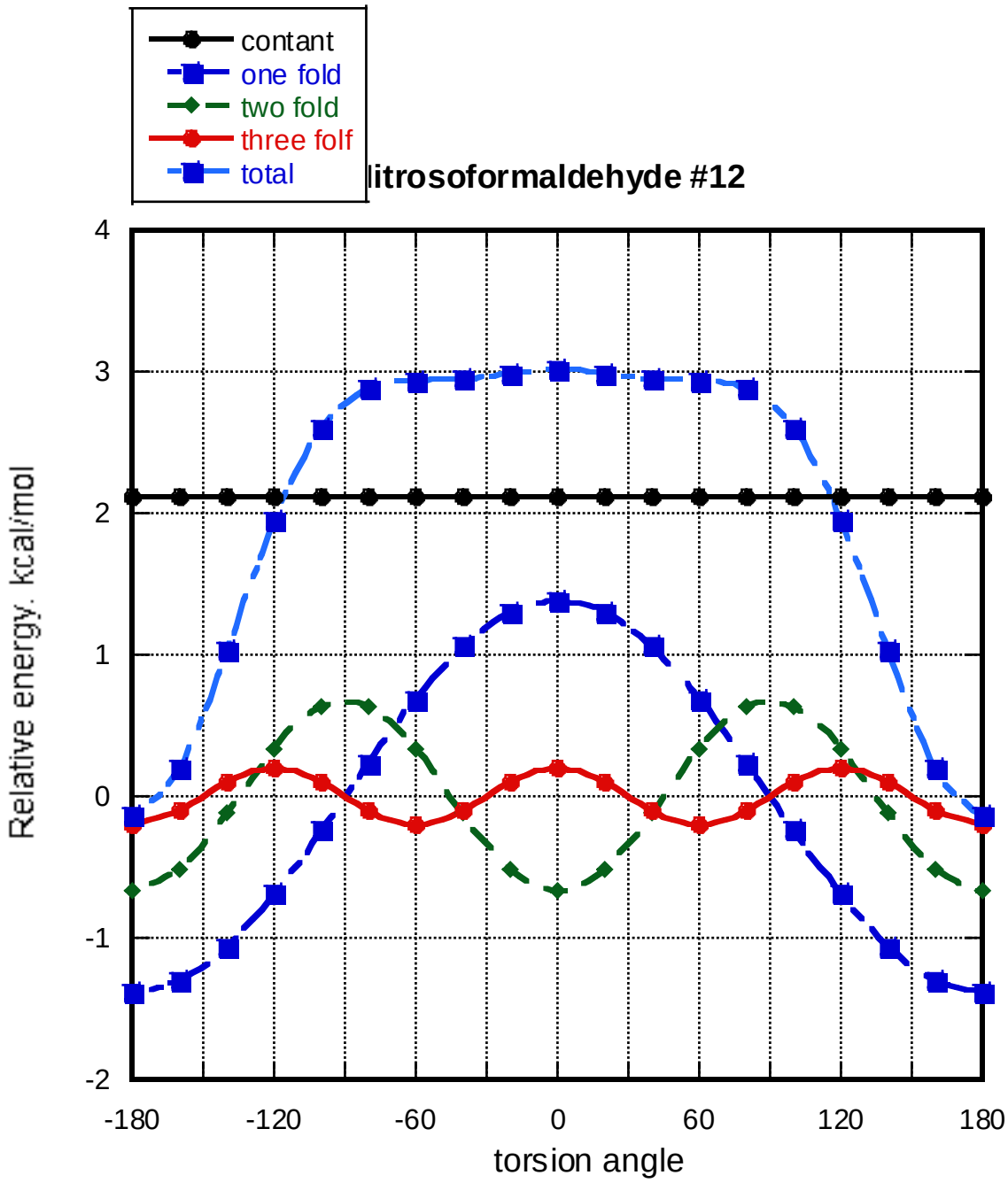


Figure S3m Z,Z-1,4-diazabutadiene

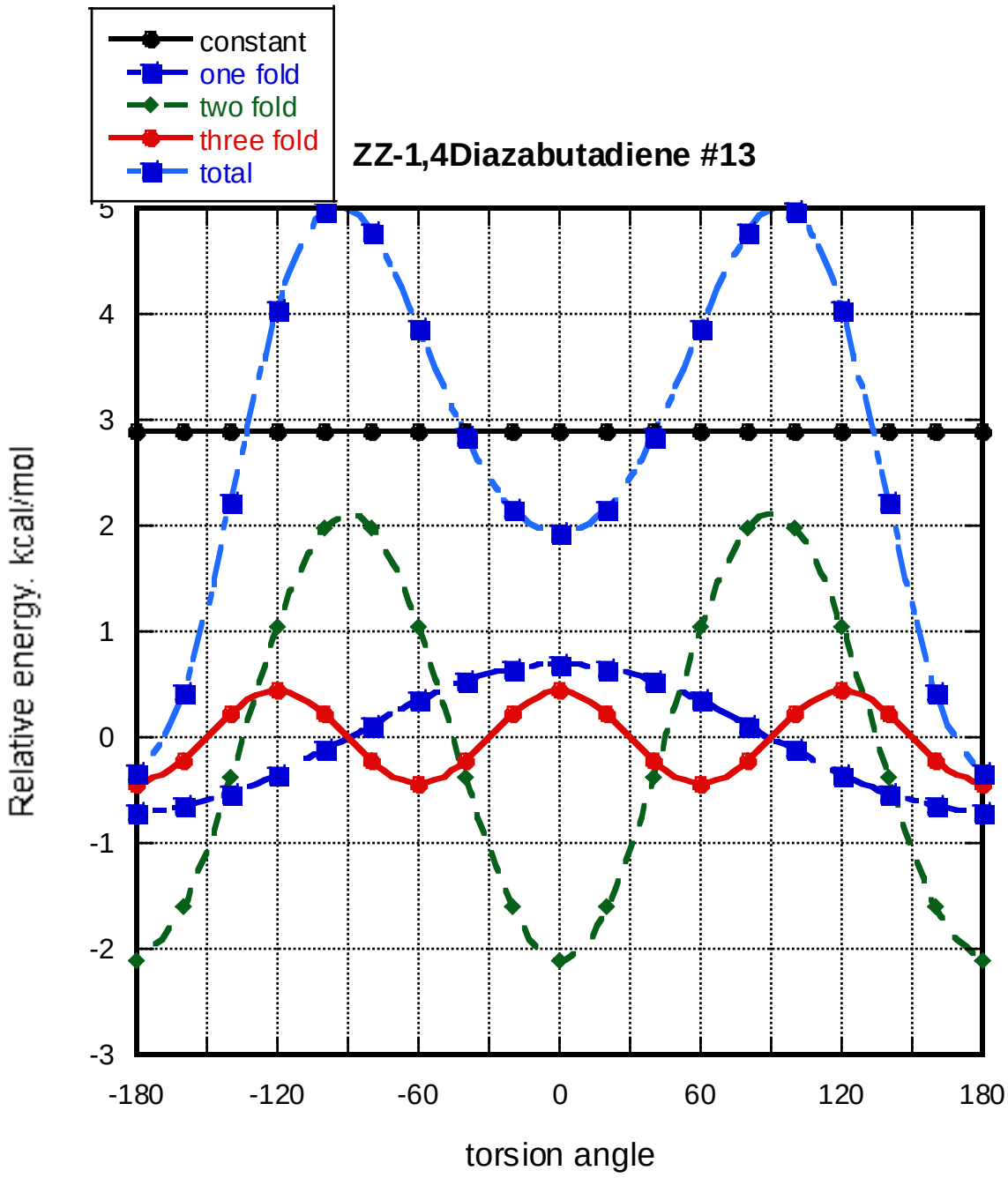


Figure S3n E,Z-1,4-diazabutadiene

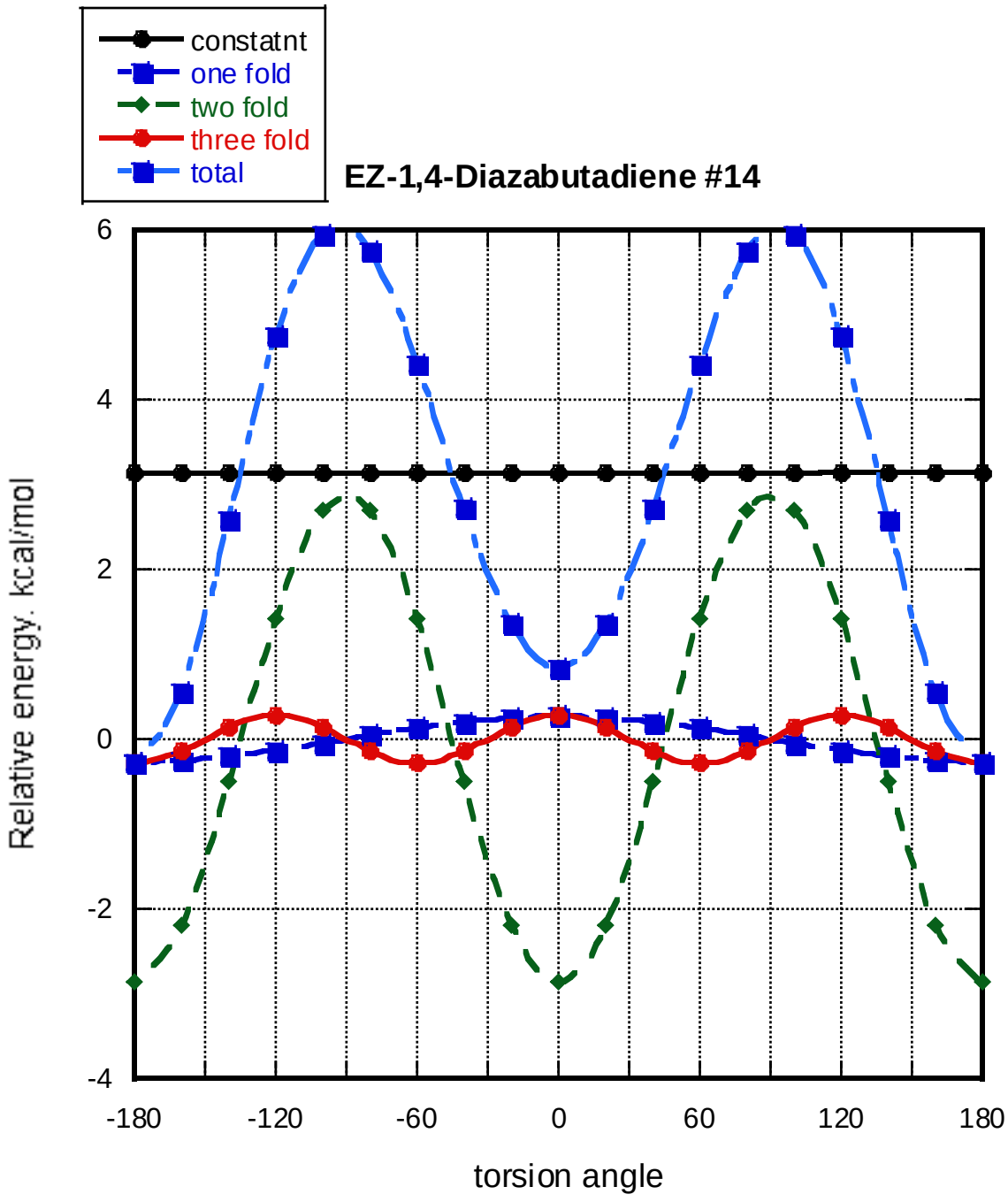


Figure S3o E,E-1,4-diazabutadiene

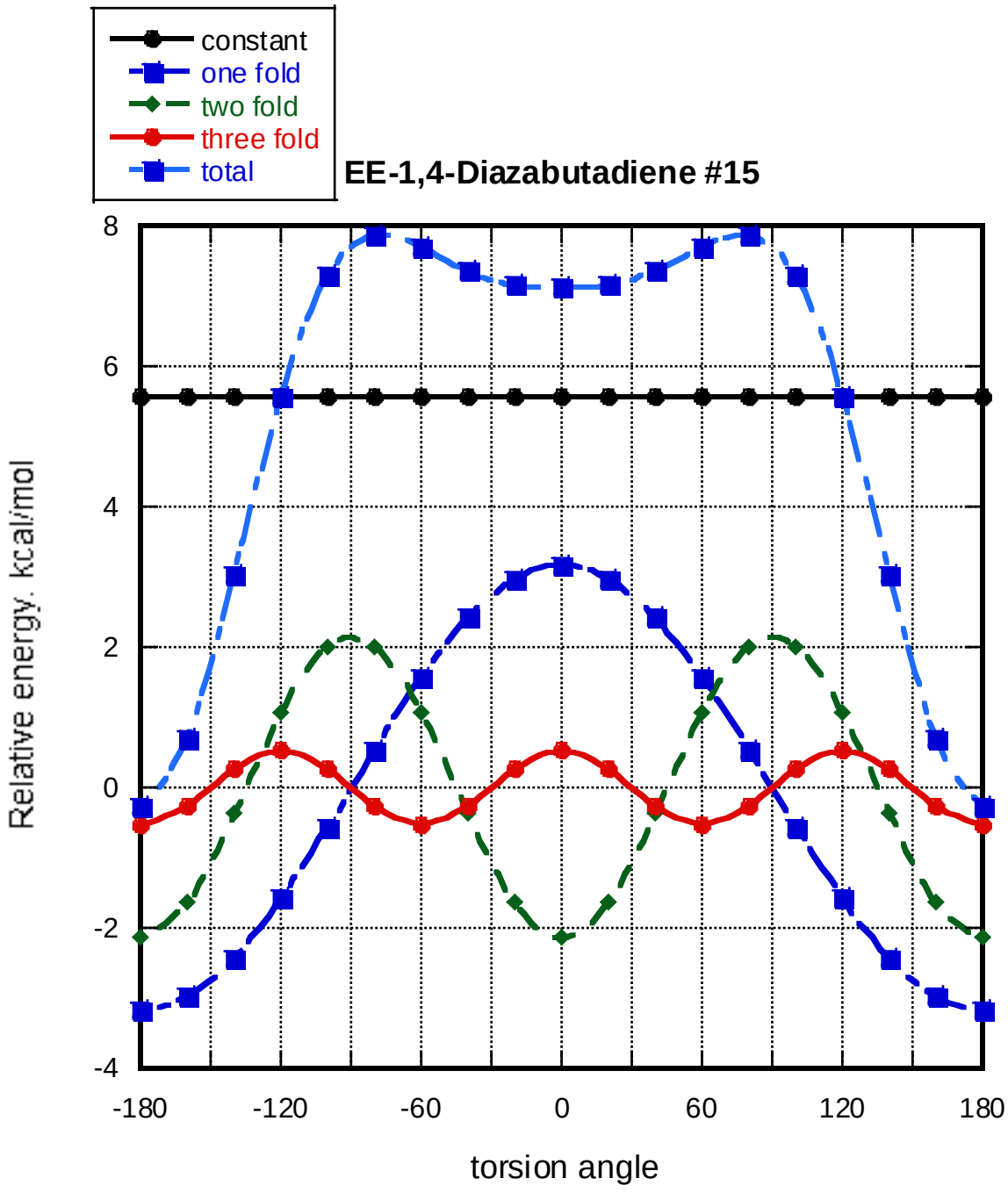


Figure S3p methyleneformamide

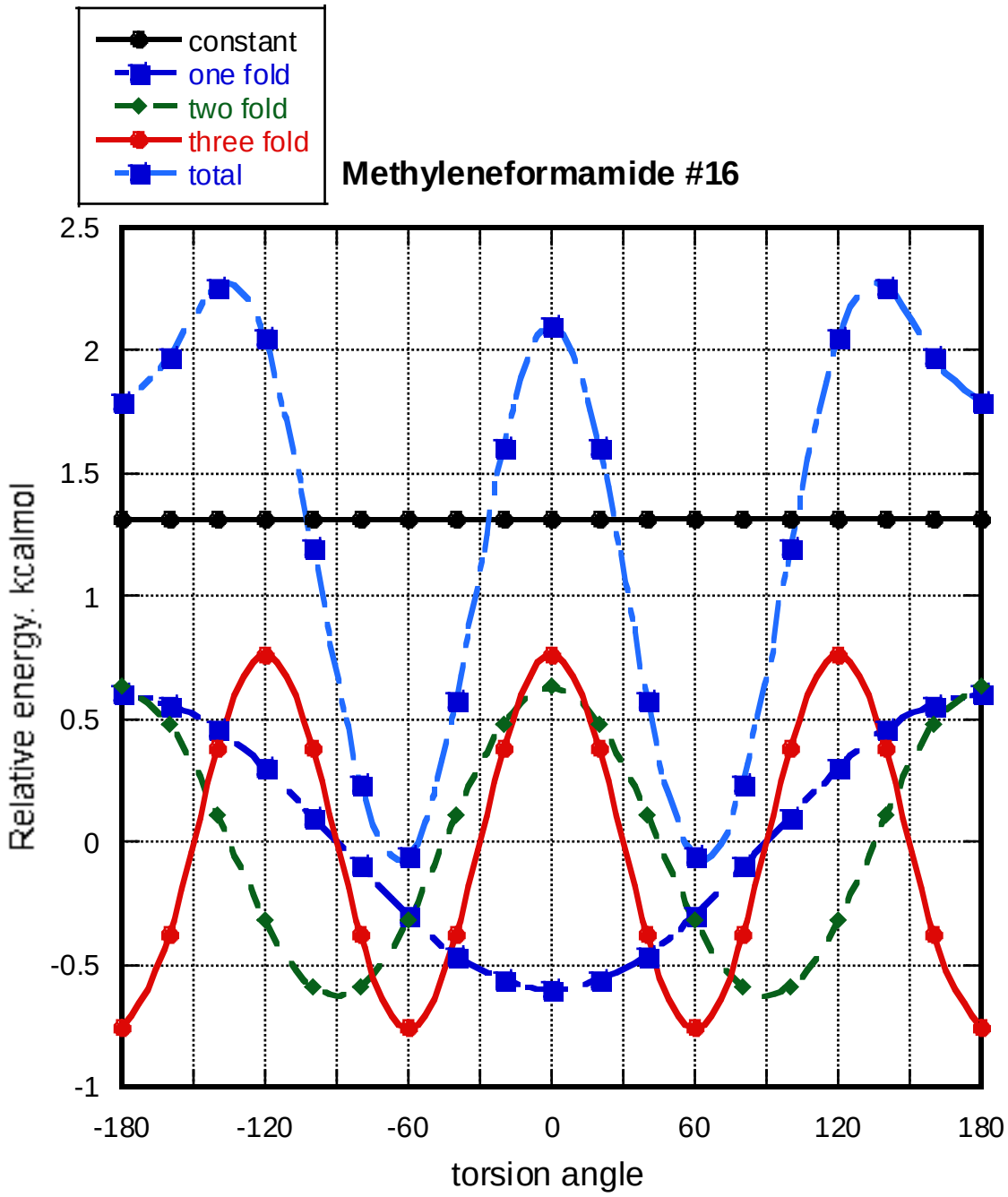


Figure S3q 2,3-diazabutadiene

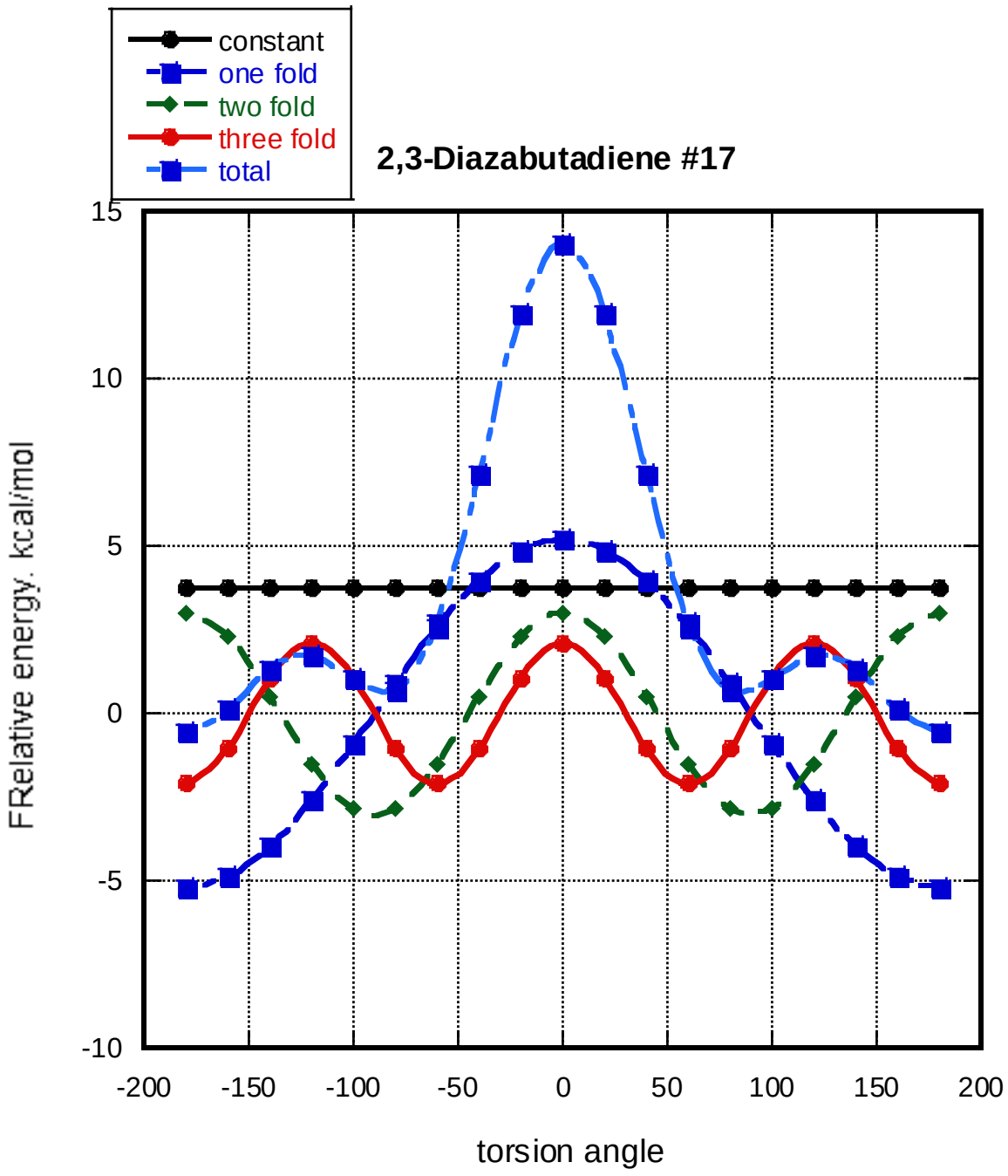


Figure S3r N-nitrosomethanimine

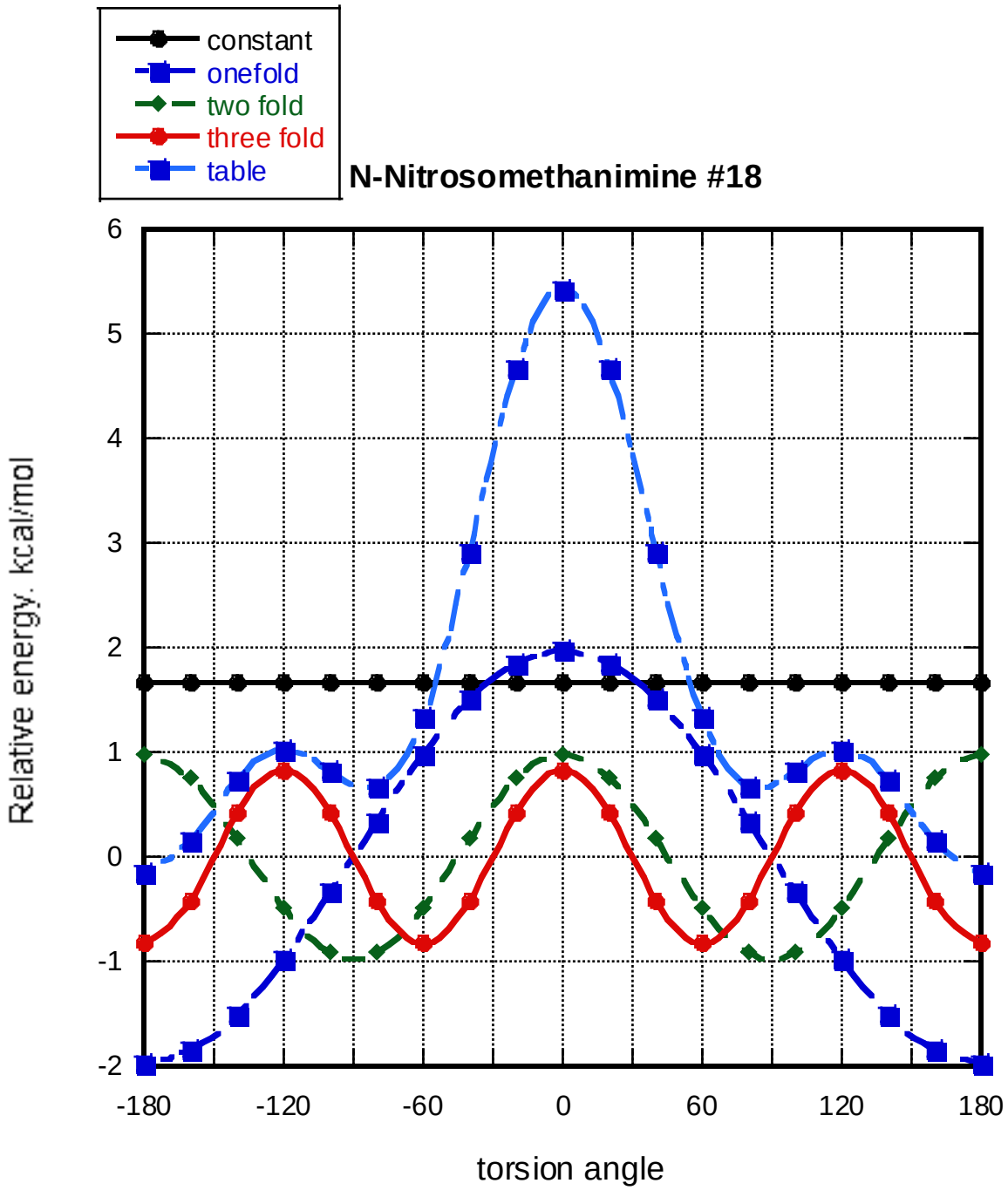


Figure S4 Components of the four-fold terms for rotational profiles

Figure S4a butadiene

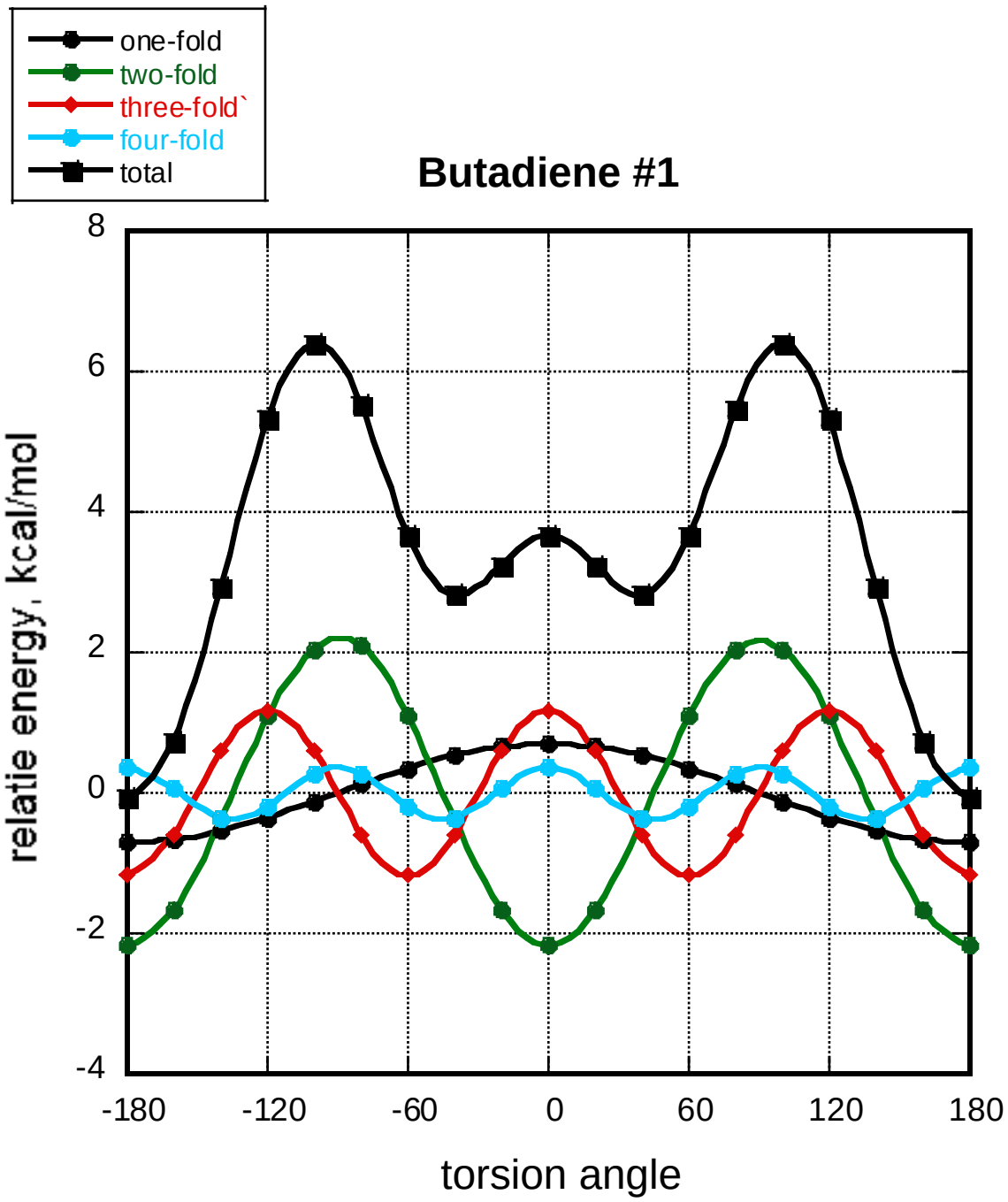


Figure S4b 2-azabutadiene

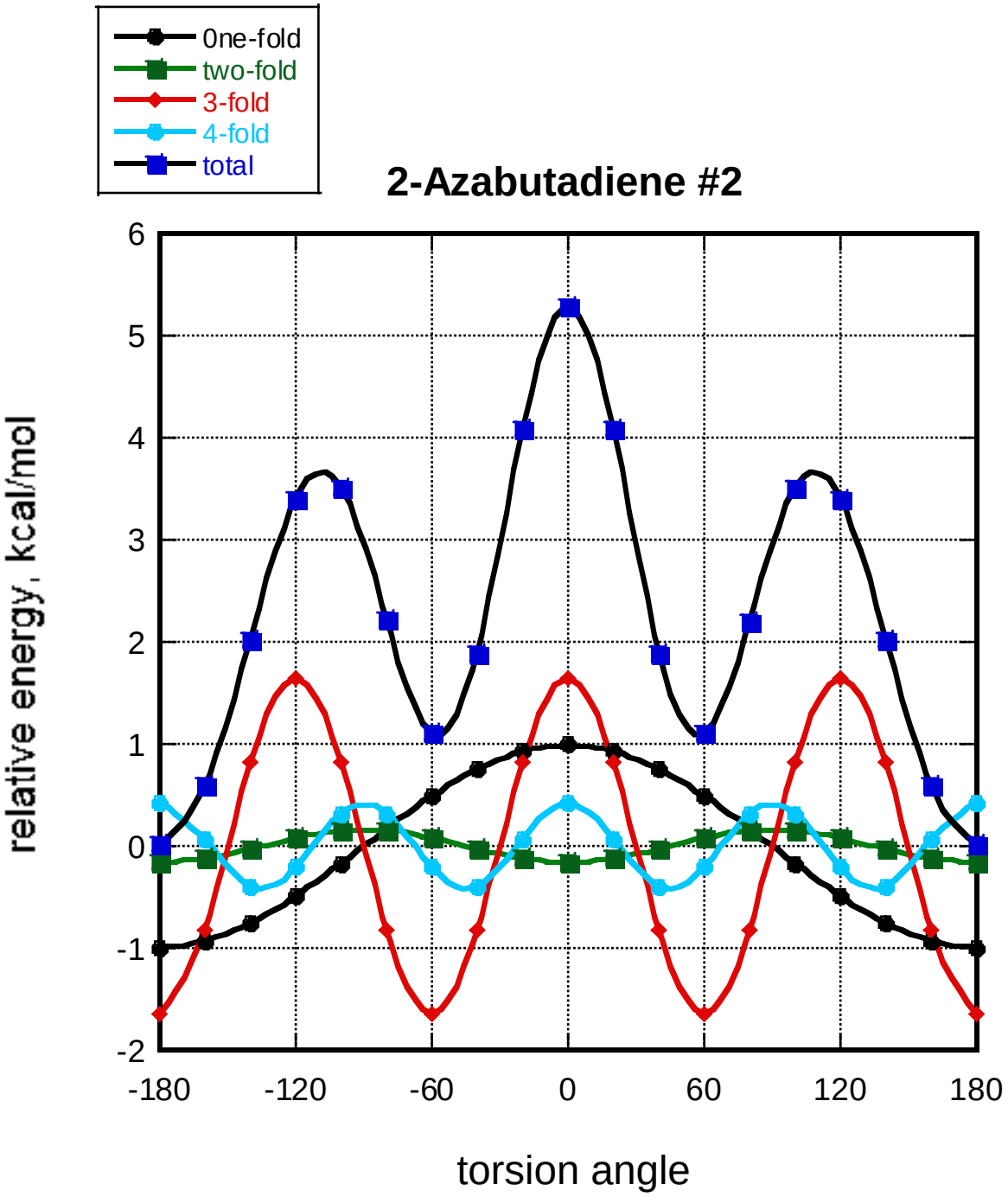


Figure S4c acrolein

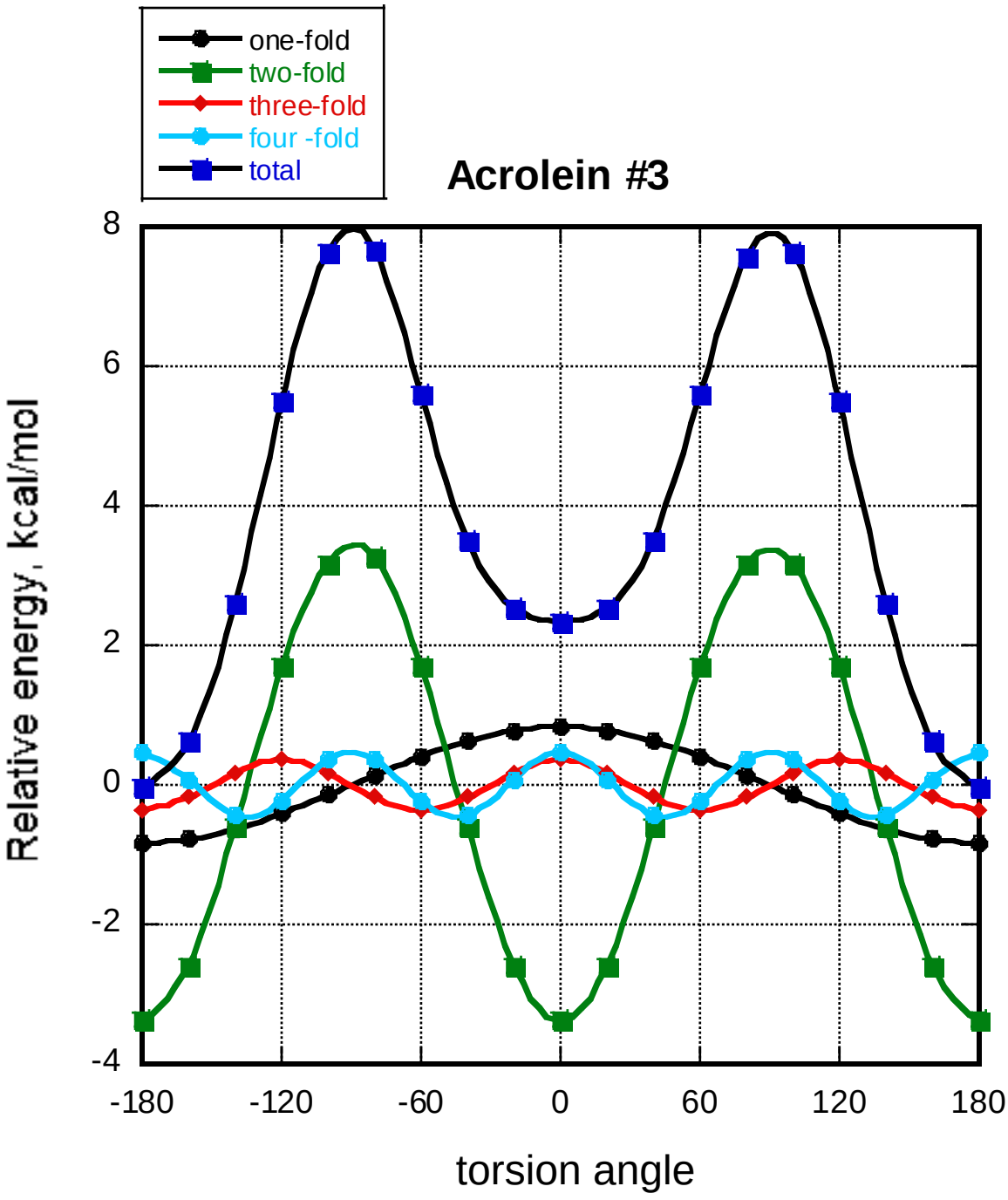


Figure S4d nitrosoethylene

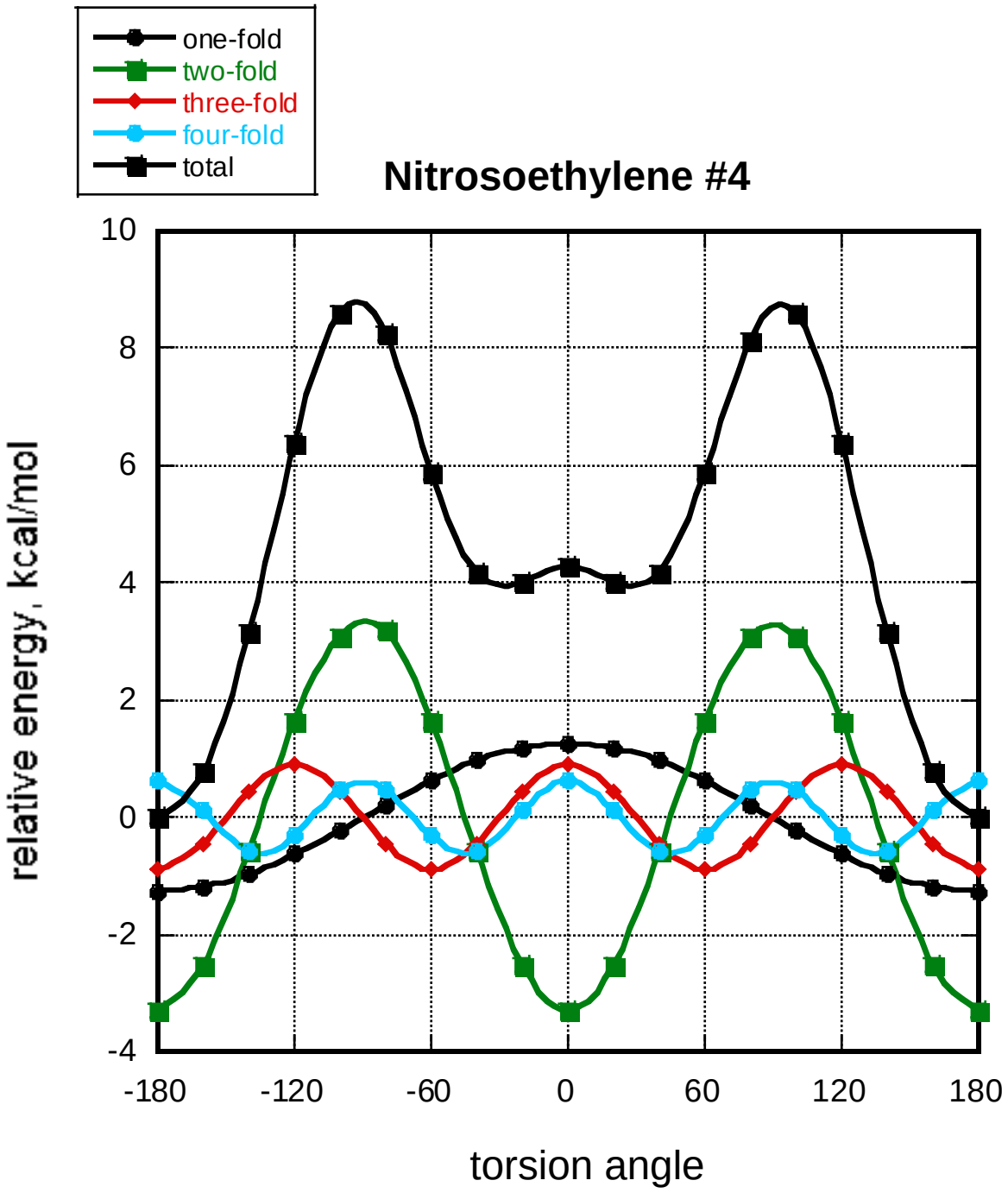


Figure S4e E-1-azabutadiene

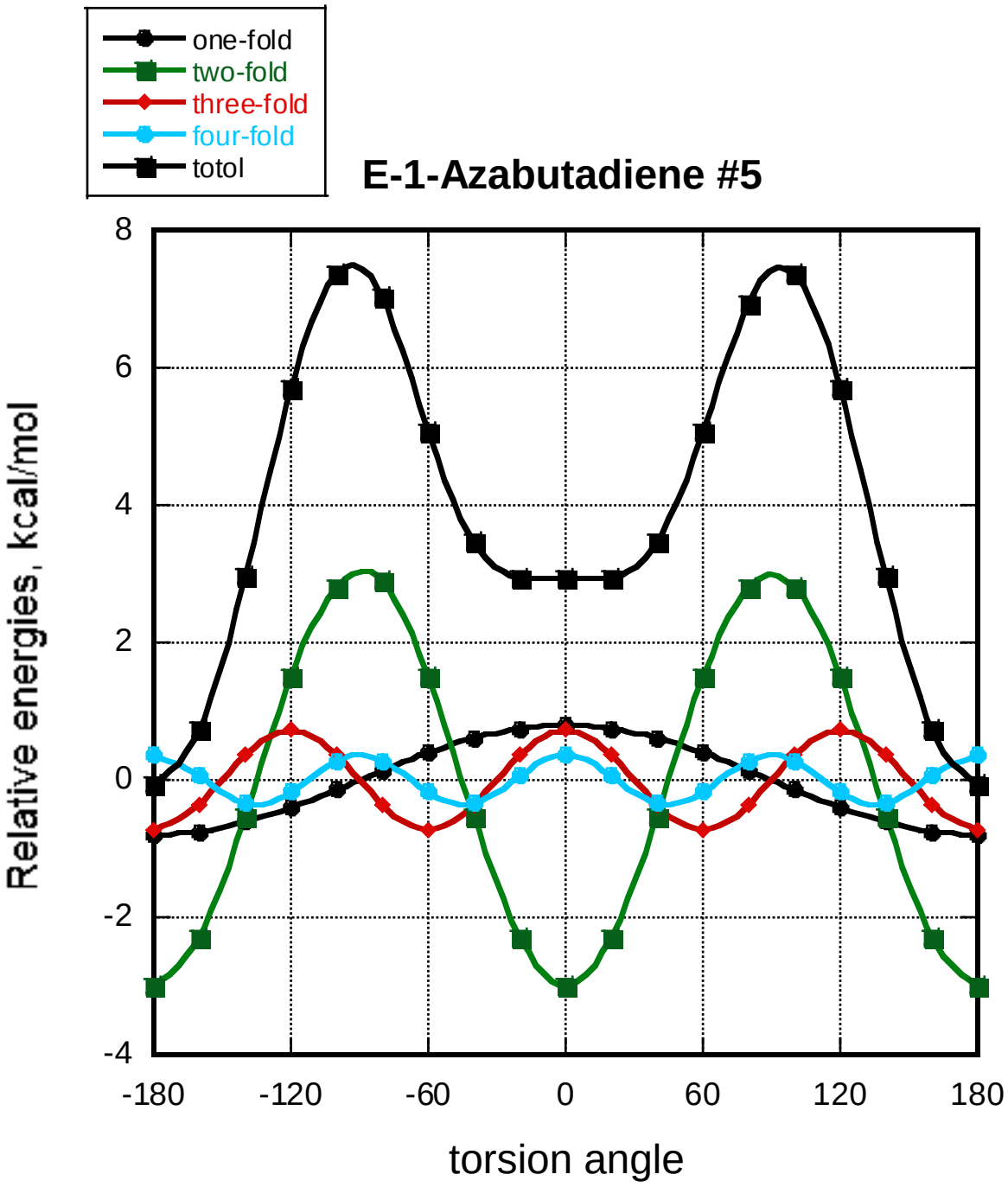


Figure S4f Z-1-azabutadiene

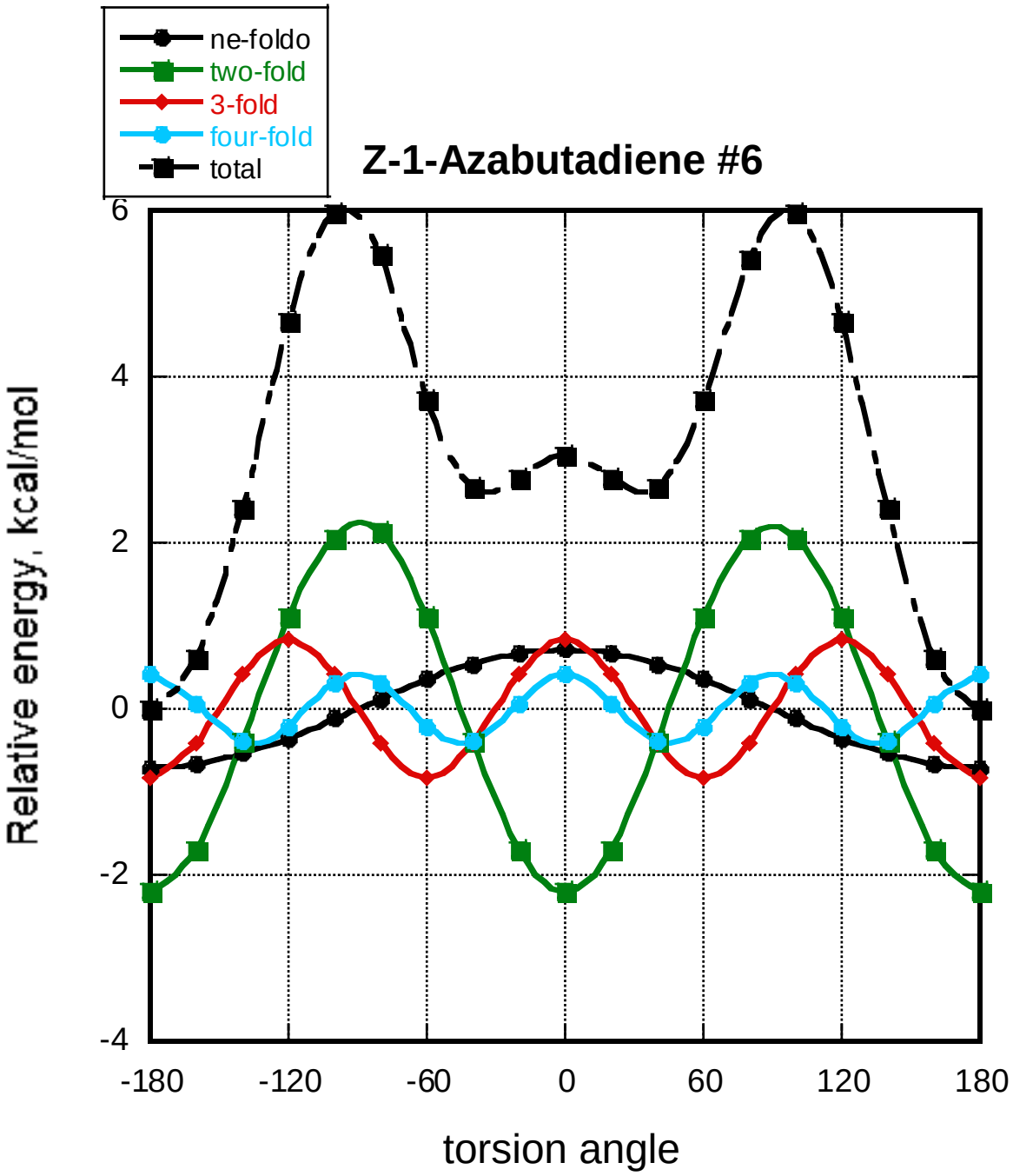


Figure S4g Z-4-azaacrolein

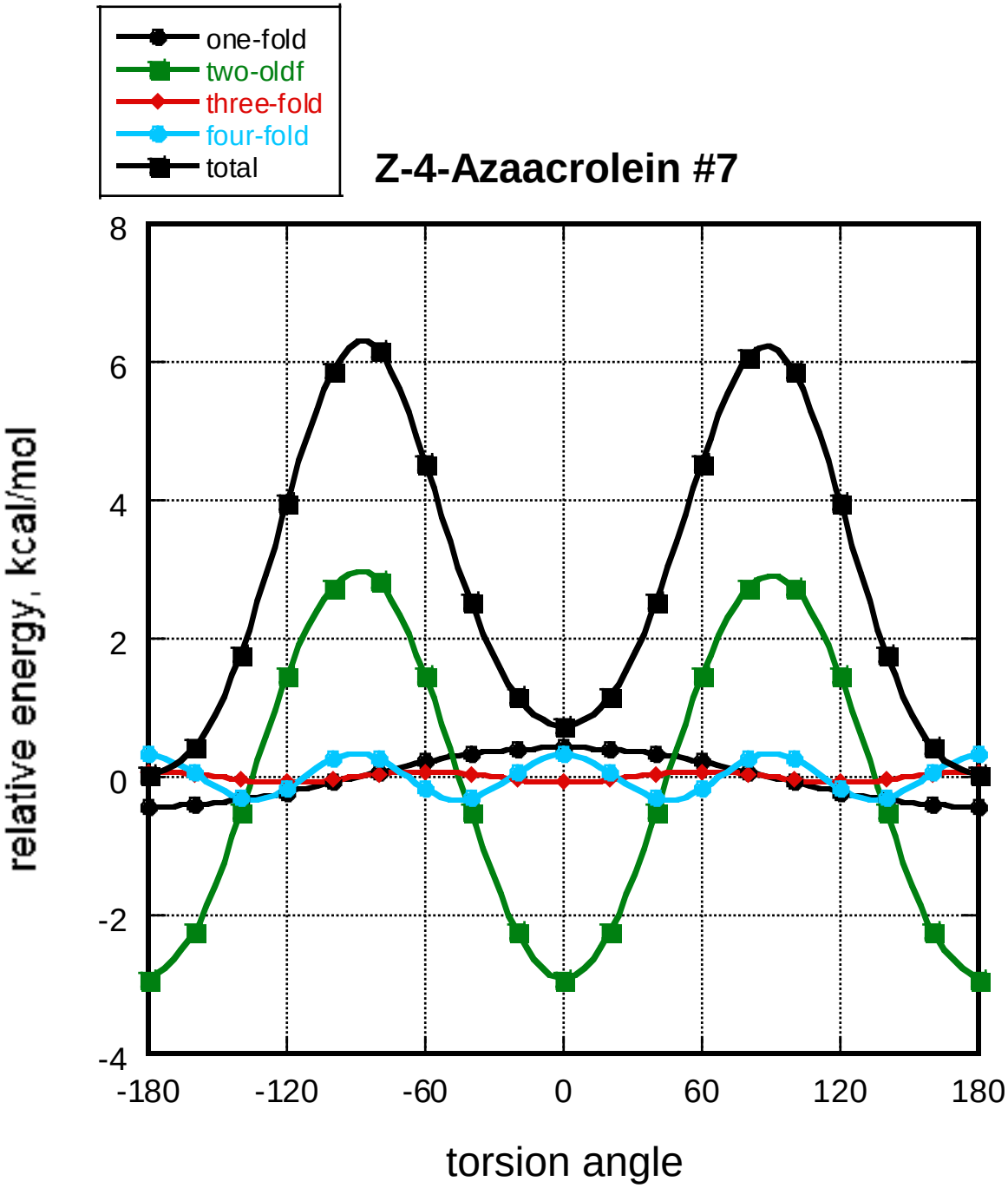


Figure S4h E-4-azabutadiene

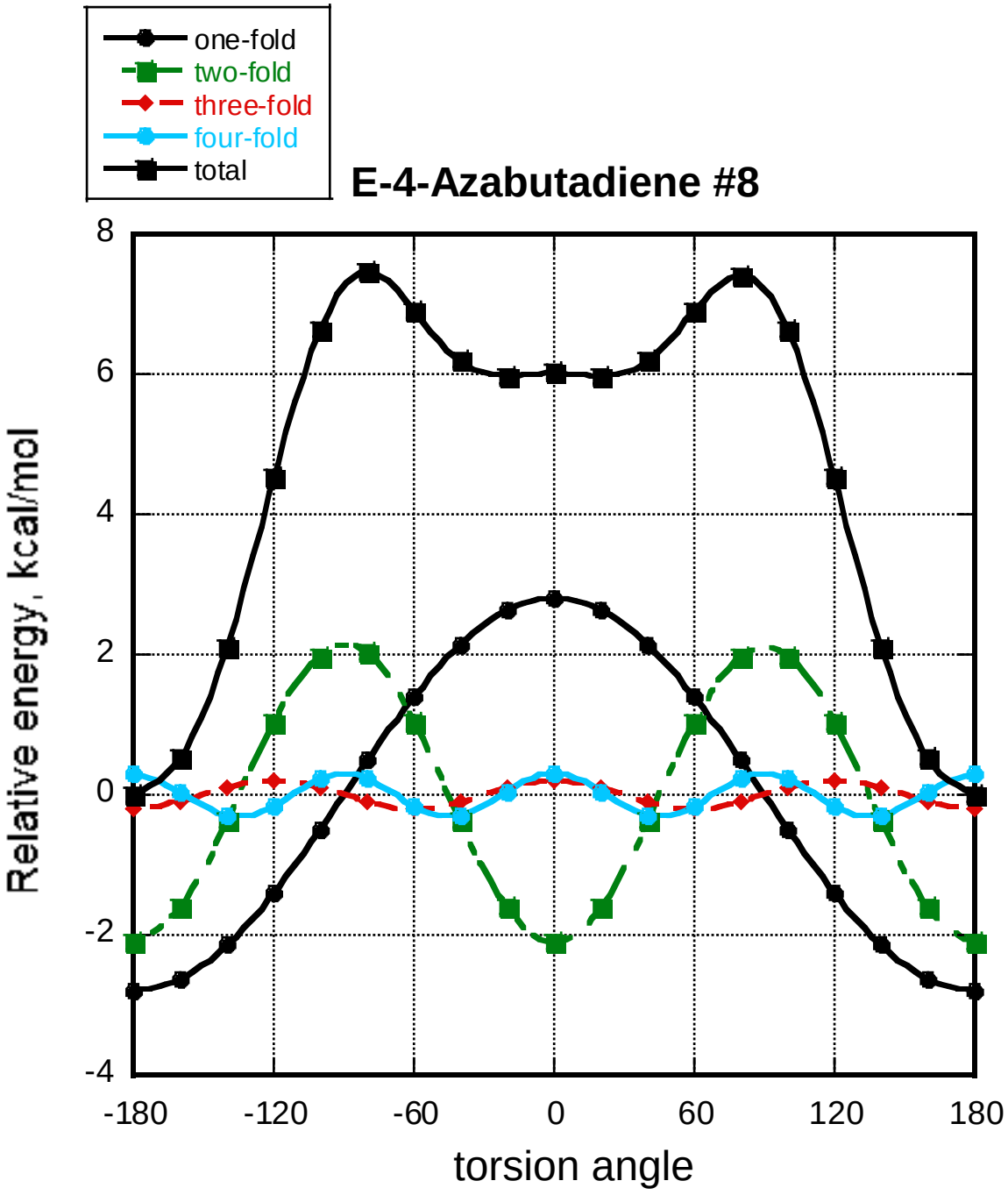


Figure S4i E-C-1-azamethaznimine

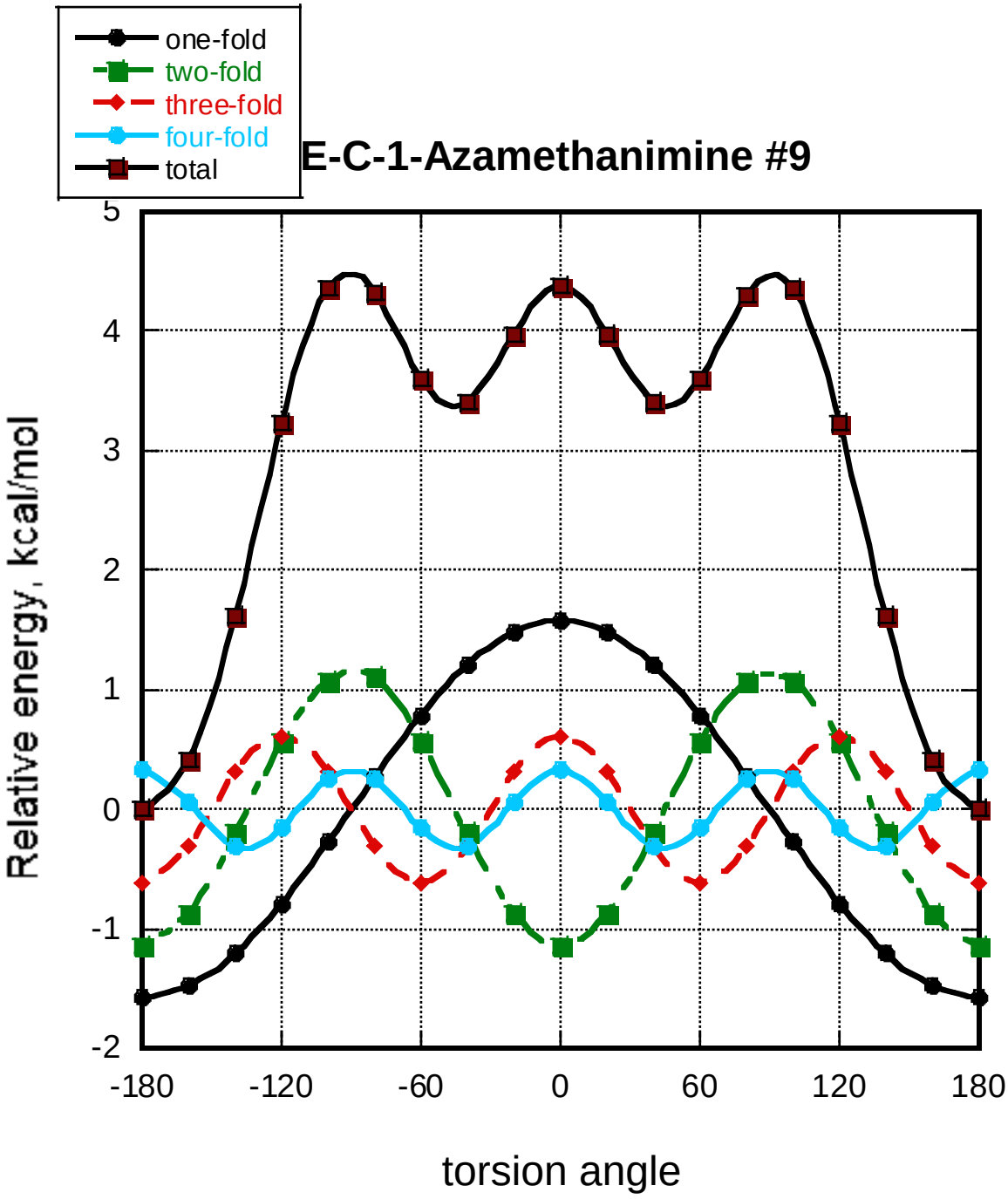


Figure S4j Z-C-nitrosomethaninimine

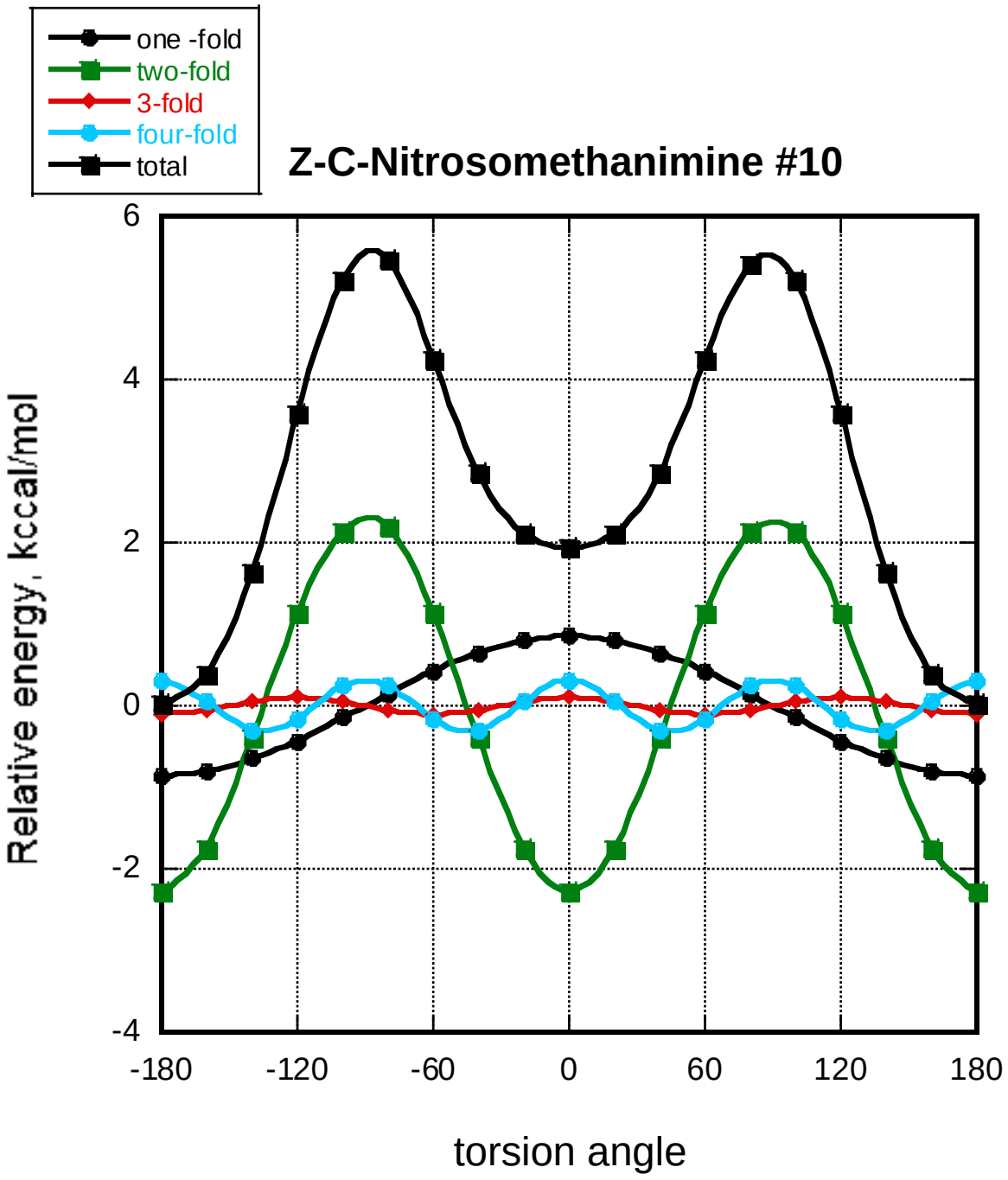


Figure S4k glyoxal

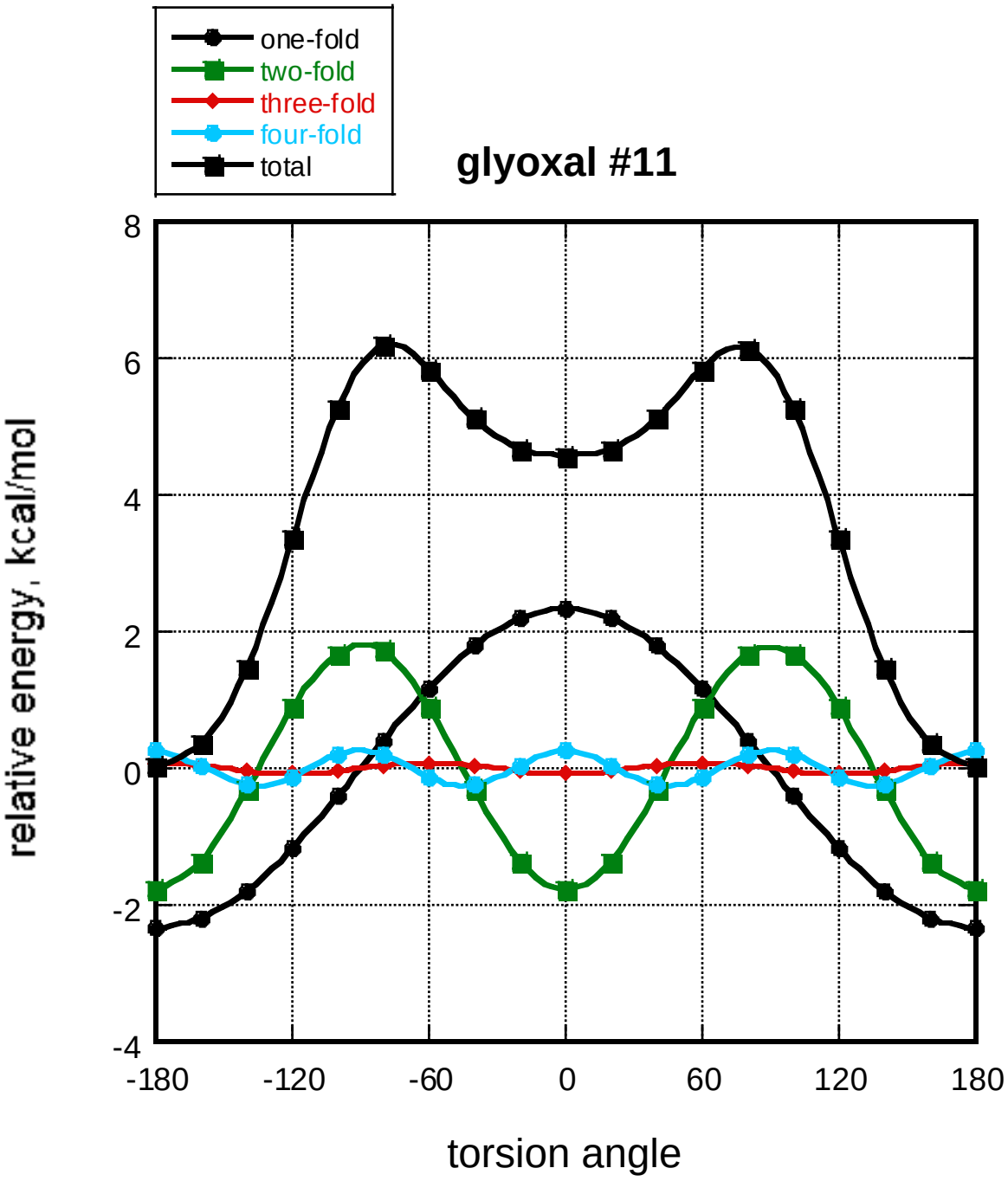


Figure S4l nitrosoformaldehyde

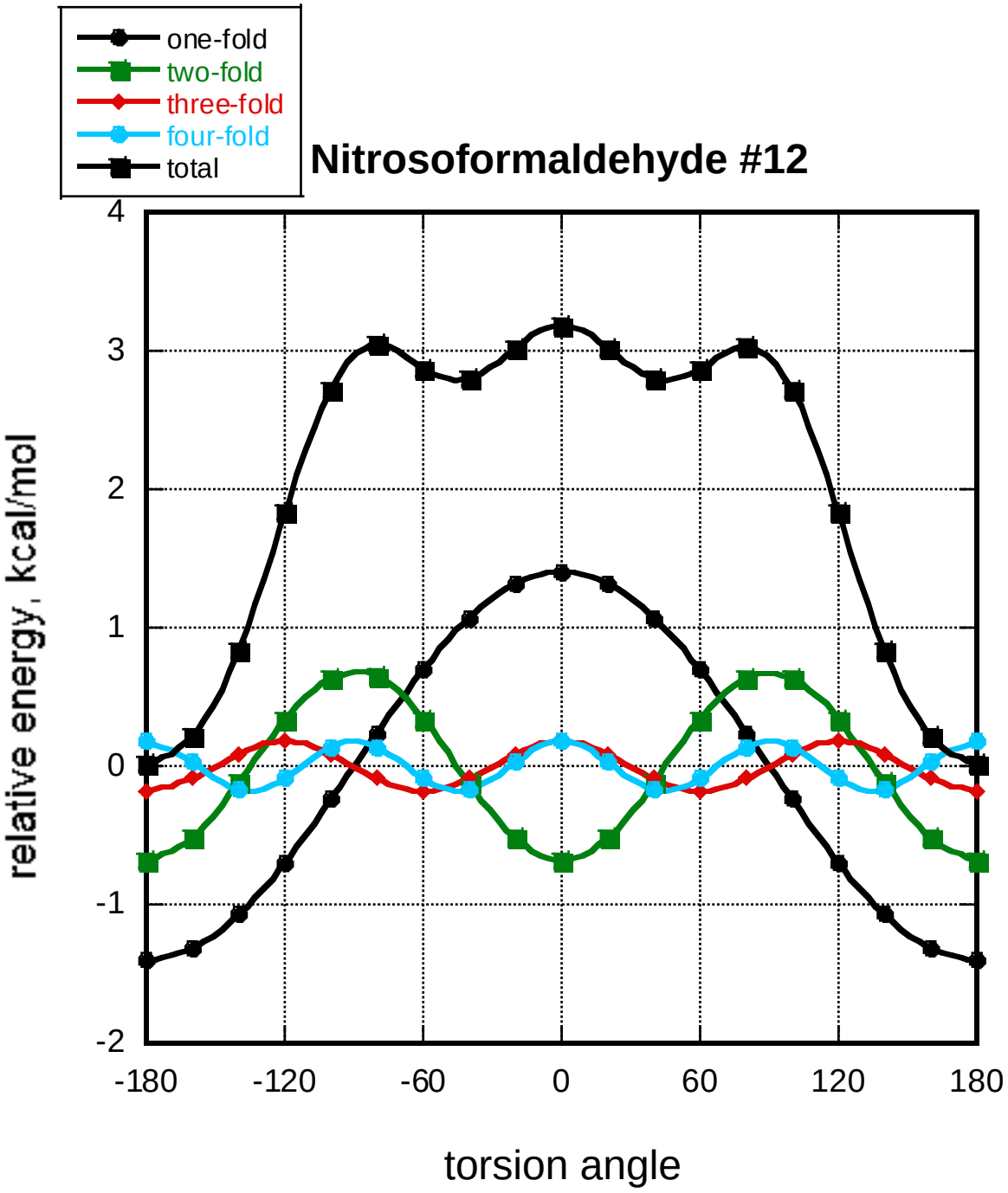


Figure S4m Z,Z-1,4-diazabutadiene

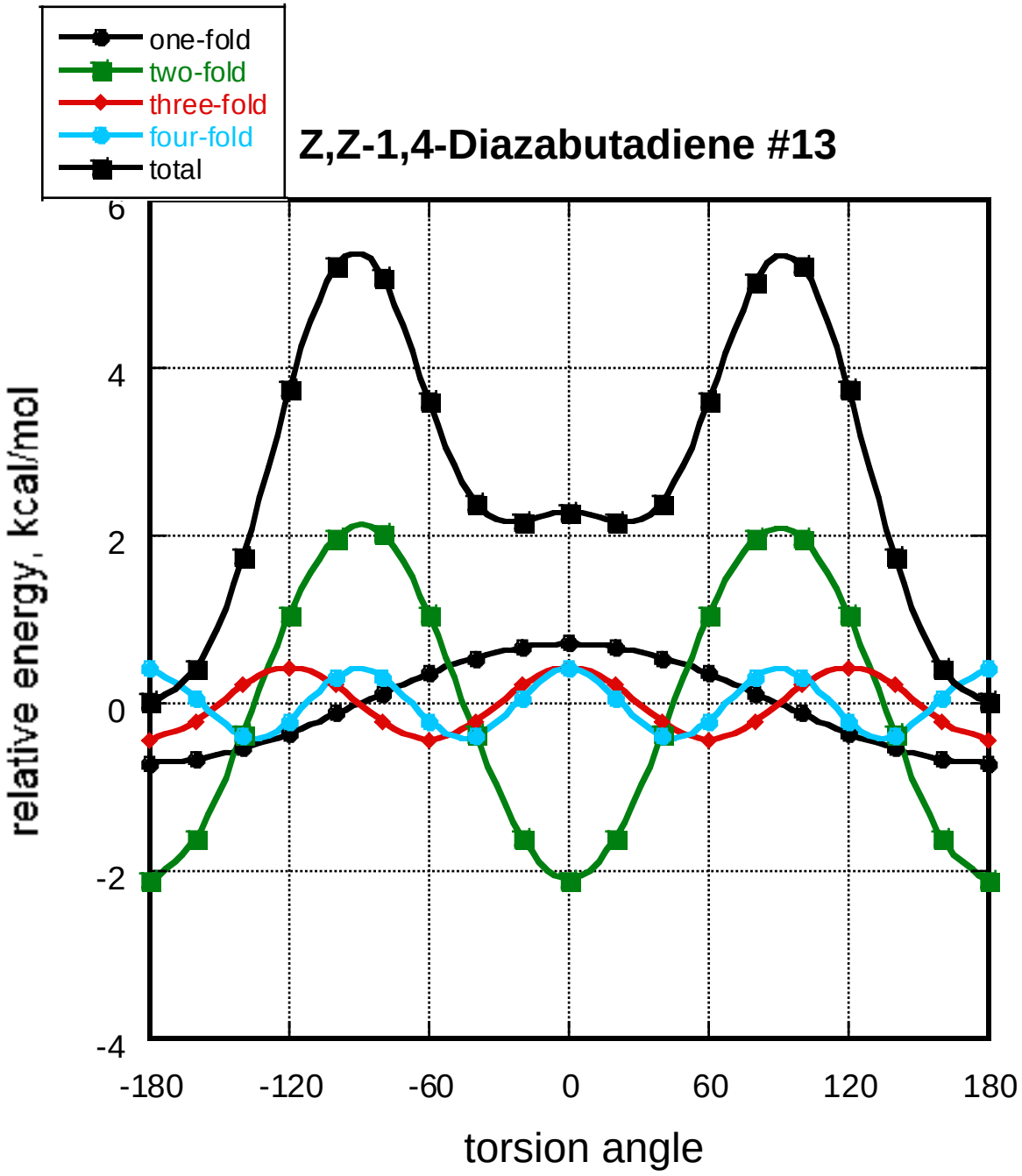


Figure S4n E,Z-1,4-diazabutadiene

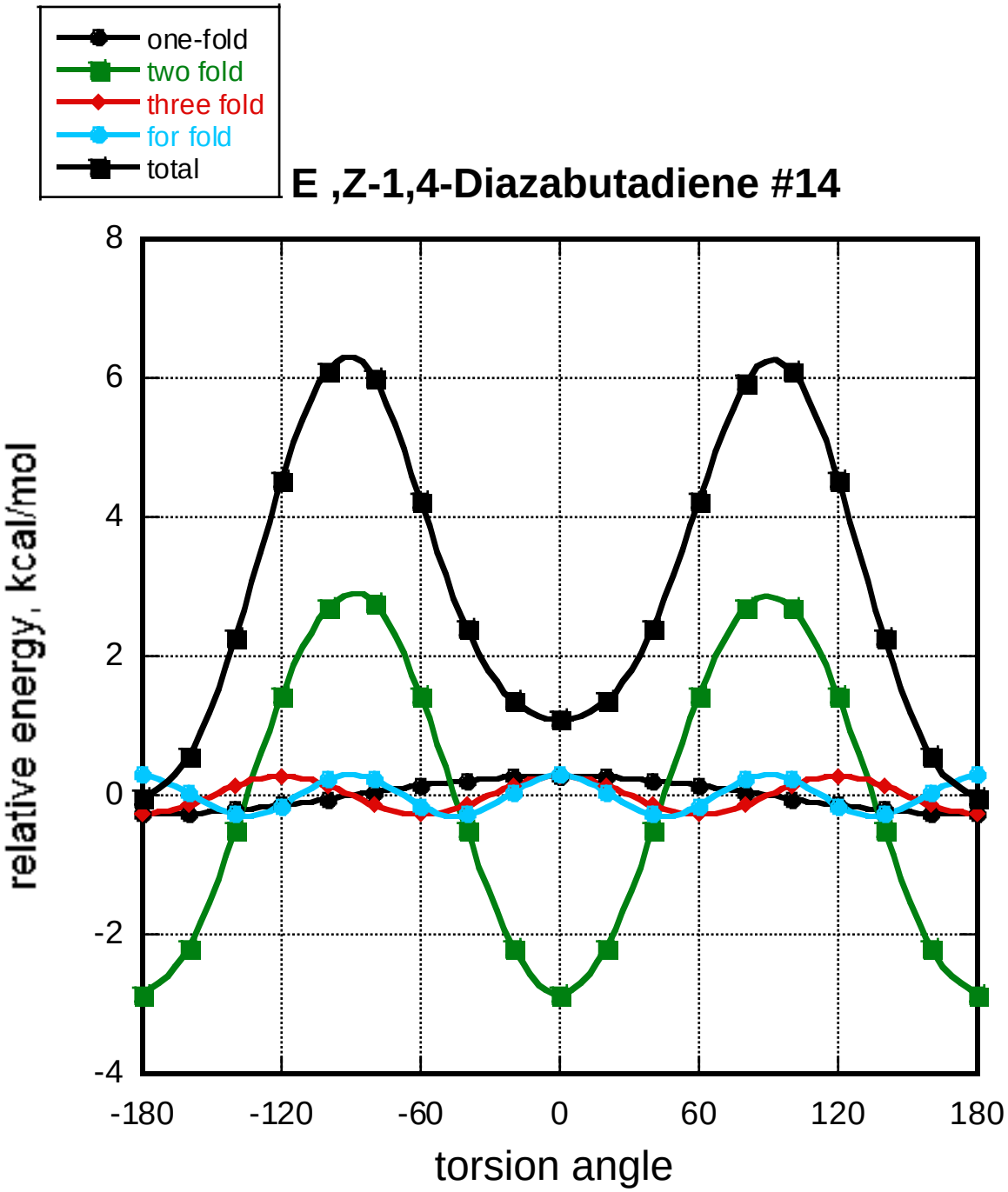


Figure S4o E,E-1,4-diazabutadiene

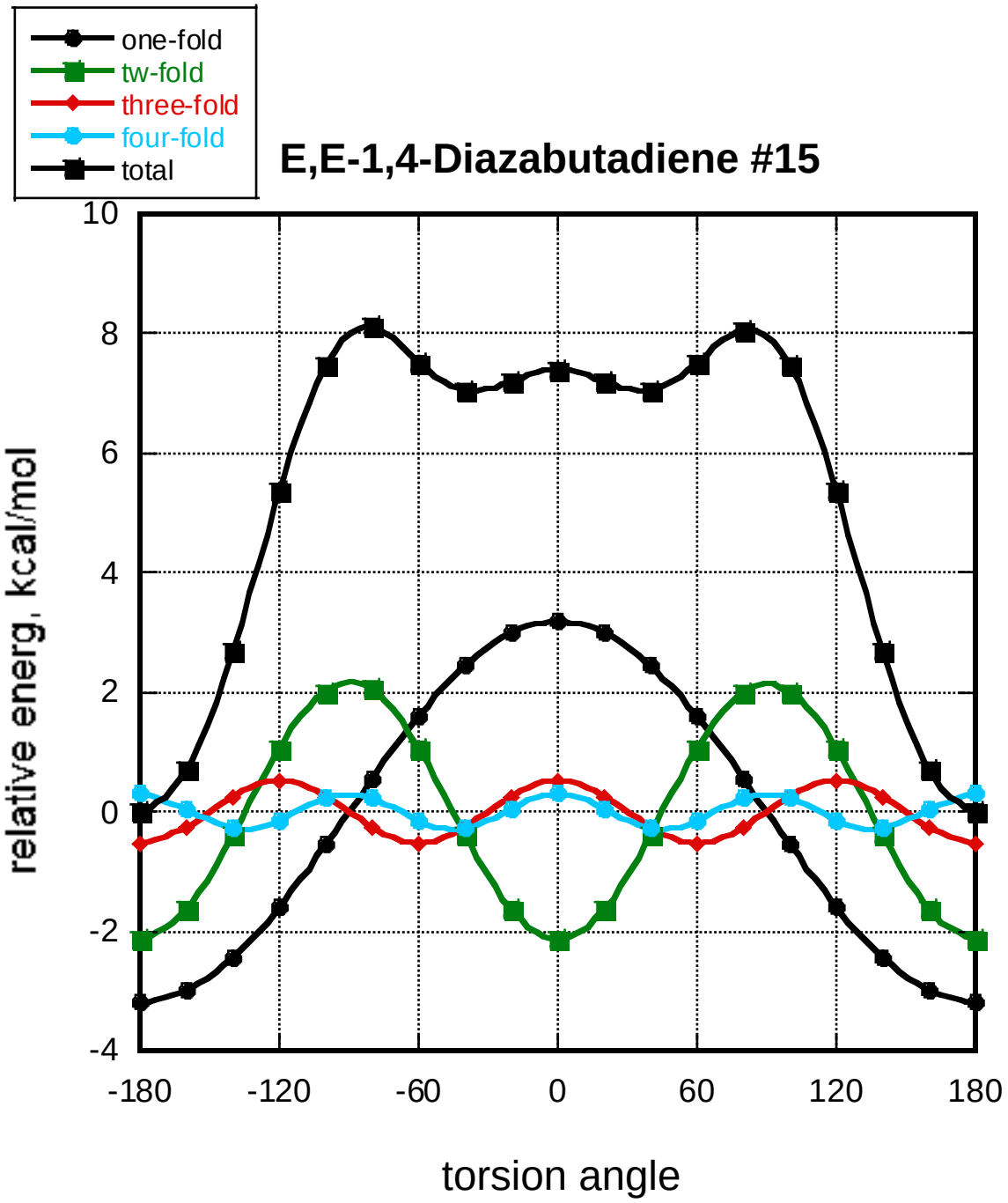


Figure S4p methyleneformamide

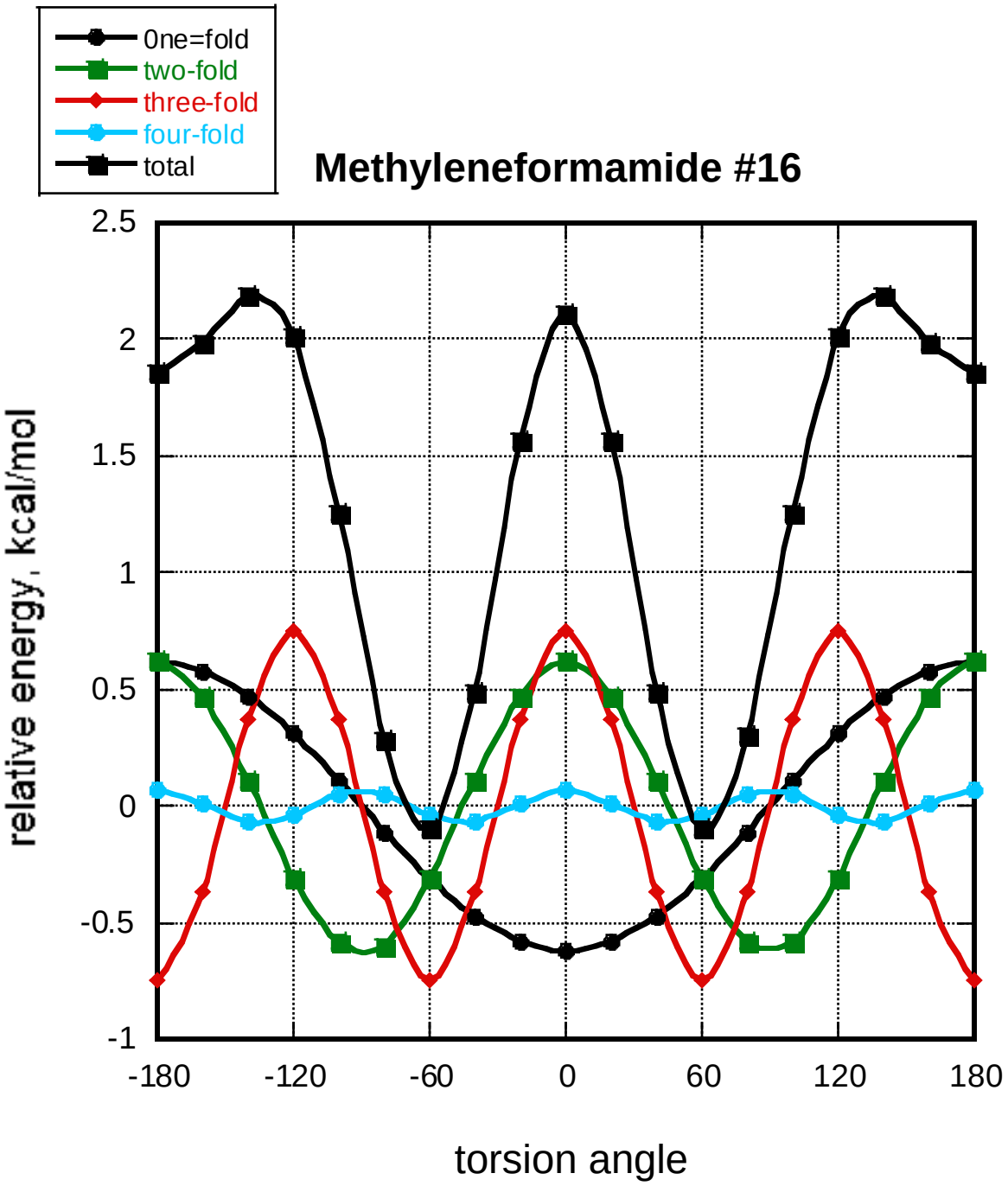


Figure S4q 2,3-diazabutadiene

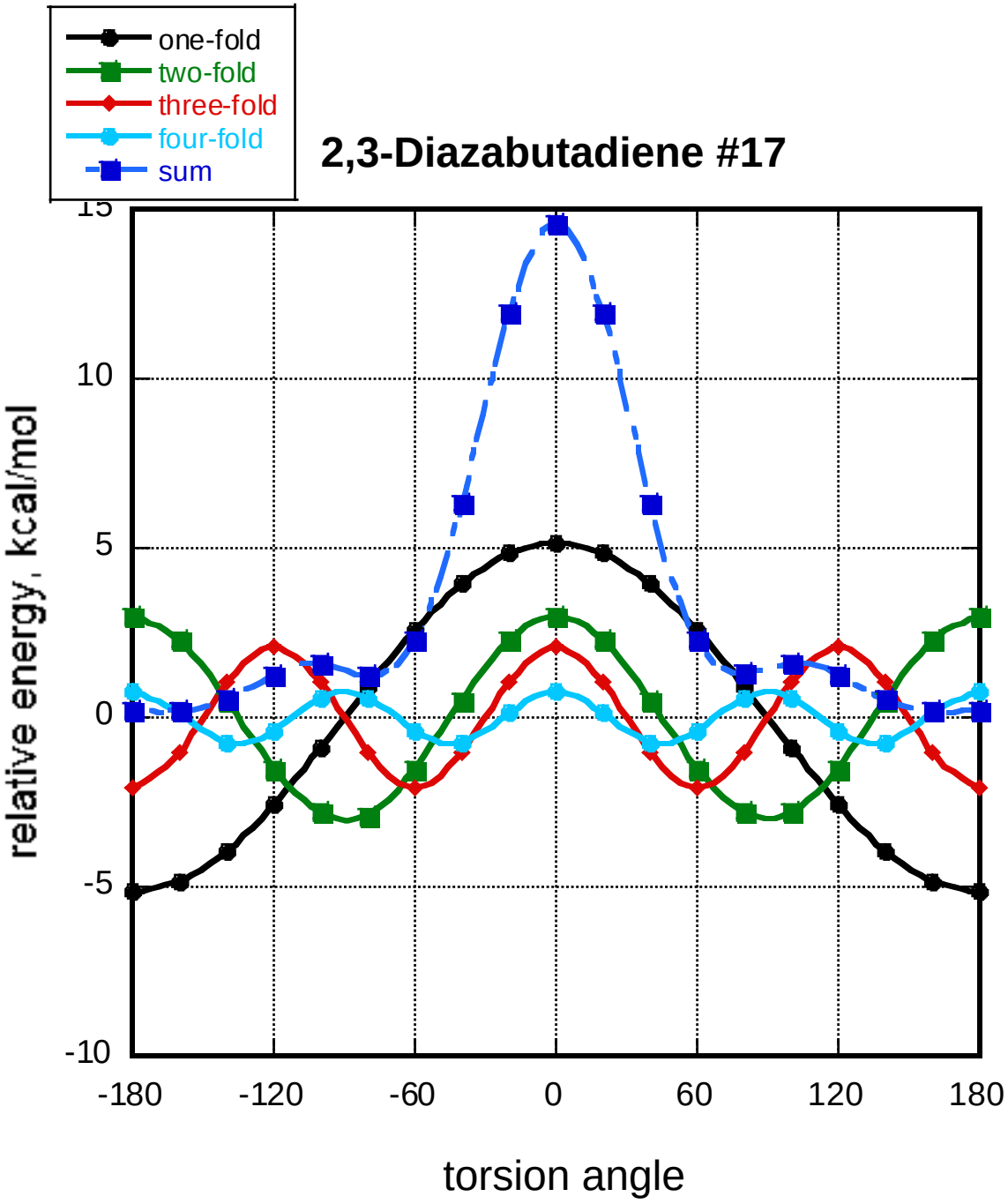


Figure S4r nitrosonethanimine

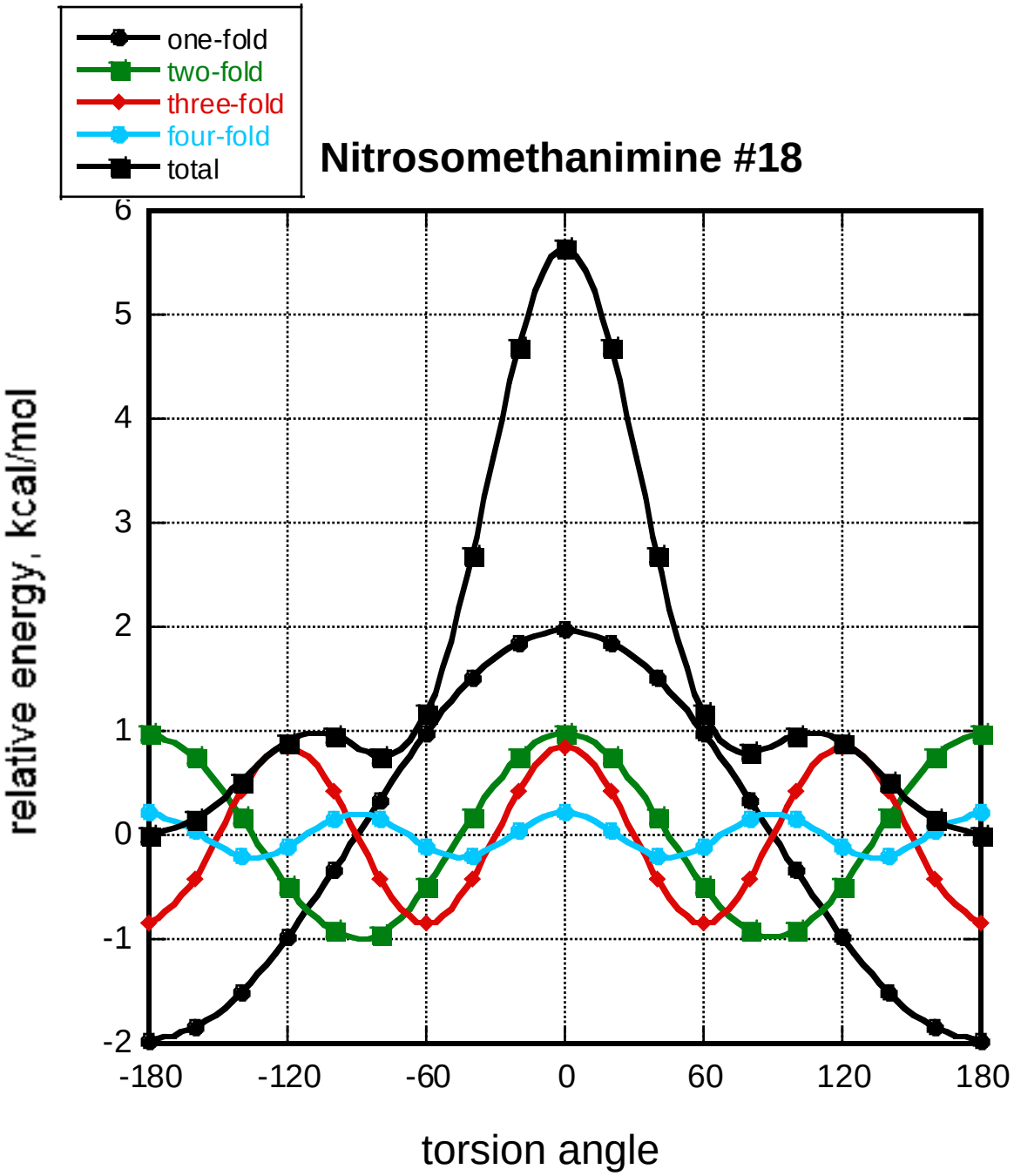


Table S3 Fourier components for heterobutadienes, using a 6-term (plus constant) Fourier expansion:

MP2/aug-cc-pVTZ energies from Ken Wiberg

6 terms plus the constant term

Equation: 0.5*m1*cos(m0)+0.5*m2*cos(2*m0)+0.5*m3*cos(3*m0)+0.5*m4*cos(4*m0)+0.5*m5*cos(5*m0)+0.5*m6*cos(6*m0)+m7

Compound	Cmpd #	1-fold	2-fold	3-fold	4-fold	5-fold	6-fold	constant
butadiene	1	1.40	-4.35	2.36	0.74	-0.11	0.12	3.60
2-azabutadiene	2	1.97	-0.32	3.28	0.84	0.24	0.20	2.39
acrolein	3	1.65	-6.76	0.72	0.93	-0.16	-0.11	4.08
nitrosoethylene	4	2.52	-6.58	1.77	1.23	-0.14	-0.09	4.81
E-1-azabutadiene	5	1.59	-5.98	1.43	0.72	-0.16	0.01	4.07
Z-1-azabutadiene	6	1.42	-4.40	1.69	0.83	-0.09	0.02	3.31
Z-4-azaacrolein	7	0.86	-5.84	-0.15	0.67	-0.05	-0.11	2.97
E-4-azabutadiene	8	5.59	-4.21	0.41	0.62	-0.01	-0.04	4.81
E-C-1-azamethanimine	9	3.15	-2.28	1.22	0.65	0.01	-0.01	3.01
Z-C-nitrosomethanimine	10	1.71	-4.54	0.20	0.63	-0.04	-0.08	2.94
glyoxal	11	4.67	-3.56	-0.15	0.51	0.04	-0.07	3.84
nitrosoformaldehyde	12	2.80	-1.35	0.36	0.36	0.00	-0.04	2.10
Z,Z-1,4-diazabutadiene	13	1.42	-4.19	0.85	0.84	0.00	-0.03	2.83
E,Z-1,4-diazabutadiene	14	0.55	-5.72	0.56	0.59	-0.11	-0.04	3.10
E,E-1,4-diazabutadiene	15	6.38	-4.27	1.04	0.60	-0.05	-0.01	5.53
methyleneformamide	16	-1.24	1.23	1.49	0.14	0.21	0.10	1.30
2,3-diazabutadiene	17	10.28	5.94	4.13	1.55	0.56	0.20	3.65
nitrosomethanimine	18	3.93	1.96	1.69	0.43	0.05	-0.02	1.63