Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

QM/MM investigation on 1,3-dipolar cycloadditions of phthalazinium dicyanomethanide with three different dipolarophiles on water and in solutions

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Table S1. Computed and experimental densities of water-acetonitrile mixture solvents at 25 °C (g.cm^{-3})

X_{H_2O}	ρ (calcd)	ρ (exptl)	ref.
0.619	0.8506	0.8707 [a]	1
0.9	0.9617	0.9847 [b]	2

[a] Based on values at 20 °C , X_{H_2O}=0.957

References:

(1) J. Chem. Eng. Data 1967, 12, 336-337.

(2) J. Chem. Eng. Data 2008, 53, 578-585.

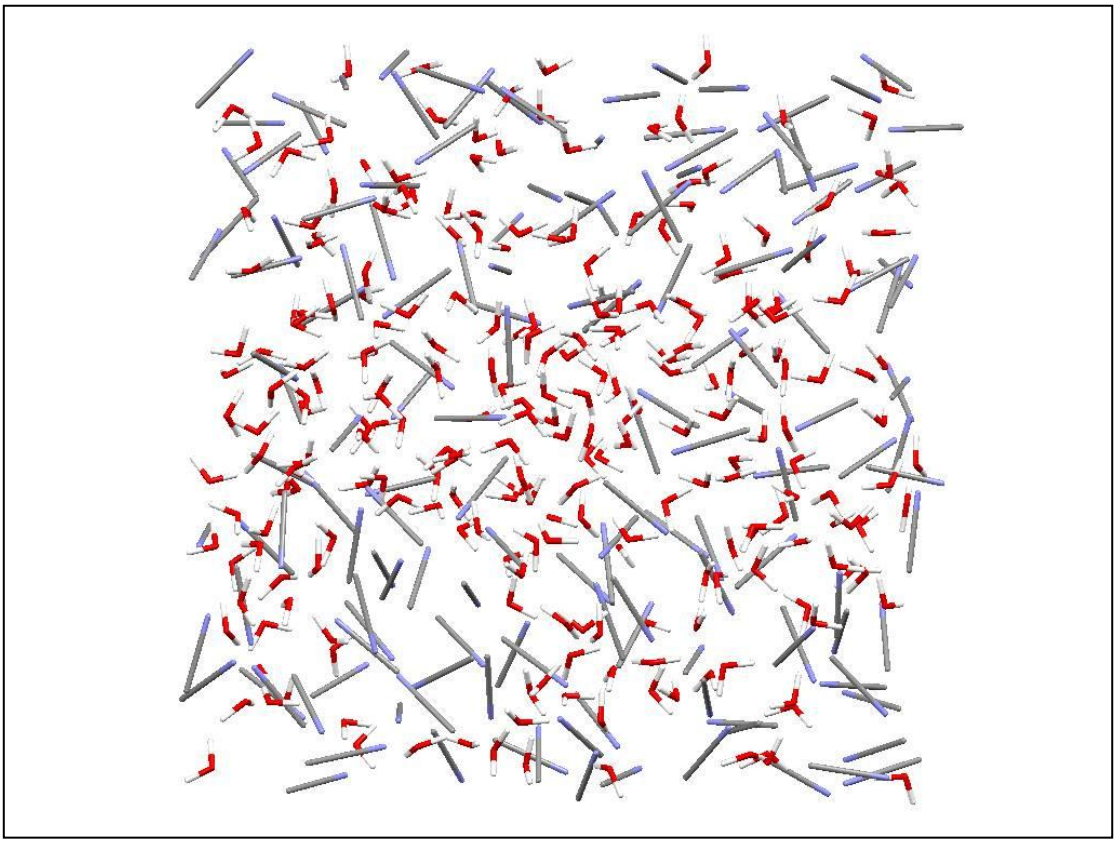

Figure S1. Illustration of the 0.619-mixture solvent box

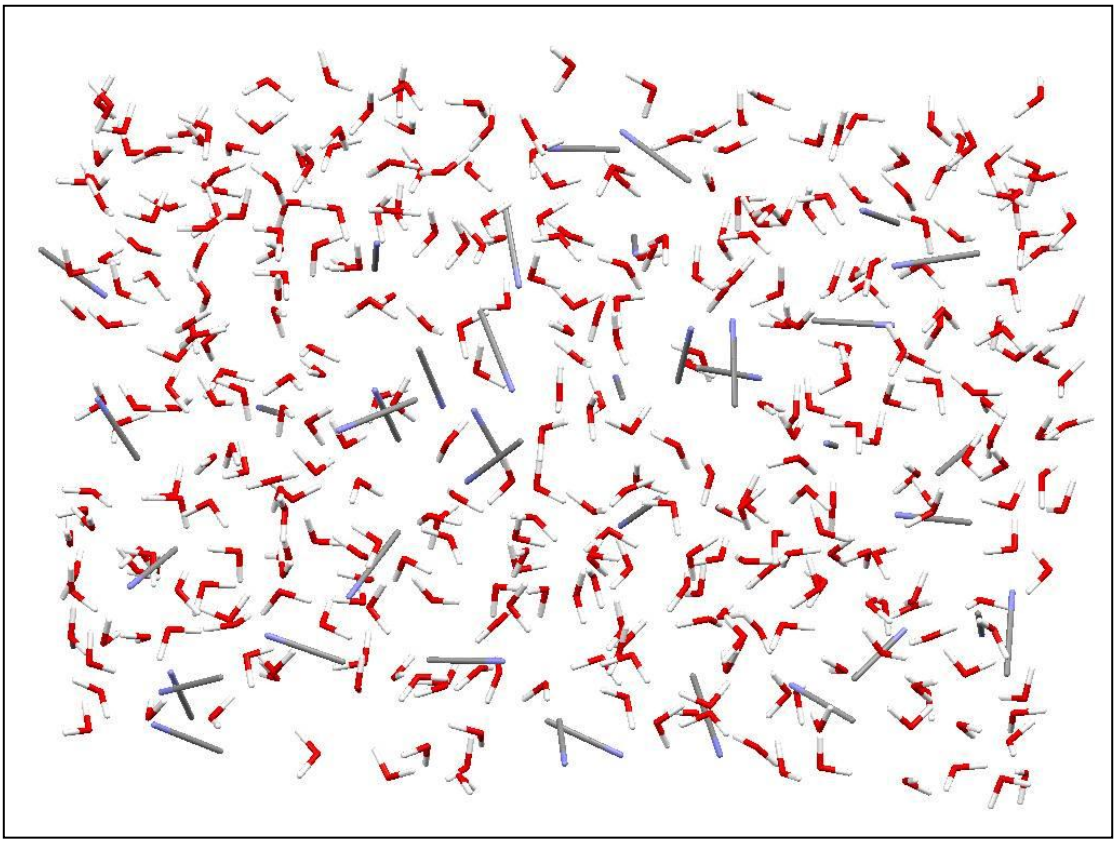

Figure S2. Illustration of the 0.9-mixture solvent box

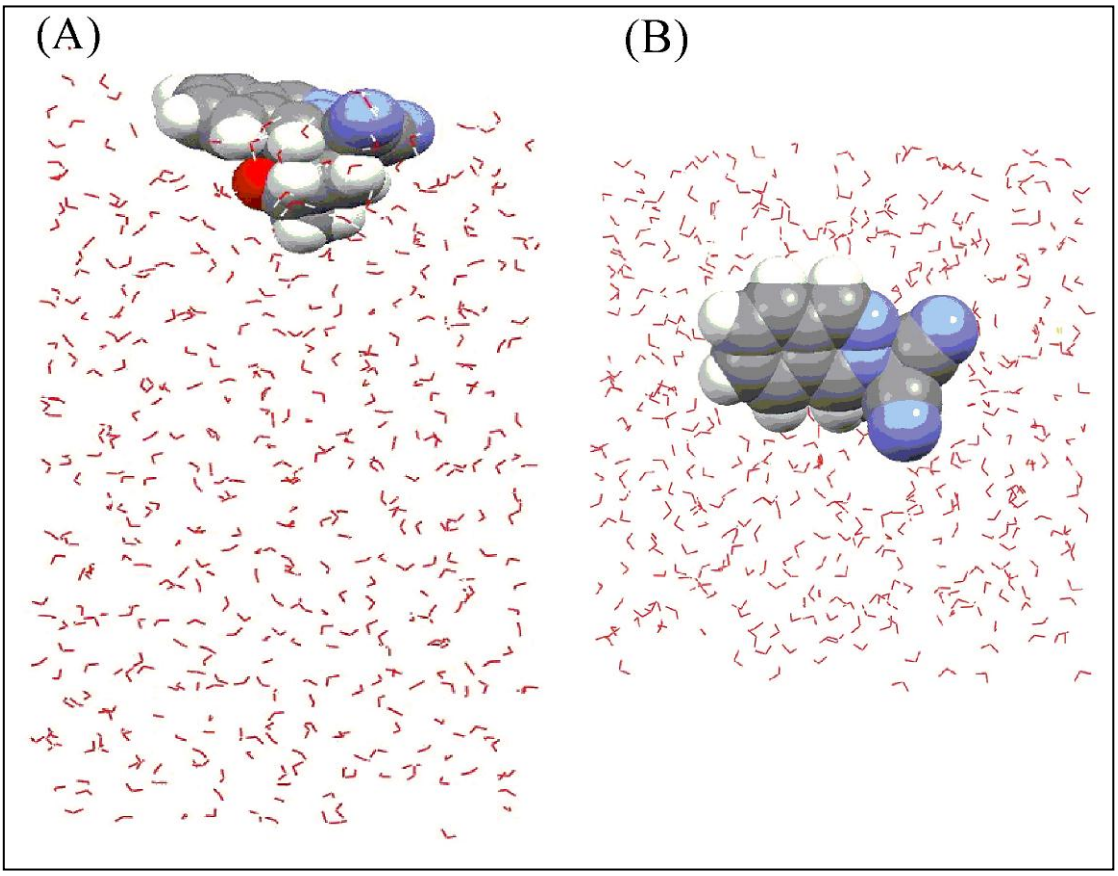

Figure S3. (A) Side and (B) overhead illustration of "on water" 1,3-dipolar cycloadditions with MVK transition structure from the QM/MM/MC calculations.

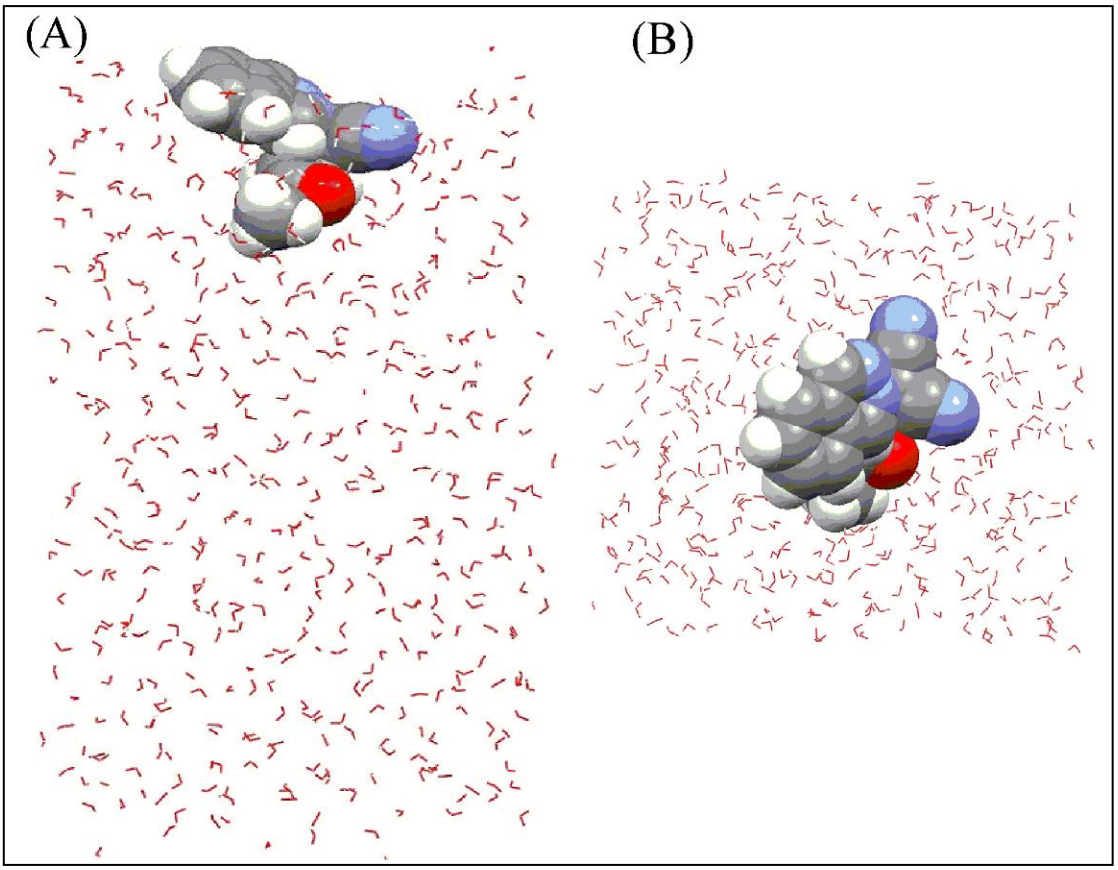

Figure S4. (A) Side and (B) overhead illustration of "on water" 1,3-dipolar cycloadditions with MAC transition structure from the QM/MM/MC calculations.

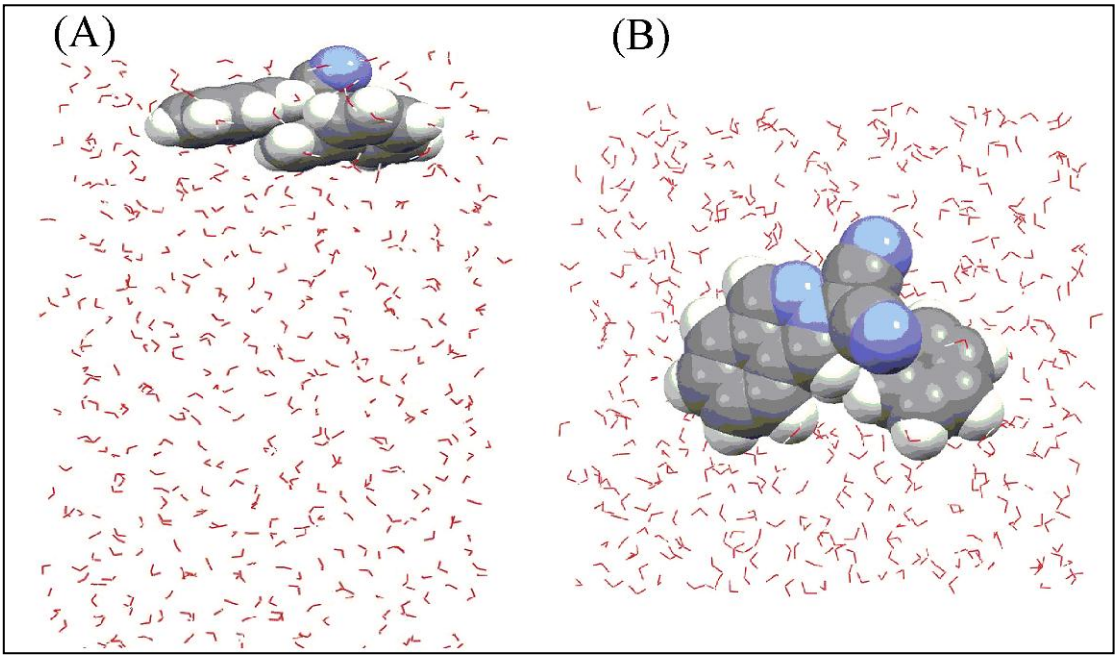

Figure S5. (A) Side and (B) overhead illustration of "on water" 1,3-dipolar cycloadditions with MVK transition structure from the QM/MM/MC calculations.

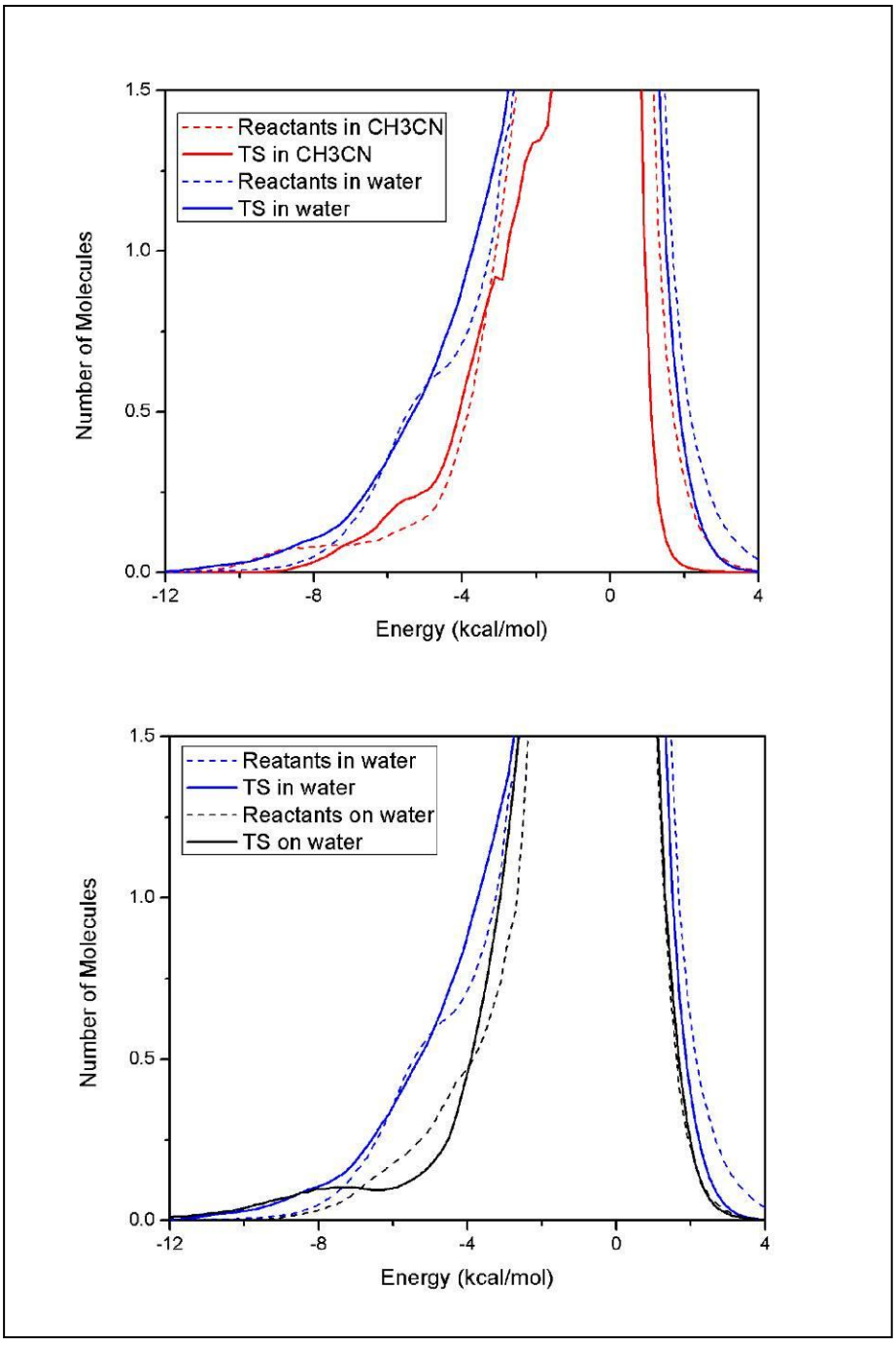

Figure S6. Solute-solvent energy pair distribution for the transition structure (solid) and reactant (solid) of the 1,3-dipolar cycloadditions of 1,3-dipolar **1** and MAC at CH3CN, in water, and on water. The ordinate records the number of solvent molecules that interact with the solutes with their interaction energy on the abscissa. Units for the ordinate are number of molecules per kcal/mol.

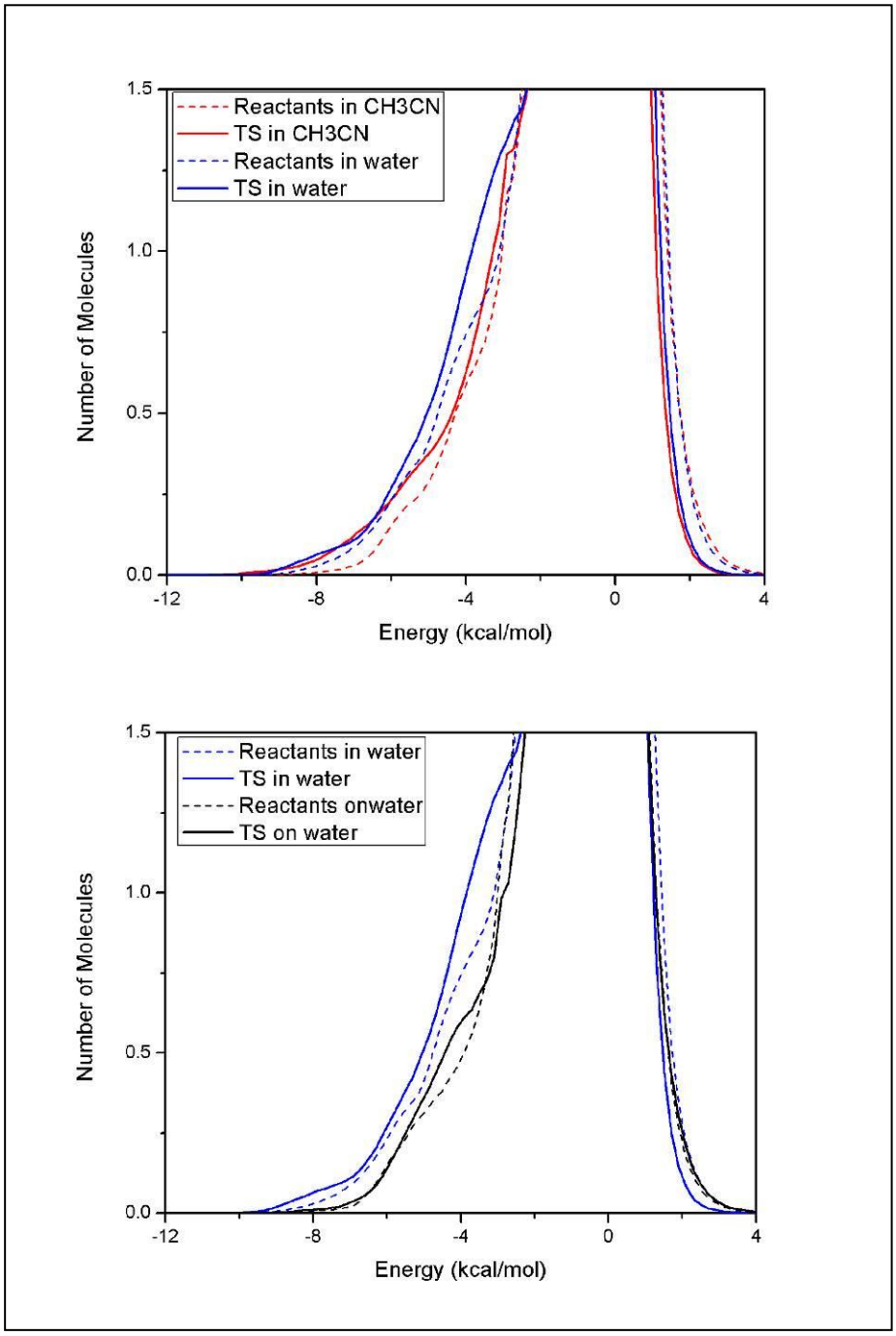

Figure S7. Solute-solvent energy pair distribution for the transition structure (solid) and reactant (solid) of the 1,3-dipolar cycloadditions of 1,3-dipolar **1** and STY at CH3CN, in water, and on water. The ordinate records the number of solvent molecules that interact with the solutes with their interaction energy on the abscissa. Units for the ordinate are number of molecules per kcal/mol.

Condensed-phase B3LYP/6-311+G(2d,p) 1,3-dipolar 1 and MVK optimizations in PCM: Water transition structure

	1	2	3
	A	A	A
Frequencies --	-353.6722	36.9766	44.5820
Red. masses --	10.5159	4.8019	7.4867
Frc consts --	0.7750	0.0039	0.0088
IR Inten --	400.4743	11.1231	20.1260

Sum of electronic and zero-point Energies=	-872.947542
Sum of electronic and thermal Energies=	-872.930029
Sum of electronic and thermal Enthalpies=	-872.929085
Sum of electronic and thermal Free Energies=	-872.993605

C	0.73341800	-1.70959800	-1.26498900
N	-0.52548500	-1.54561400	-1.00714300
H	0.94322900	-2.27878100	-2.16349600
N	-0.84043900	-0.86183400	0.13562200
C	-3.10397100	-1.14383200	-0.66251000
C	-2.70553100	-0.46119500	1.59965200
N	-3.89976600	-1.58311900	-1.36922000
N	-3.10852600	-0.40140900	2.67644700
C	-1.00851800	2.00452100	0.22666100
H	-1.03062300	2.41699600	1.22979800
C	0.11626400	2.42088100	-0.56143200
O	1.01136500	3.13610900	-0.07465800
C	-2.20650700	-0.46040300	0.23997400
C	-2.18286100	1.36547600	-0.26048300
H	-3.12077700	1.66732200	0.19552100
H	-2.27681400	1.25323300	-1.33548600
C	0.06377800	-0.22388400	0.90626700
H	-0.28511900	0.19133500	1.83694000
C	1.80478500	-1.20156000	-0.46409100
C	3.15507500	-1.43692500	-0.75394400
C	1.44740500	-0.43463100	0.66910100
C	4.12846800	-0.91441300	0.07600600
H	3.42362700	-2.02538400	-1.62248400
C	2.44838600	0.09092600	1.50245500
C	3.77372400	-0.15261000	1.20148200
H	5.17413000	-1.09206800	-0.14032800
H	2.17496600	0.67827100	2.36936400
H	4.55059600	0.24786600	1.84024200
C	0.22900700	2.03850700	-2.02843000
H	-0.37884000	1.18422100	-2.32224600

H	-0.07751700	2.89467800	-2.63636600
H	1.27421200	1.82971600	-2.25845000

CH_3CN transition structure

	1	2	3
	A	A	A
Frequencies --	-358.1136	36.3808	47.4716
Red. masses --	10.5290	4.8826	7.4787
Frc consts --	0.7956	0.0038	0.0099
IR Inten --	391.9964	9.2462	19.3566

Sum of electronic and zero-point Energies=	-872.946852
Sum of electronic and thermal Energies=	-872.929355
Sum of electronic and thermal Enthalpies=	-872.928411
Sum of electronic and thermal Free Energies=	-872.992826

C	0.72920400	-1.70993100	-1.26442700
N	-0.52944500	-1.54528600	-1.00658000
H	0.93857400	-2.27914900	-2.16305600
N	-0.84427400	-0.86191800	0.13662300
C	-3.10776400	-1.13581200	-0.66490200
C	-2.70915400	-0.45837100	1.59948900
N	-3.90425000	-1.57016100	-1.37389300
N	-3.11201500	-0.39766900	2.67631500
C	-0.99699300	2.00100100	0.22953800
H	-1.01422100	2.41342600	1.23274800
C	0.12794500	2.41436700	-0.56211600
O	1.02827000	3.12169900	-0.07586400
C	-2.20906200	-0.45871700	0.24053900
C	-2.17702200	1.37310500	-0.25650400
H	-3.11170400	1.67777000	0.20403100
H	-2.27465600	1.26283400	-1.33136500
C	0.06061400	-0.22181800	0.90592300
H	-0.28720300	0.18938900	1.83875700
C	1.80112800	-1.20264400	-0.46348700
C	3.15114300	-1.43971900	-0.75298200
C	1.44440300	-0.43489900	0.66916700
C	4.12515700	-0.91796300	0.07674900
H	3.41912300	-2.02890600	-1.62124100
C	2.44585100	0.09004500	1.50206800
C	3.77105300	-0.15513100	1.20154900
H	5.17064300	-1.09688400	-0.13944000
H	2.17305500	0.67882900	2.36818700

H	4.54818100	0.24526100	1.84006000
C	0.23127700	2.03675200	-2.03108500
H	-0.37180400	1.17775800	-2.32128400
H	-0.08911200	2.89142600	-2.63401800
H	1.27618200	1.83831000	-2.27083500

Condensed-phase B3LYP/6-311+G(2d,p) 1,3-dipolar 1 and MAC optimizations in PCM: Water transition structure

	1	2	3
	A	A	A
Frequencies --	-411.9268	25.5986	47.9038
Red. masses --	10.9107	5.2734	5.8751
Frc consts --	1.0908	0.0020	0.0079
IR Inten --	445.9180	4.6187	4.3234

Sum of electronic and zero-point Energies=	-948.198419
Sum of electronic and thermal Energies=	-948.179940
Sum of electronic and thermal Enthalpies=	-948.178995
Sum of electronic and thermal Free Energies=	-948.245965

C	-0.62587800	-0.91067000	1.89484400
N	0.63551000	-0.84270300	1.61716100
H	-0.86234500	-0.88453800	2.95264800
N	0.98519600	-0.90968500	0.29401000
C	3.19579900	-0.42715500	1.14404700
C	2.92287600	-1.29762900	-1.07572400
N	3.96324700	-0.25303900	1.98527300
N	3.40057400	-1.84797600	-1.96801300
C	0.84055800	1.34435900	-1.36973300
H	0.75286800	1.17008500	-2.43344000
C	-0.27414600	2.07475800	-0.80139900
O	-1.28542800	2.38779800	-1.41683100
C	2.32533800	-0.54511800	0.00254800
C	2.11019800	1.24929900	-0.75255100
H	2.97802300	1.24917300	-1.40204000
H	2.25464400	1.81475700	0.16033000
C	0.09620700	-0.85449500	-0.72908500
H	0.47474300	-1.08474100	-1.71121500
C	-1.67350800	-1.01970500	0.92274500
C	-3.02467000	-1.15006800	1.27038000
C	-1.29136100	-1.00958900	-0.43631500
C	-3.97576700	-1.26838700	0.27479000

H	-3.31157100	-1.15975500	2.31469100
C	-2.26785300	-1.13290600	-1.43663800
C	-3.59545100	-1.26090800	-1.07642100
H	-5.02148300	-1.36918100	0.53594700
H	-1.97694600	-1.12407200	-2.47955300
H	-4.35235900	-1.35641900	-1.84463600
O	-0.10811400	2.38546600	0.51094600
C	-1.16667400	3.13624500	1.12959500
H	-0.85071900	3.29071200	2.15813800
H	-1.30002500	4.09472300	0.62848300
H	-2.10218700	2.57878700	1.10221900

CH_3CN transition structure

	1	2	3
	A	A	A
Frequencies --	-412.7982	25.6464	48.0514
Red. masses --	10.9065	5.2833	5.9352
Frc consts --	1.0950	0.0020	0.0081
IR Inten --	435.9347	4.3281	4.4816

Sum of electronic and zero-point Energies=	-948.197829
Sum of electronic and thermal Energies=	-948.179347
Sum of electronic and thermal Enthalpies=	-948.178403
Sum of electronic and thermal Free Energies=	-948.245381

C	-0.62356200	-0.91636300	1.89332000
N	0.63771700	-0.84690600	1.61586900
H	-0.85989500	-0.89346200	2.95125800
N	0.98757700	-0.90991700	0.29260600
C	3.19805900	-0.42788400	1.14370600
C	2.92469300	-1.29037100	-1.07969900
N	3.96574400	-0.25519800	1.98502600
N	3.40141300	-1.83596600	-1.97546900
C	0.83900900	1.34764900	-1.36573800
H	0.75262400	1.17615200	-2.43002800
C	-0.27833700	2.07476000	-0.79720300
O	-1.28911500	2.38658500	-1.41335200
C	2.32728200	-0.54384200	0.00250100
C	2.10826800	1.25518300	-0.74826000
H	2.97673500	1.25795100	-1.39684000
H	2.25056900	1.81736400	0.16695000
C	0.09842200	-0.85189500	-0.73053600
H	0.47712600	-1.08060700	-1.71297000

C	-1.67122300	-1.02321900	0.92096100
C	-3.02227300	-1.15562000	1.26828100
C	-1.28912200	-1.00890400	-0.43805500
C	-3.97343000	-1.27165600	0.27250300
H	-3.30904300	-1.16864200	2.31262000
C	-2.26572000	-1.12975300	-1.43853700
C	-3.59319100	-1.25975700	-1.07865200
H	-5.01906100	-1.37391500	0.53344900
H	-1.97506300	-1.11707300	-2.48147300
H	-4.35006700	-1.35313400	-1.84716000
O	-0.11450100	2.38293900	0.51601500
C	-1.17560200	3.13025100	1.13440500
H	-0.86181300	3.28299200	2.16388400
H	-1.30996100	4.08953700	0.63511600
H	-2.11001900	2.57109600	1.10368300

Condensed-phase B3LYP/6-311+G(2d,p) 1,3-dipolar 1 and STY optimizations in PCM:

Water transition structure

	1	2	3
	A	A	A
Frequencies --	-417.8401	29.7182	46.6946
Red. masses --	11.3743	5.5301	5.5905
Frc consts --	1.1700	0.0029	0.0072
IR Inten --	851.3613	3.6999	3.9263

Sum of electronic and zero-point Energies=	-951.328931
Sum of electronic and thermal Energies=	-951.310279
Sum of electronic and thermal Enthalpies=	-951.309335
Sum of electronic and thermal Free Energies=	-951.377064

C	-2.93899700	1.53677300	-0.51609400
C	-3.33001800	0.18236800	-0.24352100
C	-2.33929300	-0.68027000	0.25808500
H	-3.63908900	2.22814000	-0.97157700
N	-1.78871000	2.04665700	-0.20606800
N	-0.87638300	1.22273100	0.38736600
C	-0.03294100	-0.65754000	-1.26597500
H	-0.74071600	-0.28022300	-1.99639200
H	-0.08843100	-1.73146600	-1.12622700
C	1.23639700	-0.06186600	-1.27929500
H	1.35083800	0.87568500	-1.80951900
C	-0.97906400	-0.16151700	0.34228000
H	-0.32004100	-0.65726400	1.04465100
C	0.38395300	1.78186700	0.61135200

C	1.20074200	1.25966700	1.62895000
C	0.69413400	3.04862300	0.08263800
N	1.88941700	0.82307800	2.45345500
N	1.01281900	4.07814000	-0.34318200
C	2.45784200	-0.64389700	-0.77217800
C	3.67284900	0.04333200	-0.96695900
C	2.50084500	-1.88341900	-0.10373900
C	4.87526900	-0.48891900	-0.52949300
H	3.65962500	1.00185800	-1.47308900
C	3.70549300	-2.41081700	0.33678300
H	1.59067400	-2.44580500	0.06241600
C	4.89763200	-1.72023100	0.12425100
H	5.79756500	0.05434900	-0.69608600
H	3.71754800	-3.36699000	0.84589900
H	5.83650100	-2.13819600	0.46650800
H	-4.22152000	-3.46657800	0.66071900
C	-3.96587400	-2.44580000	0.40523800
C	-4.95367500	-1.58903200	-0.09992300
C	-2.66613100	-2.00013100	0.58113300
C	-4.64135800	-0.28177300	-0.42271800
H	-5.96406300	-1.95388900	-0.23464100
H	-1.90637700	-2.66814200	0.96896400
H	-5.39936000	0.38976800	-0.80749500

CH_3CN transition structure

	1	2	3
	A	A	A
Frequencies --	-417.8401	29.7182	46.6946
Red. masses --	11.3743	5.5301	5.5905
Frc consts --	1.1700	0.0029	0.0072
IR Inten --	851.3613	3.6999	3.9263

Sum of electronic and zero-point Energies=	-951.328931
Sum of electronic and thermal Energies=	-951.310279
Sum of electronic and thermal Enthalpies=	-951.309335
Sum of electronic and thermal Free Energies=	-951.377064

C	-2.93689700	1.53748300	-0.51884400
C	-3.33032000	0.18396300	-0.24533200
C	-2.34140300	-0.67929400	0.25882600
H	-3.63518500	2.22945900	-0.97619700
N	-1.78637000	2.04608300	-0.20768200
N	-0.87606100	1.22171800	0.38807400

C	-0.03258900	-0.65948300	-1.26475900
H	-0.74108100	-0.28307500	-1.99494500
H	-0.08749400	-1.73330800	-1.12405400
C	1.23588900	-0.06230300	-1.27791800
H	1.34911100	0.87530300	-1.80830200
C	-0.98087900	-0.16228800	0.34437200
H	-0.32253900	-0.65877400	1.04686800
C	0.38473600	1.77905200	0.61290000
C	1.19946000	1.25504100	1.63144800
C	0.69671800	3.04584400	0.08496800
N	1.88542300	0.81621600	2.45692000
N	1.01721300	4.07477200	-0.34069800
C	2.45845900	-0.64323000	-0.77192700
C	3.67261500	0.04500800	-0.96789400
C	2.50331200	-1.88265300	-0.10364500
C	4.87594500	-0.48636300	-0.53196600
H	3.65802100	1.00376000	-1.47356000
C	3.70883600	-2.40930600	0.33520900
H	1.59368500	-2.44558300	0.06367400
C	4.90011900	-1.71776200	0.12141900
H	5.79753600	0.05789200	-0.69922100
H	3.72223500	-3.36542600	0.84440300
H	5.83970300	-2.13491700	0.46270000
H	-4.22763700	-3.46298000	0.66162400
C	-3.97035300	-2.44281600	0.40530500
C	-4.95630000	-1.58544700	-0.10246300
C	-2.67047400	-1.99838400	0.58286800
C	-4.64190100	-0.27891500	-0.42610600
H	-5.96690600	-1.94925600	-0.23840700
H	-1.91213100	-2.66658800	0.97310800
H	-5.39857800	0.39307600	-0.81274600

Gas-phase B3LYP/6-311+G(2d,p) 1,3-dipolar 1 and MVK optimizations:

transition structure

	1	2	3
	A	A	A
Frequencies --	-409.6176	31.3064	58.0059
Red. masses --	10.7654	5.3210	6.5169
Frc consts --	1.0642	0.0031	0.0129
IR Inten --	157.2157	3.3732	2.2452

Sum of electronic and zero-point Energies=	-872.924426
Sum of electronic and thermal Energies=	-872.906963

Sum of electronic and thermal Enthalpies= -872.906019
Sum of electronic and thermal Free Energies= -872.970149

C	0.66580500	-1.67952700	-1.29439300
N	-0.59030500	-1.51302400	-1.03748500
H	0.87041000	-2.22193200	-2.21168100
N	-0.90925100	-0.87308800	0.12899500
C	-3.17626500	-1.00254400	-0.71591700
C	-2.75451700	-0.45269500	1.59947800
N	-3.98064300	-1.32563700	-1.47474700
N	-3.12800600	-0.37779000	2.68731500
C	-0.81437800	1.93521900	0.31152100
H	-0.72817400	2.31912400	1.32188200
C	0.31528000	2.29879800	-0.54173200
O	1.33163400	2.78152300	-0.05413500
C	-2.25733000	-0.46456600	0.24776700
C	-2.08077400	1.51515500	-0.14126400
H	-2.95170300	1.82778600	0.42277100
H	-2.25939800	1.45858900	-1.20901300
C	0.00528300	-0.22364000	0.90251500
H	-0.33595300	0.09275400	1.87428800
C	1.74436000	-1.20697900	-0.47676400
C	3.09255000	-1.45156800	-0.76818900
C	1.39273300	-0.45788800	0.66711900
C	4.07345700	-0.95012900	0.06560900
H	3.35505300	-2.03023200	-1.64613000
C	2.40042200	0.05468000	1.49740100
C	3.72450400	-0.19494300	1.19470600
H	5.11754500	-1.13297700	-0.15561600
H	2.13481500	0.65538000	2.35763600
H	4.50355900	0.20522200	1.83145100
C	0.21990700	2.10694000	-2.04769900
H	-0.27049600	1.17524000	-2.33413200
H	-0.36075600	2.92775200	-2.47930400
H	1.22323300	2.13998300	-2.46856000

Gas-phase B3LYP/6-311+G(2d,p) 1,3-dipolar 1 and MAC optimizations:
transition structure

	1	2	3
	A	A	A
Frequencies --	-412.3038	30.2289	45.9713
Red. masses --	10.8425	5.2342	5.1990
Frc consts --	1.0860	0.0028	0.0065

IR Inten	--	145.3863	1.0663	0.4455

Sum of electronic and zero-point Energies= -948.176536
Sum of electronic and thermal Energies= -948.158068
Sum of electronic and thermal Enthalpies= -948.157124
Sum of electronic and thermal Free Energies= -948.223895

C	-0.56027500	-1.05052800	1.85504300
N	0.69774400	-0.94246500	1.58329700
H	-0.79116100	-1.10030600	2.91407200
N	1.05148700	-0.91446400	0.26243300
C	3.26565200	-0.44521500	1.12737200
C	2.95704200	-1.10494400	-1.17805800
N	4.04156400	-0.30239100	1.96696000
N	3.38978400	-1.52614400	-2.16004700
C	0.80618800	1.43490700	-1.26474000
H	0.75129100	1.32121200	-2.33935400
C	-0.38684600	2.05137100	-0.69655900
O	-1.40504000	2.27924000	-1.31991400
C	2.37961100	-0.51479100	0.00063300
C	2.05701100	1.39824100	-0.62745700
H	2.94533500	1.47075300	-1.24308500
H	2.14318000	1.86849700	0.34437200
C	0.15537500	-0.80601000	-0.75766700
H	0.53982800	-0.98474200	-1.74834400
C	-1.61070800	-1.10949500	0.88084600
C	-2.96042500	-1.27796300	1.21810700
C	-1.22927400	-1.00096300	-0.47364500
C	-3.91377900	-1.33231700	0.21993300
H	-3.24509900	-1.36528600	2.26024000
C	-2.21020800	-1.05272900	-1.47603600
C	-3.53529200	-1.21798200	-1.12615600
H	-4.95839100	-1.46049300	0.47466000
H	-1.92395300	-0.94784500	-2.51487900
H	-4.29284300	-1.25278000	-1.89914200
O	-0.26460400	2.34194500	0.62884600
C	-1.39391900	2.99573600	1.22517000
H	-1.12220500	3.15532900	2.26614500
H	-1.58871700	3.94833700	0.73248700
H	-2.28509300	2.37217400	1.15217200

Gas-phase B3LYP/6-311+G(2d,p) 1,3-dipolar 1 and STY optimizations:
transition structure

	1	2	3
	A	A	A
Frequencies --	-416.8231	24.8506	45.3160
Red. masses --	11.4991	5.3364	5.0119
Frc consts --	1.1771	0.0019	0.0061
IR Inten --	217.2986	1.3937	1.6241

Sum of electronic and zero-point Energies=	-951.306254
Sum of electronic and thermal Energies=	-951.287575
Sum of electronic and thermal Enthalpies=	-951.286631
Sum of electronic and thermal Free Energies=	-951.354427

C	-2.87675900	1.58908400	-0.53604400
C	-3.34660800	0.25902400	-0.26882700
C	-2.41212700	-0.64551500	0.26948500
H	-3.52581300	2.31676000	-1.01147600
N	-1.70986600	2.04082400	-0.20279300
N	-0.85511600	1.18054100	0.41761900
C	-0.02798700	-0.72595500	-1.24826200
H	-0.76085600	-0.38280000	-1.97019100
H	-0.05402200	-1.79656900	-1.07835800
C	1.21116300	-0.07876000	-1.25862500
H	1.28446400	0.85996100	-1.79451300
C	-1.04020700	-0.19395400	0.39330600
H	-0.40444100	-0.72224500	1.09182800
C	0.42676500	1.66305000	0.65817700
C	1.19492900	1.03839700	1.66168800
C	0.80420800	2.93671700	0.18142000
N	1.81225500	0.48540500	2.47018200
N	1.18821700	3.95197900	-0.21757000
C	2.46720200	-0.61951100	-0.78126300
C	3.65056600	0.10971700	-1.00216900
C	2.57017300	-1.85183800	-0.11160900
C	4.87958800	-0.37794700	-0.58968100
H	3.59115300	1.06975600	-1.50243000
C	3.80084100	-2.33647300	0.30279700
H	1.68233600	-2.44106700	0.08261500
C	4.96116600	-1.60561800	0.06339200
H	5.77682000	0.20119900	-0.77182700
H	3.85698900	-3.28689400	0.81985200
H	5.92118100	-1.98647200	0.39006900
H	-4.43625900	-3.34302700	0.61429400
C	-4.12491900	-2.33617000	0.36420500
C	-5.05501200	-1.43687900	-0.17609800

C	-2.81507100	-1.94871400	0.58417300
C	-4.67078800	-0.14756300	-0.48971300
H	-6.07639000	-1.75514100	-0.34368600
H	-2.10134500	-2.64775400	1.00478600
H	-5.38499100	0.55649500	-0.90113500