Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information—Proton transfer in nonpolar solvents: An approach to generate electrolytes in aprotic media

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Molecular volumes and radii

The molecular volumes (v_m) along with their sphere-equivalent radii (r_m) were calculated from the molar masses and mass densities at 25 °C provided by the commercial supplier.[1]

Table S1: Molecular volumes and sphere-equivalent radii of **1**–**5**.

Species	v_m / Å^3	r_m / Å
Acid		
Bis(2-ethylhexyl)phosphoric acid (**1**)	555	5.10
Bases		
Bis(2-ethylhexyl)amine (**2**)	498	4.92
Tris(2-ethylhexyl)amine (**3**)	719	5.56
Dioctylamine (**4**)	502	4.93
Trioctylamine (**5**)	726	5.58

Small-angle neutron scattering (SANS)

SANS measurements were performed on a 2 wt.% solution of RAFT synthesized $PLMA_{48}$ in *n*-dodecane-d_{26} (Cambridge Isotope Laboratories, 98%), and the data are shown in Figure S1. Measurements were performed on the instrument Sans2d at the ISIS Pulsed Neutron Source (STFC Rutherford Appleton Laboratory, Didcot, UK).[2] A simultaneous Q-range of 0.006–0.68 $Å^{-1}$ was achieved by utilizing an incident wavelength range of 1.75–16.5 Å and employing an instrument setup with source–sample and sample–detector distances of L1 = L2 = 4 m and the 1 m^2 detector offset vertically 60 mm and sideways 100 mm. Q is the momentum transfer vector defined in Equation S1, where θ is half the scattering angle and λ is the incident neutron wavelength.

$$Q = \frac{4\pi \sin\theta}{\lambda} \tag{S1}$$

Raw scattering data sets were corrected for the detector efficiency, sample transmission, and background scattering and converted to scattering cross sections using the instrument-specific software Mantid.[3,4] These data were placed on an absolute scale (cm^{-1}) using the scattering from a standard sample (a solid blend of hydrogenous and perdeuterated polystyrene).[5] Data have been fit to models as described below using the SasView small-angle scattering software package.[6]

As for other long-alkyl methacrylates in *n*-dodecane-d_{26},[7] the scattering from $PLMA_{48}$ does not agree with a model assuming that it is a Gaussian chain. This likely arises from the bottlebrush nature of the polymers, due to the long lauryl (C_{12}) side chains. The scattering curve was first modeled using the Guinier–Porod function[8,9] to determine the radius of gyration (R_g) of the object; the dimensionality, which is determined from the shape parameter, s ($3 - s$, equal to 3 for globular objects); and the Porod exponent (m). The fitting parameters for are shown in Table S2.

As a polymer chain, $PLMA_{48}$ can be thought of as a flexible cylinder, and the SANS data

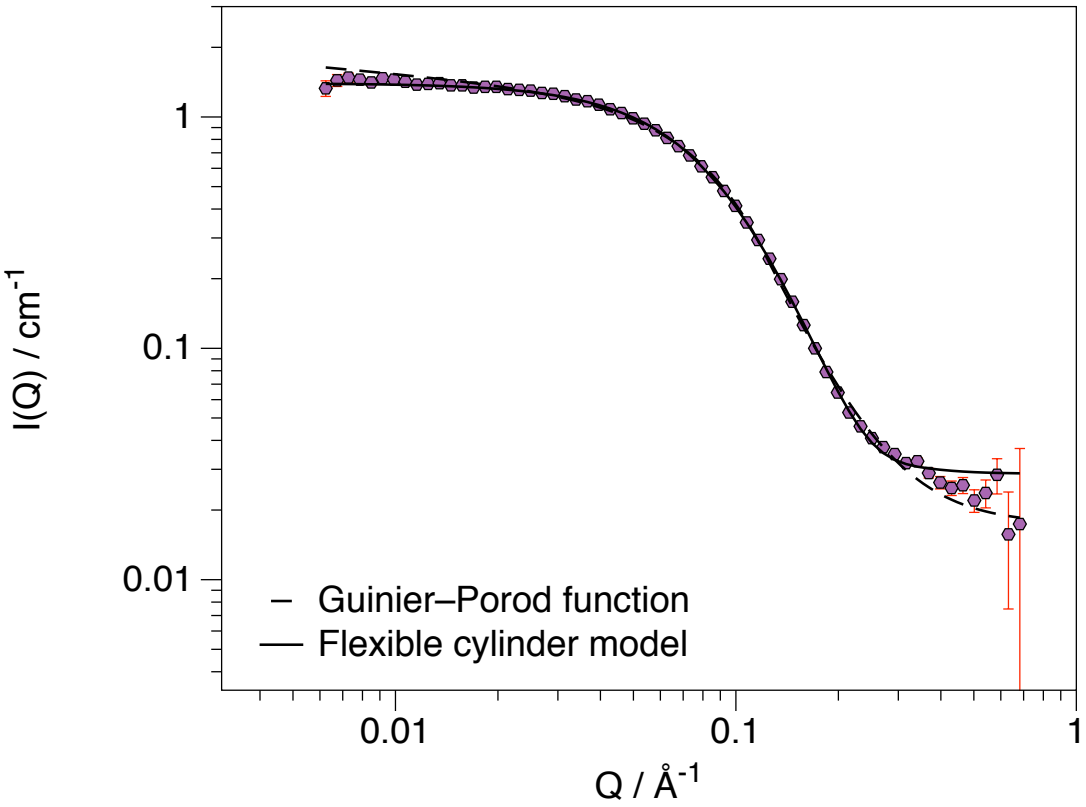

Figure S1: SANS data of a 2 wt.% solution of $PLMA_{48}$ in *n*-dodecane-d_{26} measured on Sans2d (ISIS Pulsed Neutron Source). Data have been fit to the Guinier–Porod function and to a flexible cylinder model as described in the text.

Table S2: Guinier–Porod function fitting parameters.

	R_g / Å	Dimensionality parameter	m
2 wt.% $PLMA_{48}$ in *n*-dodecane-d_{26}	17.2	2.87	3.1

have also been fit to such a model.[10,11] The contour length (L)was fixed, as the polymer is a methacrylate with a known degree of polymerization, to 123 Å. The Kuhn length (b) and cylinder radius (r_c), with a Gaussian distribution (σ_G), were allowed to vary. The R_g from this fitting is calculated from fit parameters ($R_g = \sqrt{L \cdot (b/6)}$) and compared to that from the Guinier–Porod function (Table S2). The fitting parameters for are shown in Table S3.

Table S3: Flexible cylinder model fitting parameters.

	b / Å	r_c / Å	σ_G	R_g calculated / Å
2 wt.% $PLMA_{48}$ in n-dodecane-d_{26}	15.8	11.8	0.26	18.0

Fuoss–Krauss triple ion theory

If the Fuoss–Krauss model of ion conductivity[12] can be applied to a system, a plot of the product of the molar conductivity and the square root of concentration ($\Lambda\sqrt{c}$) against concentration (c) should be a straight line. This is indeed the case as shown in Figure S2. The gradient and intercept (shown adjacent to the lines) are determined from an error weighted linear fit.

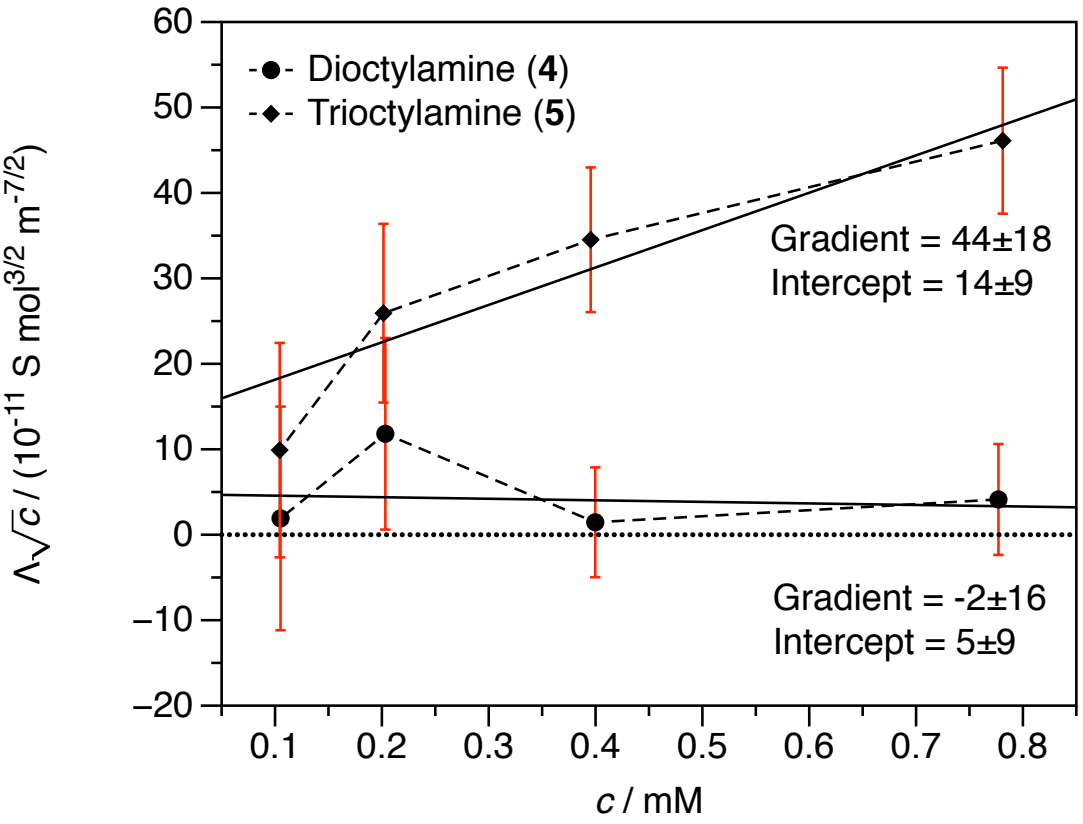

Figure S2: Plot of $\Lambda\sqrt{c}$ against c for analysis using the Fuoss–Krauss triple ion conductivity theory.[12]

Computational chemistry output files

These are output files from computational chemistry calculations run in Orca,[13] as described in the text.

H_2O

PBE0 ma-def2-SVP

```
SCF_Energy:  -76.2917730859751089
Number of atoms:  3
Coordinates:
H 0.622034530351 -0.027113765530 0.480365985111
O 0.154814047057 0.031371921444 -0.358071740034
H -0.776838577408 -0.004268155914 -0.122294245077
```

PBE0 ma-def2-TZVP

```
SCF_Energy:  -76.3790250121623586
Number of atoms:  3
Coordinates:
H 0.623564206260 -0.027014609113 0.479469707735
O 0.153682466193 0.031142240565 -0.355450109791
H -0.777236672453 -0.004137631452 -0.124019597944
Zero point energy ...  0.02145794 Eh 13.47 kcal/mol
Thermal vibrational correction ...  0.00000307 Eh 0.00 kcal/mol
Thermal rotational correction ...  0.00141627 Eh 0.89 kcal/mol
Thermal translational correction ...  0.00141627 Eh 0.89 kcal/mol
-----------------------------------------------------------------------
Total thermal correction 0.00283562 Eh 1.78 kcal/mol
```

Non-thermal (ZPE) correction 0.02145794 Eh 13.47 kcal/mol

Total correction 0.02429356 Eh 15.24 kcal/mol

MP2 cc-aug-pVTZ

MP2_Total_EN: -76.3289610464063912

H_3O^+

PBE0 ma-def2-SVP

SCF_Energy: -76.5659835839494463

Number of atoms: 4

Coordinates:

H 0.704339022299 -0.031201086005 0.511680259030

O 0.244364792419 -0.005627295592 -0.354125173902

H -0.726949926684 0.100275136058 -0.269006182696

H 0.646156111966 0.629633245540 -0.984118902432

PBE0 ma-def2-TZVP

SCF_Energy: -76.6547274868706410

Number of atoms: 4

Coordinates:

H 0.703048022716 -0.030302429821 0.509516262993

O 0.244365640321 -0.005991859230 -0.354207839179

H -0.724366364025 0.100794958370 -0.269013245225

H 0.644862700987 0.628579330681 -0.981865178589

Zero point energy ... 0.03455683 Eh 21.68 kcal/mol

Thermal vibrational correction ... 0.00008183 Eh 0.05 kcal/mol

Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol

Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol

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Total thermal correction 0.00291437 Eh 1.83 kcal/mol

Non-thermal (ZPE) correction 0.03455683 Eh 21.68 kcal/mol

Total correction 0.03747120 Eh 23.51 kcal/mol

MP2 cc-aug-pVTZ

MP2_Total_EN: -76.6000996014160052

$C_2H_4O_2$ (Acetic acid)

PBE0 ma-def2-SVP

SCF_Energy: -228.6780952195176155

Number of atoms: 8

Coordinates:

C 0.988269916844 -0.122527688751 1.303967334547

C 0.295635246105 -0.045887137522 -0.021910475753

O 0.824623147426 -0.146701286884 -1.098763670683

O -1.026300303223 0.156723741264 0.110968825768

H -1.400048628891 0.196067524215 -0.782338197459

H 2.060559823350 -0.285733940748 1.151175243514

H 0.562752690216 -0.942486950060 1.901042177830

H 0.823838108174 0.808585738486 1.866348762236

PBE0 ma-def2-TZVP

SCF_Energy: -228.9321711556677315

Number of atoms: 8

Coordinates:

C 0.987681689863 -0.122448351486 1.303002270927

C 0.298877852609 -0.045350446620 -0.021731689053

O 0.825348982309 -0.145504861486 -1.096044453930

O -1.025207101104 0.155730954766 0.116530028141

H -1.394095639176 0.194137423085 -0.777122851916

H 2.051417657072 -0.285525777638 1.152169127950

H 0.561836851429 -0.935627549926 1.894140693563

H 0.823469706999 0.802628609305 1.859546874318

Zero point energy ... 0.06195537 Eh 38.88 kcal/mol

Thermal vibrational correction ... 0.00172911 Eh 1.09 kcal/mol

Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol

Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol

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Total thermal correction 0.00456165 Eh 2.86 kcal/mol

Non-thermal (ZPE) correction 0.06195537 Eh 38.88 kcal/mol

Total correction 0.06651702 Eh 41.74 kcal/mol

MP2 cc-aug-pVTZ

MP2_Total_EN: -228.7222985605508256

$C_2H_3O_2$ (Acetate anion)

PBE0 ma-def2-SVP

SCF_Energy: -228.1148753104439777

Number of atoms: 7

Coordinates:

C 0.989011057101 -0.122530560297 1.303853547591

C 0.191130714540 -0.029249034862 -0.027151958593

O 0.854001354878 -0.148576377379 -1.080803720154

O -1.039086457700 0.156806826561 0.107261992898

H 2.063654278472 -0.288518259635 1.130535298016

H 0.585272844857 -0.945147177967 1.918053389865

H 0.849896207853 0.806234583579 1.882821450377

PBE0 ma-def2-TZVP

SCF_Energy: -228.3662141403986254

Number of atoms: 7

Coordinates:

C 0.988611827171 -0.122700806751 1.304306012550

C 0.192676175681 -0.029594353044 -0.024459442685

O 0.856680991158 -0.146723232321 -1.075609677487

O -1.035753528946 0.154534697375 0.110862666278

H 2.054220343554 -0.288467929532 1.128802804867

H 0.586314007893 -0.938631277399 1.913739829743

H 0.851130183490 0.800602901673 1.876927806735

Zero point energy ... 0.04808197 Eh 30.17 kcal/mol

Thermal vibrational correction ... 0.00073478 Eh 0.46 kcal/mol

Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol

Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol

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Total thermal correction 0.00356732 Eh 2.24 kcal/mol

Non-thermal (ZPE) correction 0.04808197 Eh 30.17 kcal/mol

Total correction 0.05164929 Eh 32.41 kcal/mol

MP2 cc-aug-pVTZ

MP2_Total_EN: -228.1604715480006575

C_2H_7N (Dimethylamine)

PBE0 ma-def2-SVP

SCF_Energy: -134.9044427030284794

Number of atoms: 10

Coordinates:

C -0.369180057937 1.274454355843 -0.153076083208

N -1.299126335305 0.199110268755 0.079134358583

C -2.685832797138 0.578231335904 -0.014040536024

H 0.664334302784 0.914621082867 -0.036370988570

H -0.506877452805 2.150051297372 0.519470173029

H -0.470909538220 1.640646838904 -1.188393703979

H -1.107592005630 -0.260261742564 0.964381398990

H -2.979946190258 1.406361360978 0.668621207202

H -3.331367496028 -0.286431245695 0.201582464941

H -2.915552429463 0.907126447636 -1.041318290963

PBE0 ma-def2-TZVP

SCF_Energy: -135.0476947423943841

Number of atoms: 10

Coordinates:

C -0.375986935654 1.272907310750 -0.154006687627

N -1.294148743371 0.179516430797 0.064104065345

C -2.679577671850 0.580711462536 -0.015371975415

H 0.652252110915 0.927909230035 -0.026655275932

H -0.538476713685 2.134374923744 0.516472893593

H -0.477137517715 1.634681378906 -1.181566855581

H -1.109891410177 -0.254314892357 0.958803878948

H -2.945426470826 1.409173065341 0.663763585245

H -3.327644284880 -0.268911088161 0.208920316275

H -2.906012362757 0.907862178409 -1.034473944852

Zero point energy ... 0.09246378 Eh 58.02 kcal/mol

Thermal vibrational correction ... 0.00158349 Eh 0.99 kcal/mol

Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol

Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol

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Total thermal correction 0.00441603 Eh 2.77 kcal/mol

Non-thermal (ZPE) correction 0.09246378 Eh 58.02 kcal/mol

Total correction 0.09687981 Eh 60.79 kcal/mol

MP2 cc-aug-pVTZ

MP2_Total_EN: -134.8809432155585171

$C_2H_8N^+$ (Protonated dimethylamine cation)

PBE0 ma-def2-SVP

SCF_Energy: -135.2691977030902706

Number of atoms: 11

Coordinates:

C -0.242543924240 1.451088851400 -0.107844110956

N -1.094829766873 0.292214923777 0.276870803464

C -2.552160244480 0.474514903560 0.030510376684

H 0.806520604355 1.216784905672 0.113283146748

H -0.560184873948 2.329717102959 0.466396466697

H -0.367143622507 1.641176365653 -1.180971969698

H -2.902939927784 1.339265377791 0.606925745448

H -3.087514572533 -0.429723795925 0.346168431633

H -2.710539690647 0.650450386596 -1.040513961720

H -0.945839038774 0.080698319711 1.271646957231

H -0.770754942570 -0.544457341195 -0.224521885531

PBE0 ma-def2-TZVP

SCF_Energy: -135.4143637791007961

Number of atoms: 11

Coordinates:

C -0.248114327439 1.450555279367 -0.108019852758

N -1.091273223369 0.284295589390 0.280248581580

C -2.547903509691 0.478056059091 0.029546823456

H 0.794358219236 1.223849574166 0.109336785105

H -0.572477196598 2.317461041233 0.463595707786

H -0.379850322289 1.633885794692 -1.172557890623

H -2.885937274096 1.339688316987 0.601722316866

H -3.084547112543 -0.416038965591 0.341925349777

H -2.695675390163 0.654194385344 -1.034015493858

H -0.945774950853 0.080023627044 1.270821433991

H -0.770734912195 -0.544240701721 -0.224653761320

Zero point energy ... 0.10817793 Eh 67.88 kcal/mol

Thermal vibrational correction ... 0.00165434 Eh 1.04 kcal/mol

Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol

Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol

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Total thermal correction 0.00448689 Eh 2.82 kcal/mol

Non-thermal (ZPE) correction 0.10817793 Eh 67.88 kcal/mol

Total correction 0.11266481 Eh 70.70 kcal/mol

MP2 cc-aug-pVTZ

MP2_Total_EN: -135.2466042784705849

C_3H_9N (Trimethylamine)

PBE0 ma-def2-SVP

SCF_Energy: -174.1360195315113231

Number of atoms: 13

Coordinates:

C 1.381853807262 -0.005204184295 -0.099214781851

N -0.015739650306 -0.201715893749 -0.385517632371

C -0.656853970333 -1.087090236807 0.551904194121

C -0.729298565758 1.036926736746 -0.558266786021

H 1.561497444262 0.505368902765 0.876385296350

H 1.903441979619 -0.974070142850 -0.071035782269

H -1.695498973584 -1.280737811165 0.242399562851

H -0.682602005892 -0.680070169680 1.590088839054

H -0.253467695342 1.642522519788 -1.345261761377

H -0.765281482536 1.654223367152 0.370065782588

H 1.849146259874 0.605425006474 -0.887235883417

H -0.130407999159 -2.053385953123 0.583738518088

H -1.766789148109 0.837807858742 -0.868059565745

PBE0 ma-def2-TZVP

SCF_Energy: -174.3197637121143089

Number of atoms: 13

Coordinates:

C 1.374216526770 -0.006656895949 -0.101525132771

N -0.017109816620 -0.218485469200 -0.417355024643

C -0.653423535150 -1.082686826198 0.546322012198

C -0.725435492416 1.030017945106 -0.557662228724

H 1.520909230025 0.502014276829 0.870556779167

H 1.897528211819 -0.964457693316 -0.062411629242

H -1.687713987727 -1.272978558699 0.250825764854

H -0.663928692761 -0.652740952245 1.565963173545

H -0.253536863429 1.641052893028 -1.330746217028

H -0.744956956574 1.619498439233 0.378640857627

H 1.843340540197 0.605513640064 -0.875219338644

H -0.131229332816 -2.040990912203 0.590196077738

H -1.758659831321 0.840900113548 -0.857595094079

Zero point energy ... 0.12022151 Eh 75.44 kcal/mol

Thermal vibrational correction ... 0.00263807 Eh 1.66 kcal/mol

Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol

Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol

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Total thermal correction 0.00547061 Eh 3.43 kcal/mol

Non-thermal (ZPE) correction 0.12022151 Eh 75.44 kcal/mol

Total correction 0.12569212 Eh 78.87 kcal/mol

MP2 cc-aug-pVTZ

MP2_Total_EN: -174.1005758447179232

$C_3H_{10}N^+$ (Protonated trimethylamine cation)

PBE0 ma-def2-SVP

SCF_Energy: -174.5066138898436350

Number of atoms: 14

Coordinates:

C 1.444603353975 -0.002423452709 -0.171949815016

N 0.009726985269 -0.217617025170 -0.510501686296

C -0.656934786156 -1.141955703503 0.448720412612

C -0.729573039247 1.068342729917 -0.649300871604

H 1.504550832140 0.485823855936 0.809275069936

H 1.957117055334 -0.971538776513 -0.138260915677

H -1.690185235805 -1.316120016155 0.124188785162

H -0.651752320012 -0.679246853703 1.443921576792

H -0.234398131594 1.689805168552 -1.405684450690

H -0.722598248322 1.583697779446 0.319569142746

H 1.904223803309 0.637732870881 -0.935128017656

H -0.109279395002 -2.091647204136 0.476146012344

H -1.762728369540 0.860308043537 -0.953708445837

H -0.013802504352 -0.674671416380 -1.430156796816

PBE0 ma-def2-TZVP

SCF_Energy: -174.6926561485580862

Number of atoms: 14

Coordinates:

C 1.440530235988 -0.002393040406 -0.171536547883

N 0.009530248011 -0.221836981186 -0.518873165585

C -0.655127550904 -1.138805971180 0.447246048672

C -0.727294645736 1.065450782165 -0.647478060721

H 1.487510676646 0.481858413437 0.802675596914

H 1.949380155374 -0.963770003835 -0.135279661949

H -1.681269874328 -1.309986746938 0.127053087826

H -0.644727486176 -0.669730116463 1.429862338776

H -0.235174144744 1.683490001760 -1.396365085090

H -0.713199039440 1.567752555909 0.318440729258

H 1.896385972469 0.635365812180 -0.926830131394

H -0.110081615415 -2.080121233639 0.477533816647

H -1.753632051078 0.859569315593 -0.945997303909

H -0.013860880670 -0.676352787398 -1.433321661560

Zero point energy ... 0.13614754 Eh 85.43 kcal/mol

Thermal vibrational correction ... 0.00277258 Eh 1.74 kcal/mol

Thermal rotational correction ... 0.00141627 Eh 0.89 kcal/mol

Thermal translational correction ... 0.00141627 Eh 0.89 kcal/mol

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Total thermal correction 0.00560512 Eh 3.52 kcal/mol

Non-thermal (ZPE) correction 0.13614754 Eh 85.43 kcal/mol

Total correction 0.14175266 Eh 88.95 kcal/mol

MP2 cc-aug-pVTZ

MP2_Total_EN: -174.4736384346398950

References

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