

Influence of anion and ether group on the polarity of ammonium and imidazolium ionic liquids

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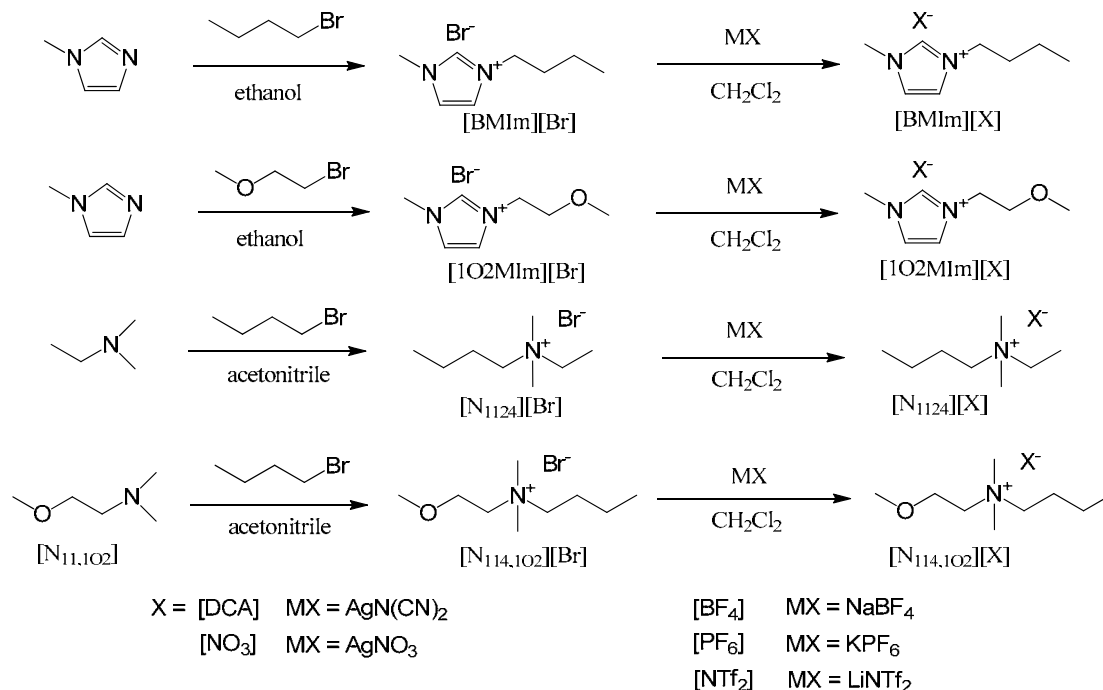
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General:

All chemicals were commercially available. *N*-methylimidazole, *N,N*-dimethylethylamine, 1-bromobutane, 2-bromoethyl methyl ether, 4-Nitroaniline and *N,N*-dimethyl-4-nitroaniline were from Alfa Aesar. 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino) phenolate (Reichardt's dye 30), 2,6-dichloro-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (Reichardt's dye 33) were from Aldrich. 6-nitro-BIPS was from Tokyo Chemical Industry.

¹H-NMR spectra were conducted on a Bruker AMX FT 400-MHz NMR spectrometer and chemical shifts were reported downfield in parts per million (ppm, δ) from a tetramethylsilane reference. Elemental analyses were performed with an Elementar Analysensysteme GmbH VarioEL using the software version V3.00. Water content in the ILs was determined by a coulometric Karl-Fisher analysis (Metrohm KF coulometer).

Synthesis:



Scheme S1 Synthetic procedures of ionic liquids used in this work

As shown in Scheme S1, all ILs were synthesized according to a typical two-step protocol.¹ Noting that in order to be convenient for AgNO₃ test, instead of alkyl chloride, alkyl bromide was used for synthesis of precursors. [N_{11,102}] was synthesized according to procedures described in the literature.²

[Cation][Br], [Cation] = [BMIm], [1O2MIm], [N₁₁₂₄], [N_{114,102}].

RBr: 1-bromobutane, 2-bromoethyl methyl ether.

Under vigorous stirring, 0.60 mol of 1-bromoethane or 2-bromoethyl methyl ether was added dropwise to a solution of 0.45 mol of either 1-methylimidazole, *N,N*-dimethylethylamine or [N_{11,102}] in 200 mL of ethanol. The mixture was heated under reflux for 2 h and then the solvent and excess reactant (RBr) was removed under reduced pressure, leaving a pale yellow solid. Recrystallization from ethyl acetate afforded a white solid, which was dried under reduced pressure at 80 °C for 4 h for further reaction.

[BMIm][Br].

White solid (92%). δ_{H} (DMSO-d₆, 400 MHz, ppm) 0.884-0.922 (t, 3H), 1.235-1.291 (m, 2H), 1.739-1.8136 (m, 2H), 3.882 (s, 3H), 4.185-4.220 (t, 2H), 7.777 (s, 1H), 7.847 (s, 1H), 9.293 (s, 1H).

[1O2MIm][Br].

White solid (95%). δ_{H} (DMSO-d₆, 400 MHz, ppm) 3.275 (s, 3H), 3.688-3.714 (t, 2H), 3.899 (s, 3H), 4.382-4.406 (t, 2H), 7.764 (s, 1H), 7.806 (s, 1H), 9.246 (s, 1H).

[N₁₁₂₄][Br].

White solid (93%). δ_{H} (acetone-d₆, 400 MHz, ppm) 0.975-1.012 (t, 3H), 1.385-1.453 (m, 5H), 1.781-1.852 (m, 2H), 3.386 (s, 3H), 3.679-3.721 (t, 2H), 3.747-3.802 (q, 2H).

[N_{114,102}][Br].

White solid (95%). δ_{H} (acetone-d₆, 400 MHz, ppm) 0.953-0.990(t, 3H), 1.366-1.422 (m, 2H), 1.798-1.877 (m, 2H), 3.400 (s, 3H), 3.453 (s, 6H), 3.758-3.801 (t, 2H), 3.945-3.980 (m, 4H).

[BMIm][X], [1O2MIm][X], [N₁₁₂₄][X], [N_{114,102}][X].

[X] = [NO₃], [DCA], [BF₄], [PF₆], [NTf₂].

Salts: AgNO₃, AgN(CN)₂, NaBF₄, KPF₆, LiNTf₂.

The respective metal salt (27.5 mmol), required to give the desired ionic liquid, was added to a solution of either [BMIm][Br], [1O2MIm][Br], [N₁₁₂₄][Br] or [N_{114,102}][Br] (25.0 mmol) in dichloromethane and stirred for 48 hours. The suspension was filtered to remove the precipitated bromide salt and the organic phase repeatedly washed with small volumes of water (ca. 30 mL) until no precipitation of a pale yellow precipitate occurred in the aqueous phase on addition of a concentrated AgNO₃ solution. Bromide content is evaluated from the above “AgNO₃ test”. AgBr has a solubility of 0.14 mg/L (20 °C) in water, hence all of the ILs synthesised will have bromide content below this value. The organic phase was then washed further two times with water to ensure complete removal of the bromide salt. The resulting organic phase stirred with activated charcoal for 12 hours, after which the suspension was filtered to remove the activated charcoal,

and the solvent was removed in vacuo, giving a colourless liquid, which was dried at ca. 80 °C in vacuo for ca. 4 h for further analysis.

[BMIm][DCA].

Colorless liquid (83%). δ_{H} (CDCl_3 , 400 MHz, ppm) 0.978-1.016 (t, 3H), 1.366-1.440 (m, 2H), 1.880-1.956 (m, 2H), 4.038 (s, 3H), 4.216-4.274 (t, 2H), 7.446 (s, 1H), 7.455 (s, 1H), 9.195 (s, 1H). Water content: 212 ppm. Elemental analysis (calc.): C, 58.3 (58.5); H, 7.2 (7.4); N, 34.1 (34.1).

[BMIm][NO₃].

Colorless liquid (85%). δ_{H} (acetone- d_6 , 400 MHz, ppm) 0.911-0.948 (t, 3H), 1.312-1.406 (m, 2H), 1.870-1.945 (m, 2H), 4.053 (s, 3H), 4.356-4.397 (t, 2H), 7.823 (s, 1H), 7.892 (s, 1H), 9.758 (s, 1H). Water content: 224 ppm. Elemental analysis (calc.): C, 47.9 (47.8); H, 7.5 (7.5); N, 20.8 (20.9).

[BMIm][BF₄].

Colorless liquid (82%). δ_{H} (acetone- d_6 , 400 MHz, ppm) 0.928-0.964 (t, 3H), 1.357-1.451 (m, 2H), 1.803-1.880 (m, 2H), 4.038 (s, 3H), 4.331-4.369 (t, 2H), 7.704 (s, 1H), 7.759 (s, 1H), 8.987 (s, 1H). Water content: 150 ppm. Elemental analysis (calc.): C, 42.4 (42.5); H, 6.7 (6.7); N, 12.3 (12.4).

[BMIm][PF₆].

Colorless liquid (78%). δ_{H} (acetone- d_6 , 400 MHz, ppm) 0.929-0.966 (t, 3H), 1.358-1.415 (m, 2H), 1.892-1.966 (m, 2H), 4.050 (s, 3H), 4.339-4.376 (t, 2H), 7.693 (s, 1H), 7.748 (s, 1H), 8.956 (s, 1H). Water content: 123 ppm. Elemental analysis (calc.): C, 33.9 (33.8); H, 5.3 (5.3); N, 9.7 (9.9).

[BMIm][NTf₂].

Colorless liquid (81%). δ_{H} (CDCl_3 , 400 MHz, ppm) 0.930-0.967 (t, 3H), 1.360-1.417 (m, 2H), 1.899-1.973 (m, 2H), 4.075 (s, 3H), 4.362-4.398 (t, 2H), 7.730 (s, 1H), 7.786 (s, 1H), 9.046 (s, 1H). Water content: 97 ppm. Elemental analysis (calc.): C, 28.5 (28.6); H, 3.5 (3.6); N, 9.8 (10.0).

[1O2MIm][DCA].

Colorless liquid (80%). δ_{H} (CDCl_3 , 400 MHz, ppm) 3.408 (s, 3H), 3.713-3.789 (t, 2H), 4.039 (s, 3H), 4.424-4.448 (t, 2H), 7.430 (s, 1H), 7.520 (s, 1H), 9.032 (s, 1H). Water content: 196 ppm. Elemental analysis (calc.): C, 52.0 (52.2); H, 6.2 (6.3); N, 33.7 (33.8).

[1O2MIm][NO₃].

Colorless liquid (81%). δ_{H} (acetone- d_6 , 400 MHz, ppm) 3.327 (s, 3H), 3.790-3.814 (t, 2H), 4.056 (s, 3H), 4.529-4.553 (t, 2H), 7.794 (s, 1H), 7.824 (s, 1H), 9.529 (s, 1H). Water content: 167 ppm. Elemental analysis (calc.): C, 41.2 (41.4); H, 6.5 (6.5); N, 20.6 (20.7).

[1O2MIm][BF₄].

Colorless liquid (73%). δ_{H} (acetone- d_6 , 400 MHz, ppm) 3.341 (s, 3 H), 3.802 (t, 2H), 4.048 (s, 3H), 4.511 (t, 2H), 7.682 (s, 1 H), 7.709 (s, 1H), 8.950 (s, 1H). Water content: 150 ppm. Elemental

analysis (calc.): C, 36.3 (36.9); H, 6.0 (5.8); N, 12.1 (12.3).

[1O2MIm][PF₆].

Colorless liquid (78%). δ_{H} (acetone-d₆, 400 MHz, ppm) 3.348 (s, 3 H), 3.793-3.817 (t, 2H), 4.060 (s, 3H), 4.506-4.529 (t, 2H), 7.677 (s, 1 H), 7.714 (s, 1H), 8.981 (s, 1H). Water content: 98 ppm. Elemental analysis (calc.): C, 29.3 (29.4); H, 4.6 (4.6); N, 9.8 (9.8).

[1O2MIm][NTf₂].

Colorless liquid (85%). δ_{H} (CDCl₃, 400 MHz, ppm) 3.357 (s, 3H), 3.684 -3.708 (t, 2H), 3.931 (s, 3H), 4.301-4.360 (t, 2H), 7.368 (s, 1H), 7.420 (s, 1H), 8.663 (s, 1H). Water content: 65 ppm. Elemental analysis (calc.): C, 25.5 (25.7); H, 3.1 (3.1); N, 9.8 (10.0).

[N₁₁₂₄][DCA].

Colorless liquid (80%). δ_{H} (CDCl₃, 400 MHz, ppm) 1.201-1.057 (t, 3H), 1.442-1.517 (m, 2H), 1.720-1.800 (m, 2H) 3.159 (s, 6H), 3.329-3.371 (t, 2H), 3.463-3.516 (q, 2H). Water content: 233 ppm. Elemental analysis (calc.): C, 61.0 (61.2); H, 10.4 (10.3); N, 28.4 (28.5).

[N₁₁₂₄][NTf₂].

Colorless liquid (82%). δ_{H} (CDCl₃, 400 MHz, ppm) 0.986-1.023 (t, 3H), 1.351-1.431 (m, 2H), 1.658-1.696 (m, 2H), 3.063 (s, 6H), 3.214-3.257 (t, 2H), 3.374-3.410 (q, 2H). Water content: 103 ppm. Elemental analysis (calc.): C, 29.2 (29.3); H, 4.8 (4.9); N, 6.8 (6.8).

[N_{114,102}][DCA].

Colorless liquid (79%). δ_{H} (CDCl₃, 400 MHz, ppm) 1.010-1.047 (t, 3H), 1.410-1.502 (m, 2H), 1.742-1.822 (m, 2H), 3.230 (s, 6H), 3.421 (s, 3H), 3.421-3.462 (t, 2H), 3.616-3.640 (t, 2H), 3.845-3.861 (t, 2H). Water content: 203 ppm. Elemental analysis (calc.): C, 58.6 (58.4); H, 9.7 (9.8); N, 24.6 (24.8).

[N_{114,102}][NO₃].

Colorless liquid (81%). δ_{H} (acetone-d₆, 400 MHz, ppm) 0.955-0.992 (t, 3H), 1.352-1.445 (m, 2H), 1.812-1.892 (m, 2H), 3.322 (s, 6H), 3.385 (s, 3H), 3.577-3.619 (t, 2H), 3.786-3.809 (t, 2H), 3.916 (t, 2H). Water content: 186 ppm. Elemental analysis (calc.): C, 48.4 (48.6); H, 10.1 (10.0); N, 12.4(12.6).

[N_{114,102}][BF₄].

Colorless liquid (74%). δ_{H} (acetone-d₆, 400 MHz, ppm) 0.959-0.995 (t, 3H), 1.358-1.455 (m, 2H), 1.822-1.907 (m, 2H), 3.310 (s, 6H), 3.386 (s, 3H), 3.540-3.583 (t, 2H), 3.741-3.764 (t, 2H), 3.910-3.925 (t, 2H). Water content: 147 ppm. Elemental analysis (calc.): C, 43.9 (43.8); H, 8.8 (9.0); N, 5.7 (5.7).

[N_{114,102}][PF₆].

Colorless liquid (70%). δ_{H} (acetone-d₆, 400 MHz, ppm) 0.961-0.998 (t, 3H), 1.367-1.459 (m, 2H), 1.831-1.912 (m, 2H), 3.293 (s, 6H), 3.389 (s, 3H), 3.521-3.564 (t, 2H), 3.715-3.738 (t, 2H), 3.921-3.931 (t, 2H). Water content: 124 ppm. Elemental analysis (calc.): C, 35.5 (35.4); H, 7.0

(7.3); N, 4.5 (4.6).

[N_{114,102}][NTf₂].

Colorless liquid (80%). δ_{H} (CDCl₃, 400 MHz, ppm) 0.960-0.997 (t, 3H), 1.342-1.435 (m, 2H), 1.672-1.752 (m, 2H), 3.109 (s, 6H), 3.295-3.339 (t, 2H), 3.369 (s, 3H), 3.491-3.495 (t, 2H), 3.761-3.766 (t, 2H). Water content: 103 ppm. Elemental analysis (calc.): C, 30.2 (30.0); H, 4.9 (5.0); N, 6.4(6.4).

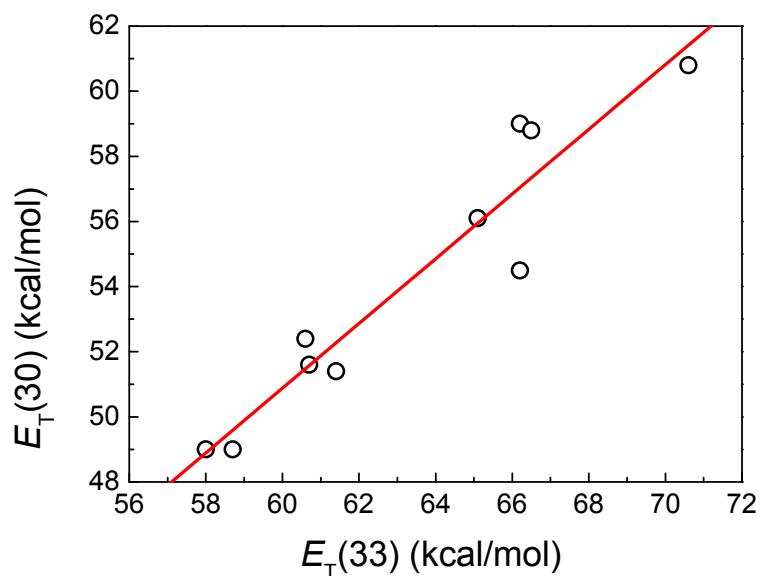


Figure S1: Plot of the $E_T(30)$ Scales vs $E_T(33)$ Scales of ILs listed in Table S1. The result of linear correlation analysis is the following: $E_T(30) = 0.99382 (\pm 0.1109) \times E_T(33) - 8.74797 (\pm 7.04428)$ ($r = 0.95363$, $s = 1.36007$, $n=10$).

Atom Coordinates Calculated at the B3LYP/6-31+G(d,p) level of theory; Gaussian standard orientation.

[BMIm][DCA]

N	-0.06328600	-1.34270800	-0.50708200
C	-1.16575900	-0.68129000	-0.13137400
N	-2.13258600	-1.56938400	0.13866900
C	-1.63198500	-2.84121300	-0.06986300
C	-0.33543100	-2.69850400	-0.47161200
H	-1.29651800	0.39065600	-0.04883100
H	-2.23278500	-3.72433500	0.07800900
H	0.40513500	-3.43596400	-0.73650600
C	-3.49550000	-1.22322700	0.57504900
H	-4.21209000	-1.60543800	-0.15507200
H	-3.68223100	-1.67376900	1.55215900

H	-3.56567200	-0.13377100	0.64053900
C	1.24100900	-0.72665300	-0.85054500
H	1.05842200	0.32431000	-1.09333800
H	1.60167600	-1.23748700	-1.74859100
C	2.25108500	-0.82702000	0.29605000
H	2.41108600	-1.87940700	0.57083000
N	-0.99099500	3.53349500	-0.01864100
C	0.15451300	2.99948100	-0.38128100
C	-1.95856100	2.69934700	0.25691900
N	-2.84760500	1.96206400	0.50953900
N	1.19560500	2.55333800	-0.71005700
H	1.83380000	-0.32144700	1.17580300
C	3.58598000	-0.16986800	-0.08378000
C	4.61017100	-0.22405300	1.05497000
H	3.39310700	0.87142700	-0.36455000
H	3.99858300	-0.67025400	-0.97132600
H	5.55307600	0.24446000	0.75545900
H	4.24335900	0.30850100	1.93970600
H	4.82999500	-1.25711900	1.35151900

[BMIm][NTf₂]

N	-2.34373500	2.06508500	-0.40522600
C	-1.12550300	2.09212800	0.15464800
N	-0.96414300	3.27985200	0.75783900
C	-2.11302800	4.02917300	0.57984600
C	-2.97840700	3.26613400	-0.14753200
H	-0.38984300	1.28286300	0.11844700
H	-2.21116700	5.02765200	0.97507400
H	-3.97450700	3.47539000	-0.50322900
C	0.23821400	3.71113100	1.48637200
H	0.63930000	4.61124800	1.01582600
H	-0.02754200	3.92017000	2.52478800
H	0.97821200	2.91034200	1.44784200
C	-2.92479500	0.91474500	-1.13457700
C	-3.94809700	0.15042500	-0.29167700
H	-2.09397600	0.26243600	-1.41034300
H	-3.37618200	1.31418900	-2.04810400
H	-3.45799100	-0.21044900	0.62052200
H	-4.76053400	0.82168200	0.01946900
F	3.36764300	-0.26201500	-1.93349500
C	3.32776700	0.68784900	-0.99524600
F	2.69017100	1.76399600	-1.50188600
F	4.58004700	1.04850000	-0.68248800
S	2.44104000	0.07733600	0.55814400

N	0.93968900	-0.25168400	0.01440500
O	2.31763200	1.29860300	1.37497200
O	3.23147700	-1.04814200	1.04689000
S	0.44498000	-1.70617200	-0.52984700
O	-0.76379800	-1.45249300	-1.33376200
O	1.47528000	-2.61317600	-1.02631200
C	-0.24312600	-2.52648200	1.02823500
F	-0.76467100	-3.72092900	0.71503500
F	0.70722700	-2.69292700	1.95130600
F	-1.22504500	-1.76417400	1.55984400
C	-4.52963900	-1.04325700	-1.06754300
C	-5.54750300	-1.83624300	-0.24451600
H	-3.70698800	-1.69868900	-1.37481400
H	-5.00328800	-0.67972100	-1.98938200
H	-5.94459100	-2.67939900	-0.81773600
H	-5.09196600	-2.24176500	0.66536400
H	-6.39630600	-1.21136000	0.05720000

[N₁₁₂₄][DCA]

C	1.54080900	1.24233100	-0.03508700
C	2.25633400	-0.08944700	0.19773100
H	1.84606500	1.97492600	0.71871200
H	1.79262200	1.64930900	-1.01907300
C	3.74344300	0.03112400	-0.17811900
H	2.17751300	-0.37634900	1.25188300
H	1.79509900	-0.90198400	-0.37302200
C	4.52609100	-1.25095500	0.12702700
H	3.82947800	0.26642000	-1.24769000
H	4.19709400	0.87468400	0.36150000
H	5.57602000	-1.14731700	-0.16481500
H	4.49730100	-1.48719500	1.19649800
H	4.10708200	-2.10670700	-0.41245300
C	-0.47406400	2.65467200	0.05536300
H	0.09424500	3.18484200	-0.71462900
H	-0.15559700	3.03442500	1.02995900
C	-0.45560200	0.47088300	1.24215600
H	-0.00674100	0.94885100	2.11495000
H	-1.54349400	0.51158500	1.28439100
H	-0.14460200	-0.57028200	1.16476400
C	-0.51766100	0.52190000	-1.22833800
H	-0.10585800	-0.48565300	-1.27756500
H	-1.60256500	0.45653100	-1.15117500
H	-0.22173400	1.11316800	-2.09709600
N	0.01318400	1.20623000	0.00905300

C	-3.12829400	-1.35654800	0.10811400
N	-3.61792800	-0.28780500	0.22354400
N	-2.60609500	-2.55292100	-0.01887300
C	-1.30157700	-2.63033500	-0.12783300
N	-0.12840700	-2.71766000	-0.23527200
C	-1.97198200	2.85885000	-0.14717000
H	-2.19688500	3.90125800	0.09951800
H	-2.27578700	2.69212400	-1.18274300
H	-2.58952100	2.21761400	0.48584500

[N₁₁₂₄][NTf₂]

C	-3.52937600	1.54297300	-0.04001900
C	-3.70002100	0.02533800	-0.11335300
H	-3.86673000	2.01202100	-0.96937500
H	-4.12734500	1.95271600	0.77984700
C	-5.12741700	-0.32824600	-0.56765800
H	-2.97802400	-0.42459500	-0.80223500
H	-3.51817400	-0.42283100	0.86908500
C	-5.37077100	-1.84131700	-0.59558500
H	-5.85804600	0.14854000	0.10071900
H	-5.30383600	0.08928500	-1.56812100
H	-6.38669300	-2.06704700	-0.93437800
H	-4.67029300	-2.34154600	-1.27247300
H	-5.24407400	-2.28198800	0.39939900
C	-2.20832500	3.55782100	0.44562500
H	-2.77158200	3.65525200	1.37755000
H	-2.82287000	3.96062600	-0.36454900
C	-1.27834500	1.80595800	-1.05467700
H	-1.71507800	2.38158100	-1.87350900
H	-0.25414200	2.11409700	-0.86542100
H	-1.27122800	0.74156000	-1.28087700
C	-1.48836200	1.37188800	1.37798000
H	-1.38560500	0.31237900	1.16483400
H	-0.48957200	1.76777300	1.55258900
H	-2.13944000	1.54091100	2.23809500
N	-2.10626800	2.05622900	0.18304400
C	-0.88491700	4.30957100	0.53593500
H	-1.11372900	5.34080700	0.82221500
H	-0.21016100	3.89925300	1.29030300
H	-0.35733400	4.34412100	-0.41930000
S	0.64895500	-1.64960900	-0.72357200
N	0.87944900	-0.23558600	0.03255500
O	-0.60281700	-1.48510100	-1.48890800
O	1.81108900	-2.27737100	-1.34880200

C	0.13561900	-2.82398800	0.66728800
S	2.24580500	0.30462500	0.71898000
F	-0.20840700	-4.01114800	0.14867100
F	1.11961900	-3.00241100	1.55088100
F	-0.93905100	-2.32569100	1.32433100
O	1.83810200	1.43441000	1.57495800
O	3.18233200	-0.69762300	1.22330400
C	3.15123300	1.16363800	-0.70159000
F	3.49190300	0.30202700	-1.66233600
F	2.35998000	2.11763700	-1.24817600
F	4.25706500	1.75913800	-0.23428300

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