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

An accurate cost effective DFT approach to study sensor behaviour of polypyrrole for nitrate ion in gas and aqueous phase

Fatima Wasim, Tariq Mahmood, Khurshid Ayub,*

Department of Chemistry, COMSATS Institute of Information Technology, Abbottabad

Supporting Information

Table S1. Optimized Geometric parameters of nPy and nPy-NO_3^- in gas phase and solvent phase at B3LYP/6-31G(d)

nPy	N_4---H_5(Å)	O_9--H_5 (Å)	$C_3N_4C_6$	$N_4H_5O_9$	$C_2C_3N_4C_6$	$N_4C_6C_7N_8$	$N_1C_2C_3N_4$
1Py (gas phase)	1.00	------	109.81	------	------	------	------
1Py-NO_3^-	1.04	1.77	109.34	174.74	------	------	------
1Py (solvent phase)	1.00		109.93	------	------	------	------
1Py-NO_3^-	1.02	1.86	109.44	174.16	------	------	------
3Py(gas phase)	1.00	------	110.82	------	-179.78	-155.23	-155.22
3Py-NO_3^-	1.04	1.75	109.97	167.41	-179.49	170.53	162.86
3Py (solvent phase)	1.00	------	110.76	------	179.62	164.90	-164.90
3Py-NO_3^-	1.02	1.86	110.08	169.43	179.63	168.71	162.75
5Py (gas phase)	1.00	------	110.64	------	179.35	157.65	-157.65
5Py-NO_3^-	1.04	1.74	109.94	167.00	179.89	170.57	167.77
5Py (solvent phase)	1.00	------	110.63	------	179.79	163.81	163.80
5Py-NO_3^-	1.02	1.85	110.07	169.052	179.41	165.22	170.98
7Py (gas phase)	1.00	------	110.66	------	-179.44	-157.13	159.71
7Py-NO_3^-	1.04	1.73	109.90	166.92	179.86	170.57	167.58
7Py (solvent phase)	1.00	------	110.65	------	-179.89	-164.03	168.41
7Py-NO_3^-	1.02	1.85	110.06	169.19	179.94	171.55	165.11
9Py (gas phase)	1.00	------	110.63	------	179.29	157.12	-157.22
9Py-NO_3^-	1.04	1.73	109.90	167.54	-179.89	171.85	167.17
9Py (solvent phase)	1.00	------	110.61	------	179.92	163.87	-163.74
9Py-NO_3^-	1.02	1.85	110.06	169.37	179.63	169.083	166.16

Table S2. Intermolecular bond distance *(dO_9-H_5)* with different level of theories

Species	B3LYP/6-31G(d)	M05-2x/6-31G(d)	B3LYP-DCP/631G(d) & 6-31+G(2d,2p)	B3LYP-D3/6-31G(d)	B3LYP-CP/6-31G(d)
1Py- NO_3^-	1.77 Å	1.82 Å	1.80 Å	1.76 Å	1.79 Å
3Py- NO_3^-	1.75 Å	1.76 Å	1.77 Å	1.72 Å	1.80 Å
5Py- NO_3^-	1.74 Å	1.73 Å	1.76 Å	1.71 Å	1.80 Å
7Py- NO_3^-	1.73 Å	1.72 Å	1.75 Å	1.70 Å	1.78 Å
9Py- NO_3^-	1.73 Å	1.72 Å	1.75 Å	1.69 Å	1.78 Å

Mullikan and NBO charge analysis

Transfer of charge is mostly related with the interaction of two or more than two species. Interaction of species causes the electronic properties to change due to transfer of charge [42]. Charge transfer gives the information about the conductivity, resistivity and selectivity of species toward each other [57]. For conducting polymers, charge transfer defines the sensing abilities of polymer towards analyte. The amount of charge transfer between PPy and nitrate ions are simulated in gas phase and in aqueous medium. Charge analysis for pyrrole, nitrate and pyrrole nitrate complex are given in Tables. 5 and Table 6.

In case of NBO charge analysis, the charge on isolated pyrrole monomer in the gas phase is -0.001 e^- while charge on nitrate ion is -0.999 e^- which can be expected for a neutral pyrrole and anionic nitrate species. However, in 1Py-NO_3^- complex, nitrate ion transfers approximately about -0.082 e^- charge to pyrrole monomer based on NBO. Furthermore, in case of Mulliken charge analysis, the monomer contains about 0.00 e^- charge and nitrate have -1.00 e^- charge, after the formation of complex, NO_3^- ion transfers -0.132 e^- charge to the pyrrole ring. The amount of NBO charge transfer is a bit lower than the Mulliken charge transfer.

The amount of charge transfer increases with increase in the chain length which is indicative of stronger sensing response of oligopyrrole with nitrate ion. This observation is consistent with the inferences obtained from the interaction energy analysis. The amount of Mulliken charge transfer from nitrate to 3Py in 3Py-NO3 complex is -0.194 e^- which further increases to -0.198 e^-, -0.202 e^- and -0.204 e^- for 5Py- NO_3^-, 7Py- NO_3^- and 9Py- NO_3^-, respectively. The charge transferred from the nitrate ion to oligopyrrole is not all restricted to the ring interacting with the nitrate ion, rather it is dispersed to the neighboring pyrrole ring. For example, for 3Py, the net charge transferred is -0.194 e^- (vide supra) but the pyrrole ring interacting with nitrate ion accepts only -0.047 e^- charge. The spread of charge to the neighboring rings in 3Py and high oligomers indicates an increase in conjugation in oligomer backbone upon adsorption. This increases in conjugation is also supported by the geometric parameters (vide supra). A similar trend in charge transfer is also obtained with NBO charge analysis. The NBO charge transferred from nitrate ion to 3Py in 3Py-NO_3^- is -0.108 e^- which further increases to -0.111 e^- in 5Py-NO_3^-. The charge transfer to 7Py and 9Py from nitrate ion in their complexes is -0.113 e^- and -0.115 e^- respectively. These results show that with increasing the number of repeating units increase the amount of charge transfer is also increased. Transfer of charge from nitrate ion to nPy is referred as the doping process of polymer and these results also illustrate the sensing ability of PPy toward nitrate ion.

The amount of charge transferred from nitrate ion to the pyrrole and higher oligomer in aqueous medium is relatively less pronounced, compared to gas phase. Net Mulliken charges on nitrate ion and pyrrole monomer are -1.001 e^-, and 0.004 e^-, respectively. After complexation of nitrate ion with pyrrole, the nitrate ion transfers about -0.109 e^- charge to pyrrole monomer. Based on NBO, nitrate is having -1.001 e^- charge and total charge on pyrrole monomer is -0.001 e^- while upon interaction nitrate transfer -0.064 e^- charge to monomer. In both cases (Mulliken and NBO), approximately -0.002 e^- charge is dispersed in environment which contain water ions. In case of 3Py- NO_3^-nitrate transfer about -0.146 e- charge (based on Mulliken) to 3Py, out of which only -0.044 e- charge is transfer to central pyrrole ring that is in

direct contact with nitrate ion while rest of charge is dispersed on other rings and environment. Based on NBO nitrate loses about -0.081 e- charge in case of 3Py- NO_3^-. In case of 5Py- NO_3^-, -0.152 e- charge is transferred to 5Py (based on Mulliken), and -0.08 e- charge based on NBO. In 7Py- NO_3^- and 9Py- NO_3^-, based on Mulliken 7Py oligomers gain about -0.152 e- charge from analyte and 9Py takes -0.149 e- charge from nitrate ion. However, nitrate ion transfer -0.081 and -0.08 e- charge to 7Py and 9Py oligomers, respectively. For infinite polymer total charge transfer is about -0.15 e- based on Mulliken, and -0.079 e- charge based on NBO.

Table.5 Mulliken charge Analysis and NBO of Py and nPy-NO_3^- in gas phase

Complex	Species	Py isolated	NO_3^-	PPy in complex	Nitrate in complex	Amount of charge transfer
			Mullikan			
Py-NO_3^-	1Py	0.00	-1.00	-0.132	-0.868	-0.132
3Py-NO_3^-	3Py	0.014	-1.00	-0.047	-0.806	-0.194
5Py-NO_3^-	5Py	0.001	-1.00	-0.043	-0.802	-0.198
7Py-NO_3^-	7Py	0.001	-1.00	-0.038	-0.798	-0.202
9Py-NO_3^-	9Py	-0.002	-1.00	-0.034	-0.796	-0.204
∞Py-NO_3^-	∞	-0.015	-1.00	-0.036	-0.793	-0.206
			NBO			
Py-NO_3^-	1Py	-0.001	-0.999	-0.083	-0.917	-0.082
3Py-NO_3^-	3Py	-0.01	-0.999	-0.057	-0.891	-0.108
5Py-NO_3^-	5Py	-0.002	-0.999	-0.034	-0.888	-0.111
7Py-NO_3^-	7Py	-0.002	-0.999	-0.028	-0.886	-0.113
9Py-NO_3^-	9Py	-0.002	-0.999	-0.024	-0.884	-0.115
∞Py-NO_3^-	∞	0.006	-0.999	0	-0.882	-0.12

Table. 6 Mulliken charge analysis and NBO of nPy-NO_3^- in solvent phase

Complex	Species	Py isolated	NO_3^-	PPy in complex	Nitrate in complex	Amount of charge transfer
			Mullikan			
Py-NO_3^-	1Py	0.004	-1.001	-0.107	-0.892	-0.109
3Py-NO_3^-	3Py	0.016	-1.001	-0.044	-0.855	-0.146
5Py-NO_3^-	5Py	-0.003	-1.001	-0.059	-0.849	-0.152
7Py-NO_3^-	7Py	0	-1.001	-0.057	-0.849	-0.152
9Py-NO_3^-	9Py	-0.003	-1.001	-0.056	-0.852	-0.149
∞Py-NO_3^-	∞	-0.017	-1.001	-0.078	-0.850	-0.15
			NBO			
Py-NO_3^-	1Py	-0.001	-1.001	-0.062	-0.937	-0.064
3Py-NO_3^-	3Py	-0.009	-1.001	-0.05	-0.92	-0.081
5Py-NO_3^-	5Py	-0.006	-1.001	-0.039	-0.921	-0.08
7Py-NO_3^-	7Py	-0.002	-1.001	-0.037	-0.92	-0.081
9Py-NO_3^-	9Py	0	-1.001	-0.034	-0.921	-0.08
∞Py-NO_3^-	∞	0.006	-1.001	-0.023	-0.922	-0.079

Coordinates of optimized structures in gas phase

Specie 1a: Pyrrole monomer

C	-1.01685347	-2.96495692	0.00010400
C	0.38489653	-2.96495692	0.00010400
C	0.80889453	-1.59416092	0.00010400
C	-0.34816247	-0.80270792	0.00000000
N	-1.45658047	-1.64444892	0.00009500
H	-2.39690847	-1.35374792	-0.00012200
H	-1.71844147	-3.79818992	0.00020200
H	1.02926953	-3.83766292	0.00012900
H	1.83345753	-1.23766892	0.00007900
H	-0.45708447	0.28106408	-0.00014700

Specie 1b. Nitrate ion (NO_3^-):

N	0.00000000	0.00001500	0.00000000
O	-0.17618000	-1.22636500	0.00000000
O	-0.97395300	0.76569200	0.00000000
O	1.15013300	0.46065900	0.00000000

Specie 1c. Pyrrole- NO_3^- complex:

C	-1.58938332	1.16244576	0.56891769
C	-2.97061114	1.06168852	0.57500241
C	-3.28597198	-0.32654549	0.64342514
C	-2.08184370	-1.00991434	0.67599276
N	-1.06460448	-0.09672609	0.63023160
H	-0.92532163	2.01308229	0.52678297
H	-3.67104741	1.88766483	0.53493119
H	-4.27366807	-0.77238599	0.66594195
H	-1.87039818	-2.06956603	0.72763741
H	-0.04647410	-0.31011157	0.64061003

O	1.36824404	-0.05381980	0.17910475
O	1.30463139	1.91605612	0.16235869
N	2.21818300	0.94819272	0.44211553
O	3.38236606	1.34546621	1.02215999

Specie 2a: 3Py oligomers

C	0.06631866	-2.65547917	0.00010400
C	1.46806866	-2.65547917	0.00010400
C	1.89206666	-1.28468317	0.00010400
C	0.73500966	-0.49323017	0.00000000
N	-0.37340834	-1.33497117	0.00009500
H	-1.31373634	-1.04427017	-0.00012200
H	2.11244166	-3.52818517	0.00012900
H	2.91662966	-0.92819117	0.00007900
C	-0.92558264	-3.83349945	0.00024255
C	-2.32743093	-3.83385426	0.00023975
N	-0.48561145	-5.15393260	0.00042389
C	-2.75104620	-5.20476854	0.00059015
H	-2.97203757	-2.96133025	0.00010768
C	-1.59387010	-5.99587317	0.00069125
H	0.45471316	-5.44464458	0.00064089
H	-3.77551903	-5.56154261	0.00072228
H	-1.48494455	-7.07968042	0.00083826
C	0.58101132	1.03905064	-0.00020783
C	-0.57604568	1.83050364	-0.00031183
N	1.68942932	1.88079163	-0.00034860
C	-0.15204768	3.20129959	-0.00068719
H	-1.60060868	1.47401165	-0.00023353
C	1.24970232	3.20129959	-0.00069591

H	2.62975732	1.59009058	-0.00049240
H	-0.79642068	4.07400556	-0.00089547
H	1.95129032	4.03453258	-0.00082883

Specie 2b: 3Py-NO_3^- complex

C	-1.35937472	-2.43954709	-0.00596232
C	0.04237528	-2.43954709	-0.00596232
C	0.46637328	-1.06875109	-0.00596232
C	-0.69068372	-0.27729809	-0.00606632
N	-1.79910172	-1.11903909	-0.00597132
H	-2.73942972	-0.82833809	-0.00618832
H	0.68674828	-3.31225309	-0.00593732
H	1.49093628	-0.71225909	-0.00598732
C	-2.35127602	-3.61756737	-0.00582377
C	-3.75312431	-3.61792219	-0.00582657
N	-1.91130483	-4.93800052	-0.00564244
C	-4.17673957	-4.98883647	-0.00547617
H	-4.39773094	-2.74539817	-0.00595865
C	-3.01956347	-5.77994109	-0.00537507
H	-0.97098022	-5.22871250	-0.00542544
H	-5.20121240	-5.34561053	-0.00534404
H	-2.91063793	-6.86374834	-0.00522806
C	-0.84468206	1.25498272	-0.00627416
C	-2.00173906	2.04643572	-0.00637816
N	0.26373594	2.09672371	-0.00641492
C	-1.57774106	3.41723167	-0.00675351
H	-3.02630206	1.68994372	-0.00629985
C	-0.17599106	3.41723166	-0.00676223
H	1.20406394	1.80602266	-0.00655873

H	-2.22211406	4.28993764	-0.00696179
H	0.52559694	4.25046466	-0.00689515
N	-5.80578443	0.00752585	0.47011165
O	-4.48176751	-0.19249223	0.23226306
O	-6.28546633	-0.05559265	1.74114326
O	-6.65011310	0.27066144	-0.56307214

Specie 3a: 5Py oligomers

C	0.06631866	-2.65547917	0.00010400
C	1.46806866	-2.65547917	0.00010400
C	1.89206666	-1.28468317	0.00010400
C	0.73500966	-0.49323017	0.00000000
N	-0.37340834	-1.33497117	0.00009500
H	-1.31373634	-1.04427017	-0.00012200
H	2.11244166	-3.52818517	0.00012900
H	2.91662966	-0.92819117	0.00007900
C	-0.92558264	-3.83349945	0.00024255
C	-2.32743093	-3.83385426	0.00023975
N	-0.48561145	-5.15393260	0.00042389
C	-2.75104620	-5.20476854	0.00059015
H	-2.97203757	-2.96133025	0.00010768
C	-1.59387010	-5.99587317	0.00069125
H	0.45471316	-5.44464458	0.00064089
H	-3.77551903	-5.56154261	0.00072228
C	0.58101132	1.03905064	-0.00020783
C	-0.57604568	1.83050364	-0.00031183
N	1.68942932	1.88079163	-0.00034860
C	-0.15204768	3.20129959	-0.00068719
H	-1.60060868	1.47401165	-0.00023353

C	1.24970232	3.20129959	-0.00069591
H	2.62975732	1.59009058	-0.00049240
H	-0.79642068	4.07400556	-0.00089547
C	2.24160362	4.37931987	-0.00088383
C	3.64345192	4.37967467	-0.00089261
N	1.80163244	5.69975302	-0.00106194
C	4.06706719	5.75058899	-0.00091908
H	4.28805855	3.50715065	-0.00078865
C	2.90989109	6.54169362	-0.00102957
H	0.86130783	5.99046505	-0.00092054
H	5.09154002	6.10736308	-0.00088885
H	2.80096555	7.62550087	-0.00117865
C	-1.43987175	-7.52815397	0.00089909
C	-0.28281475	-8.31960697	0.00100309
N	-2.54828975	-8.36989497	0.00099409
C	-0.70681275	-9.69040297	0.00100309
H	0.74174825	-7.96311497	0.00097809
C	-2.10856275	-9.69040297	0.00100309
H	-3.48861775	-8.07919397	0.00077709
H	-0.06243975	-10.56310897	0.00102809
H	-2.81015075	-10.52363597	0.00110109

Specie 3b: 5Py-NO_3^- complex

C	-0.73674172	-2.52368492	0.12044386
C	0.66500828	-2.52368492	0.12044386
C	1.08900628	-1.15288892	0.12044386
C	-0.06805072	-0.36143592	0.12033986
N	-1.17646872	-1.20317692	0.12043486
H	-2.11679672	-0.91247592	0.12021786

H	1.30938128	-3.39639092	0.12046886
H	2.11356928	-0.79639692	0.12041886
C	-0.22204906	1.17084488	0.12013202
C	-1.37910606	1.96229788	0.12002802
N	0.88636894	2.01258588	0.11999126
C	-0.95510806	3.33309383	0.11965267
H	-2.40366906	1.60580589	0.12010633
C	0.44664194	3.33309383	0.11964395
H	1.82669694	1.72188483	0.11984745
H	-1.59948106	4.20579981	0.11944439
C	-1.72864302	-3.70170521	0.12058241
C	-3.13049131	-3.70206002	0.12057961
N	-1.28867183	-5.02213836	0.12076374
C	-3.55410658	-5.07297430	0.12093001
H	-3.77509795	-2.82953600	0.12044753
C	-2.39693048	-5.86407892	0.12103111
H	-0.34834722	-5.31285034	0.12098075
H	-4.57857941	-5.42974836	0.12106214
C	-2.24293214	-7.39635973	0.12123895
C	-1.08587514	-8.18781273	0.12134295
N	-3.35135014	-8.23810073	0.12133395
C	-1.50987314	-9.55860873	0.12134295
H	-0.06131214	-7.83132073	0.12131795
C	-2.91162314	-9.55860873	0.12134295
H	-4.29167814	-7.94739973	0.12111695
H	-0.86550014	-10.43131473	0.12136795
H	-3.61321114	-10.39184173	0.12144095
C	1.43854324	4.51111411	0.11945603

C	2.84039153	4.51146892	0.11944726
N	0.99857205	5.83154726	0.11927792
C	3.26400680	5.88238324	0.11942079
H	3.48499816	3.63894490	0.11955121
C	2.10683069	6.67348786	0.11931029
H	0.05824744	6.12225929	0.11941932
H	4.28847963	6.23915733	0.11945101
H	1.99790515	7.75729512	0.11916121
N	-5.05906276	-0.26440994	0.54306942
O	-5.94268149	-1.28616196	0.38545996
O	-3.77905393	-0.39845074	0.10351231
O	-5.45545530	0.89138543	1.14023777

Specie 4a. 7Py oligomers:

C	0.06631866	-2.65547917	0.00010400
C	1.46806866	-2.65547917	0.00010400
C	1.89206666	-1.28468317	0.00010400
C	0.73500966	-0.49323017	0.00000000
N	-0.37340834	-1.33497117	0.00009500
H	-1.31373634	-1.04427017	-0.00012200
H	2.11244166	-3.52818517	0.00012900
H	2.91662966	-0.92819117	0.00007900
C	-0.92558264	-3.83349945	0.00024255
C	-2.32743093	-3.83385426	0.00023975
N	-0.48561145	-5.15393260	0.00042389
C	-2.75104620	-5.20476854	0.00059015
H	-2.97203757	-2.96133025	0.00010768
C	-1.59387010	-5.99587317	0.00069125
H	0.45471316	-5.44464458	0.00064089

H	-3.77551903	-5.56154261	0.00072228
C	0.58101132	1.03905064	-0.00020783
C	-0.57604568	1.83050364	-0.00031183
N	1.68942932	1.88079163	-0.00034860
C	-0.15204768	3.20129959	-0.00068719
H	-1.60060868	1.47401165	-0.00023353
C	1.24970232	3.20129959	-0.00069591
H	2.62975732	1.59009058	-0.00049240
H	-0.79642068	4.07400556	-0.00089547
C	2.24160362	4.37931987	-0.00088383
C	3.64345192	4.37967467	-0.00089261
N	1.80163244	5.69975302	-0.00106194
C	4.06706719	5.75058899	-0.00091908
H	4.28805855	3.50715065	-0.00078865
C	2.90989109	6.54169362	-0.00102957
H	0.86130783	5.99046505	-0.00092054
H	5.09154002	6.10736308	-0.00088885
C	-1.43987175	-7.52815397	0.00089909
C	-0.28281475	-8.31960697	0.00100309
N	-2.54828975	-8.36989497	0.00099409
C	-0.70681275	-9.69040297	0.00100309
H	0.74174825	-7.96311497	0.00097809
C	-2.10856275	-9.69040297	0.00100309
H	-3.48861775	-8.07919397	0.00077709
H	-0.06243975	-10.56310897	0.00102809
C	2.75589275	8.07397443	-0.00124034
C	1.59883425	8.86542522	-0.00135088
N	3.86430915	8.91571753	-0.00137717

C	2.02282964	10.23622198	-0.00172626
H	0.57427193	8.50893128	-0.00127682
C	3.42457964	10.23622465	-0.00172846
H	4.80463770	8.62501827	-0.00151618
H	1.37845498	11.10892673	-0.00193881
H	4.12616605	11.06945898	-0.00185933
C	-3.10046405	-10.86842326	0.00114164
C	-4.50231234	-10.86877807	0.00113884
N	-2.66049286	-12.18885640	0.00132298
C	-4.92592761	-12.23969235	0.00148924
H	-5.14691898	-9.99625405	0.00100677
C	-3.76875151	-13.03079697	0.00159034
H	-1.72016825	-12.47956838	0.00153998
H	-5.95040044	-12.59646641	0.00162137
H	-3.65982596	-14.11460422	0.00173735

Specie 4b: 7Py-NO_3^- complex

C	-0.73674172	-2.52368492	0.12044386
C	0.66500828	-2.52368492	0.12044386
C	1.08900628	-1.15288892	0.12044386
C	-0.06805072	-0.36143592	0.12033986
N	-1.17646872	-1.20317692	0.12043486
H	-2.11679672	-0.91247592	0.12021786
H	1.30938128	-3.39639092	0.12046886
H	2.11356928	-0.79639692	0.12041886
C	-0.22204906	1.17084488	0.12013202
C	-1.37910606	1.96229788	0.12002802
N	0.88636894	2.01258588	0.11999126
C	-0.95510806	3.33309383	0.11965267

H	-2.40366906	1.60580589	0.12010633
C	0.44664194	3.33309383	0.11964395
H	1.82669694	1.72188483	0.11984745
H	-1.59948106	4.20579981	0.11944439
C	-1.72864302	-3.70170521	0.12058241
C	-3.13049131	-3.70206002	0.12057961
N	-1.28867183	-5.02213836	0.12076374
C	-3.55410658	-5.07297430	0.12093001
H	-3.77509795	-2.82953600	0.12044753
C	-2.39693048	-5.86407892	0.12103111
H	-0.34834722	-5.31285034	0.12098075
H	-4.57857941	-5.42974836	0.12106214
C	-2.24293214	-7.39635973	0.12123895
C	-1.08587514	-8.18781273	0.12134295
N	-3.35135014	-8.23810073	0.12133395
C	-1.50987314	-9.55860873	0.12134295
H	-0.06131214	-7.83132073	0.12131795
C	-2.91162314	-9.55860873	0.12134295
H	-4.29167814	-7.94739973	0.12111695
H	-0.86550014	-10.43131473	0.12136795
C	1.43854324	4.51111411	0.11945603
C	2.84039153	4.51146892	0.11944726
N	0.99857205	5.83154726	0.11927792
C	3.26400680	5.88238324	0.11942079
H	3.48499816	3.63894490	0.11955121
C	2.10683069	6.67348786	0.11931029
H	0.05824744	6.12225929	0.11941932
H	4.28847963	6.23915733	0.11945101

N	-5.05906276	-0.26440994	0.54306942
O	-5.94268149	-1.28616196	0.38545996
O	-3.77905393	-0.39845074	0.10351231
O	-5.45545530	0.89138543	1.14023777
C	-3.90352444	-10.73662902	0.12148150
C	-5.30537273	-10.73698383	0.12147870
N	-3.46355325	-12.05706216	0.12166284
C	-5.72898800	-12.10789811	0.12182910
H	-5.94997937	-9.86445981	0.12134663
C	-4.57181190	-12.89900273	0.12193020
H	-2.52322864	-12.34777414	0.12187984
H	-6.75346083	-12.46467217	0.12196123
H	-4.46288635	-13.98280998	0.12207721
C	1.95283235	8.20576867	0.11909952
C	0.79577385	8.99721946	0.11898897
N	3.06124875	9.04751177	0.11896270
C	1.21976924	10.36801622	0.11861359
H	-0.22878847	8.64072552	0.11906302
C	2.62151924	10.36801889	0.11861141
H	4.00157731	8.75681251	0.11882370
H	0.57539458	11.24072097	0.11840104
H	3.32310566	11.20125321	0.11848054

Specie 5a. 9Py oligomers

C	0.06631866	-2.65547917	0.00010400
C	1.46806866	-2.65547917	0.00010400
C	1.89206666	-1.28468317	0.00010400
C	0.73500966	-0.49323017	0.00000000
N	-0.37340834	-1.33497117	0.00009500

H	-1.31373634	-1.04427017	-0.00012200
H	2.11244166	-3.52818517	0.00012900
H	2.91662966	-0.92819117	0.00007900
C	-0.92558264	-3.83349945	0.00024255
C	-2.32743093	-3.83385426	0.00023975
N	-0.48561145	-5.15393260	0.00042389
C	-2.75104620	-5.20476854	0.00059015
H	-2.97203757	-2.96133025	0.00010768
C	-1.59387010	-5.99587317	0.00069125
H	0.45471316	-5.44464458	0.00064089
H	-3.77551903	-5.56154261	0.00072228
C	0.58101132	1.03905064	-0.00020783
C	-0.57604568	1.83050364	-0.00031183
N	1.68942932	1.88079163	-0.00034860
C	-0.15204768	3.20129959	-0.00068719
H	-1.60060868	1.47401165	-0.00023353
C	1.24970232	3.20129959	-0.00069591
H	2.62975732	1.59009058	-0.00049240
H	-0.79642068	4.07400556	-0.00089547
C	2.24160362	4.37931987	-0.00088383
C	3.64345192	4.37967467	-0.00089261
N	1.80163244	5.69975302	-0.00106194
C	4.06706719	5.75058899	-0.00091908
H	4.28805855	3.50715065	-0.00078865
C	2.90989109	6.54169362	-0.00102957
H	0.86130783	5.99046505	-0.00092054
H	5.09154002	6.10736308	-0.00088885
C	-1.43987175	-7.52815397	0.00089909

C	-0.28281475	-8.31960697	0.00100309
N	-2.54828975	-8.36989497	0.00099409
C	-0.70681275	-9.69040297	0.00100309
H	0.74174825	-7.96311497	0.00097809
C	-2.10856275	-9.69040297	0.00100309
H	-3.48861775	-8.07919397	0.00077709
H	-0.06243975	-10.56310897	0.00102809
C	2.75589275	8.07397443	-0.00124034
C	1.59883425	8.86542522	-0.00135088
N	3.86430915	8.91571753	-0.00137717
C	2.02282964	10.23622198	-0.00172626
H	0.57427193	8.50893128	-0.00127682
C	3.42457964	10.23622465	-0.00172846
H	4.80463770	8.62501827	-0.00151618
H	1.37845498	11.10892673	-0.00193881
C	-3.10046405	-10.86842326	0.00114164
C	-4.50231234	-10.86877807	0.00113884
N	-2.66049286	-12.18885640	0.00132298
C	-4.92592761	-12.23969235	0.00148924
H	-5.14691898	-9.99625405	0.00100677
C	-3.76875151	-13.03079697	0.00159034
H	-1.72016825	-12.47956838	0.00153998
H	-5.95040044	-12.59646641	0.00162137
C	4.41647869	11.41424682	-0.00191348
C	5.81832699	11.41460430	-0.00191574
N	3.97650499	12.73467913	-0.00209556
C	6.24193964	12.78551943	-0.00194223
H	6.46293528	10.54208151	-0.00180751

C	5.08476203	13.57662185	-0.00205927
H	3.03617983	13.02538937	-0.00195895
H	7.26641179	13.14229547	-0.00190777
H	4.97583442	14.66042890	-0.00221043
C	-3.61475316	-14.56307777	0.00179818
C	-2.45769616	-15.35453077	0.00190218
N	-4.72317116	-15.40481877	0.00189318
C	-2.88169416	-16.72532677	0.00190218
H	-1.43313316	-14.99803877	0.00187718
C	-4.28344416	-16.72532677	0.00190218
H	-5.66349916	-15.11411777	0.00167618
H	-2.23732116	-17.59803277	0.00192718
H	-4.98503216	-17.55855977	0.00200018

Specie 5b. 9Py-NO_3^- complex

C	-0.73674172	-2.52368492	0.12044386
C	0.66500828	-2.52368492	0.12044386
C	1.08900628	-1.15288892	0.12044386
C	-0.06805072	-0.36143592	0.12033986
N	-1.17646872	-1.20317692	0.12043486
H	-2.11679672	-0.91247592	0.12021786
H	1.30938128	-3.39639092	0.12046886
H	2.11356928	-0.79639692	0.12041886
C	-0.22204906	1.17084488	0.12013202
C	-1.37910606	1.96229788	0.12002802
N	0.88636894	2.01258588	0.11999126
C	-0.95510806	3.33309383	0.11965267
H	-2.40366906	1.60580589	0.12010633
C	0.44664194	3.33309383	0.11964395

H	1.82669694	1.72188483	0.11984745
H	-1.59948106	4.20579981	0.11944439
C	-1.72864302	-3.70170521	0.12058241
C	-3.13049131	-3.70206002	0.12057961
N	-1.28867183	-5.02213836	0.12076374
C	-3.55410658	-5.07297430	0.12093001
H	-3.77509795	-2.82953600	0.12044753
C	-2.39693048	-5.86407892	0.12103111
H	-0.34834722	-5.31285034	0.12098075
H	-4.57857941	-5.42974836	0.12106214
C	-2.24293214	-7.39635973	0.12123895
C	-1.08587514	-8.18781273	0.12134295
N	-3.35135014	-8.23810073	0.12133395
C	-1.50987314	-9.55860873	0.12134295
H	-0.06131214	-7.83132073	0.12131795
C	-2.91162314	-9.55860873	0.12134295
H	-4.29167814	-7.94739973	0.12111695
H	-0.86550014	-10.43131473	0.12136795
C	1.43854324	4.51111411	0.11945603
C	2.84039153	4.51146892	0.11944726
N	0.99857205	5.83154726	0.11927792
C	3.26400680	5.88238324	0.11942079
H	3.48499816	3.63894490	0.11955121
C	2.10683069	6.67348786	0.11931029
H	0.05824744	6.12225929	0.11941932
H	4.28847963	6.23915733	0.11945101
N	-5.05906276	-0.26440994	0.54306942
O	-5.94268149	-1.28616196	0.38545996

O	-3.77905393	-0.39845074	0.10351231
O	-5.45545530	0.89138543	1.14023777
C	-3.90352444	-10.73662902	0.12148150
C	-5.30537273	-10.73698383	0.12147870
N	-3.46355325	-12.05706216	0.12166284
C	-5.72898800	-12.10789811	0.12182910
H	-5.94997937	-9.86445981	0.12134663
C	-4.57181190	-12.89900273	0.12193020
H	-2.52322864	-12.34777414	0.12187984
H	-6.75346083	-12.46467217	0.12196123
C	1.95283235	8.20576867	0.11909952
C	0.79577385	8.99721946	0.11898897
N	3.06124875	9.04751177	0.11896270
C	1.21976924	10.36801622	0.11861359
H	-0.22878847	8.64072552	0.11906302
C	2.62151924	10.36801889	0.11861141
H	4.00157731	8.75681251	0.11882370
H	0.57539458	11.24072097	0.11840104
C	-4.41781355	-14.43128353	0.12213804
C	-3.26075655	-15.22273653	0.12224204
N	-5.52623155	-15.27302453	0.12223304
C	-3.68475455	-16.59353253	0.12224204
H	-2.23619355	-14.86624453	0.12221704
C	-5.08650455	-16.59353253	0.12224204
H	-6.46655955	-14.98232353	0.12201604
H	-3.04038155	-17.46623853	0.12226704
H	-5.78809255	-17.42676553	0.12234004
C	3.61341831	11.54604105	0.11842639

C	5.01526660	11.54639851	0.11842415
N	3.17344462	12.86647336	0.11824429
C	5.43887927	12.91731364	0.11839765
H	5.65987489	10.67387571	0.11853240
C	4.28170167	13.70841607	0.11828059
H	2.23311946	13.15718361	0.11838088
H	6.46335143	13.27408966	0.11843212
H	4.17277408	14.79222312	0.11812941

Co-ordinates of optimized structures in solvent phase

Specie 6a. 1Py

C	0.33151100	-1.12552700	-0.00002700
C	-0.98349600	-0.71273000	-0.00012500
C	-0.98345300	0.71279000	0.00008300
C	0.33157900	1.12550800	0.00000800
N	1.12233300	-0.00003400	0.00004300
H	2.13032900	-0.00006800	0.00019600
H	0.76769700	-2.11414400	-0.00006900
H	-1.84956300	-1.36087500	-0.00023700
H	-1.84947800	1.36099000	0.00014200
H	0.76783700	2.11409400	0.00003300

Specie 6b. Nitrate ion

N	0.00000000	0.00007300	0.00000000
O	-0.76257300	1.00852400	0.00000000
O	1.25468200	0.15589300	0.00000000
O	-0.49210900	-1.16448000	0.00000000

Specie 6c. 1Py-NO_3^- complex

C	-1.48734100	1.00151200	-0.00011400
C	-2.87023800	0.92654300	0.00024900
C	-3.21164300	-0.45720800	0.00016500

C	-2.02056400	-1.16382800	-0.00021700
N	-0.98631300	-0.26874300	-0.00049800
H	-0.80739900	1.84056200	-0.00000300
H	-3.55504000	1.76648100	0.00043800
H	-4.20758200	-0.88492000	0.00028000
H	-1.82898200	-2.22849600	-0.00062200
H	0.02756900	-0.50143900	-0.00005900
O	1.71497700	-1.05577000	0.00054200
O	1.84848000	1.13175500	-0.00002300
N	2.42216700	0.01075100	0.00008800
O	3.66893900	-0.07953000	-0.00022600

Specie 7a. 3Py oligomers

C	1.13523100	-0.51542000	0.02796000
C	0.70843900	-1.83824100	0.01934300
C	-0.70847300	-1.83822000	-0.01935000
C	-1.13522500	-0.51538200	-0.02804200
N	0.00001600	0.26755600	0.00007100
H	0.00004600	1.27642800	-0.00042700
H	1.35016400	-2.70814400	0.06942800
H	-1.35023400	-2.70810200	-0.06932700
C	2.46009400	0.06641100	0.06526600
C	2.91722500	1.29676600	0.52044800
N	3.56336000	-0.62064500	-0.40077200
C	4.32274500	1.34346700	0.31228100
H	2.31125700	2.05801700	0.99434300
C	4.69544100	0.14639600	-0.26108600
H	3.51401800	-1.51253100	-0.86889700
H	4.98716800	2.15777200	0.56761800
H	5.66095600	-0.22171500	-0.57618100
C	-2.46008500	0.06643400	-0.06532300

C	-2.91725500	1.29680600	-0.52042000
N	-3.56332300	-0.62069100	0.40068500
C	-4.32277700	1.34345300	-0.31221500
H	-2.31136900	2.05806100	-0.99441900
C	-4.69542200	0.14636600	0.26113100
H	-3.51383300	-1.51227400	0.86937300
H	-4.98721800	2.15776000	-0.56750200
H	-5.66093500	-0.22182800	0.57613400

Specie 7b. 3Py-NO_3^- complex

C	-1.14508600	-1.34156300	0.05648700
C	-0.73937700	-2.66703800	0.21261400
C	0.67464800	-2.68129100	0.19737300
C	1.10619600	-1.36378400	0.03861300
N	-0.01321300	-0.56940200	-0.04402400
H	-0.00345600	0.46028100	-0.20520800
H	-1.39207400	-3.51976700	0.35744800
H	1.30856200	-3.55675400	0.27692200
C	-2.48106400	-0.78344800	-0.00730000
C	-2.96108300	0.50832200	0.15961900
N	-3.57454000	-1.59710700	-0.25579200
C	-4.37389300	0.46070600	-0.00574300
H	-2.34971700	1.37348100	0.39454100
C	-4.72914900	-0.84620500	-0.26871800
H	-3.50115700	-2.56559700	-0.52372200
H	-5.05594100	1.29808700	0.07061100
H	-5.69034000	-1.30461800	-0.45650500
C	2.45529500	-0.83738700	-0.03826800
C	2.95736100	0.41295300	-0.37706800
N	3.54394000	-1.64622200	0.24394300
C	4.37544100	0.34432100	-0.28515700

H	2.35170700	1.26655100	-0.65780200
C	4.71465400	-0.93425500	0.10530500
H	3.46937800	-2.58658700	0.59715100
H	5.06996000	1.14968100	-0.48751000
H	5.67385000	-1.39700700	0.29212300
N	0.04164200	3.05877300	0.07514900
O	0.26202200	2.10254500	-0.75456200
O	-0.81086300	2.90148400	0.98461600
O	0.67518900	4.12496700	-0.04499400

Specie 8a. 5Py oligomers

C	1.13555600	-0.09023300	-0.56313600
C	0.70843800	-1.35636700	-0.94740400
C	-0.70845200	-1.35635900	-0.94737400
C	-1.13555600	-0.09020700	-0.56313500
N	0.00001500	0.66430700	-0.34421700
H	0.00005300	1.57366500	0.09263700
H	1.35064600	-2.17172700	-1.25338200
H	-1.35065700	-2.17176200	-1.25324800
C	2.45780500	0.46304900	-0.38836300
C	2.91899500	1.77437700	-0.40638200
N	3.55537900	-0.34221200	-0.15611000
C	4.31678800	1.74700700	-0.17223200
H	2.32158800	2.64927300	-0.62693300
C	4.69696700	0.41988300	-0.01200400
H	3.50164900	-1.32584800	0.06191100
H	4.98576000	2.59759700	-0.18157600
C	-2.45778500	0.46308400	-0.38828600
C	-2.91898400	1.77442300	-0.40623800
N	-3.55535500	-0.34216300	-0.15598400
C	-4.31676200	1.74703400	-0.17208400

H	-2.32160000	2.64936000	-0.62668900
C	-4.69694700	0.41990300	-0.01187300
H	-3.50162200	-1.32588400	0.06164300
H	-4.98566200	2.59768300	-0.18127500
C	-5.98283000	-0.18703000	0.25437300
C	-6.47579000	-1.45856400	-0.01187400
N	-6.99726200	0.51099300	0.87893900
C	-7.81088800	-1.51786600	0.47205900
H	-5.94640000	-2.24037000	-0.54060000
C	-8.10689400	-0.28793600	1.02028600
H	-6.89100500	1.43886000	1.25946100
H	-8.48311300	-2.36299200	0.41197500
H	-9.00479800	0.08321900	1.49253100
C	5.98283100	-0.18705600	0.25435100
C	6.47568800	-1.45871400	-0.01150400
N	6.99734300	0.51113100	0.87860900
C	7.81079600	-1.51793900	0.47242200
H	5.94622000	-2.24055200	-0.54010500
C	8.10690700	-0.28785000	1.02022300
H	6.89098400	1.43901500	1.25906500
H	8.48298200	-2.36311600	0.41260200
H	9.00483800	0.08335800	1.49237500

Specie 8b. 5Py-NO_3^- complex

C	-1.13563200	-0.73543100	0.04377900
C	-0.71682500	-2.06218400	0.16435100
C	0.69222800	-2.07065300	0.07836900
C	1.11096000	-0.74877900	-0.08989700
N	-0.01330900	0.04235800	-0.10555700
H	-0.01508100	1.07149600	-0.26904900
H	-1.35604200	-2.92272100	0.32158300

H	1.33280000	-2.94350600	0.11497300
C	2.44898300	-0.21577000	-0.22669500
C	2.92062800	1.04936900	-0.56562400
N	3.55650300	-1.01793500	-0.01267100
C	4.33523600	0.99717300	-0.53589600
H	2.29380900	1.89804200	-0.81450000
C	4.71985100	-0.29097300	-0.17959400
H	3.51930000	-1.93501900	0.40418200
H	5.00721500	1.80566100	-0.79713400
C	-2.46843000	-0.17536100	0.06722800
C	-2.91874200	1.13499100	0.20279400
N	-3.58638100	-0.98254600	-0.03279200
C	-4.33340800	1.09793300	0.18593300
H	-2.28330500	2.00759900	0.31739700
C	-4.73899600	-0.22592200	0.04235700
H	-3.56403600	-1.98715000	-0.10942300
H	-4.99207100	1.95661300	0.23573600
C	-6.05377200	-0.82136100	-0.02755200
C	-6.50675300	-2.03678300	-0.53070000
N	-7.16294600	-0.16391000	0.46722000
C	-7.91358600	-2.10047200	-0.32264100
H	-5.89571500	-2.77477500	-1.03396900
C	-8.29470800	-0.93032000	0.29768000
H	-7.11161300	0.71230000	0.96339500
H	-8.57340600	-2.90882200	-0.61012300
H	-9.26218400	-0.57761100	0.62500900
C	6.02466200	-0.88047600	0.01489000
C	6.47295700	-2.19674700	-0.02601200
N	7.12504100	-0.09912900	0.30771400
C	7.86849400	-2.19272200	0.25500800

H	5.86701700	-3.05703100	-0.27868600
C	8.24696900	-0.88332900	0.45971000
H	7.06833600	0.89226000	0.48316100
H	8.52362500	-3.05362900	0.28830200
H	9.20672200	-0.44558700	0.69383700
N	0.07309500	3.67545800	-0.01302500
O	-0.82196200	3.60208100	0.86502000
O	0.22709200	2.70025700	-0.83721600
O	0.81110700	4.67375100	-0.10978600

Specie 9a. 7Py oligomers

C	-1.13115500	0.27151300	-0.69452300
C	-0.74082900	1.55470400	-1.06205600
C	0.67134600	1.56518300	-1.17551900
C	1.13281400	0.28794500	-0.87727300
N	0.02158000	-0.48255200	-0.59783200
H	0.06198200	-1.40760400	-0.19729000
H	-1.40675900	2.37905000	-1.28184100
H	1.28346400	2.39609300	-1.50056200
C	-2.43236800	-0.29879500	-0.43770200
C	-2.87862800	-1.61656000	-0.44292400
N	-3.52280600	0.48762300	-0.12679600
C	-4.25860600	-1.61019900	-0.12684500
H	-2.27811400	-2.48480800	-0.68032800
C	-4.64707400	-0.28840600	0.06660000
H	-3.50211700	1.49337800	-0.05367900
H	-4.89686700	-2.47715600	-0.01862000
C	2.46601800	-0.26429400	-0.83355000
C	2.92655700	-1.57080400	-0.95338400
N	3.57690600	0.53484000	-0.64790500
C	4.33743600	-1.54830800	-0.82687300

H	2.31477400	-2.43651700	-1.17057500
C	4.72762300	-0.22818400	-0.63061600
H	3.53718900	1.50510100	-0.37431700
H	5.00495100	-2.39371200	-0.92935200
C	6.02878500	0.36721000	-0.43689400
C	6.49104800	1.66207300	-0.64243900
N	7.10006300	-0.36884400	0.02979800
C	7.86193500	1.69653000	-0.28370500
H	5.91705000	2.47627000	-1.06498100
C	8.22481900	0.42331300	0.13914100
H	7.02637600	-1.30066000	0.40961300
H	8.52979600	2.54232100	-0.38196600
C	-5.92257800	0.29381000	0.41270200
C	-6.25463900	1.51540000	0.98733100
N	-7.10893800	-0.37808400	0.19309600
C	-7.66631400	1.57280300	1.10286600
H	-5.55230400	2.25873300	1.34161000
C	-8.18431800	0.38659500	0.59714900
H	-7.19086100	-1.22172800	-0.35422800
H	-8.24094100	2.36645300	1.56221000
C	9.48097700	-0.10987100	0.61925900
C	9.99359300	-1.40128000	0.62173200
N	10.43667200	0.69953900	1.20051100
C	11.28018100	-1.35765600	1.22421900
H	9.51207600	-2.26954800	0.19134800
C	11.52803500	-0.04753300	1.57515000
H	10.29817000	1.67743300	1.40447500
H	11.95380100	-2.19098800	1.37091800
H	12.38073100	0.41193100	2.05347100
C	-9.54376500	-0.08849500	0.45954500

C	-10.06931800	-1.37284900	0.39033400
N	-10.61029900	0.78399200	0.37208500
C	-11.47930500	-1.25909500	0.25188800
H	-9.50177400	-2.28990700	0.47942900
C	-11.78652100	0.08492800	0.24066300
H	-10.51458400	1.78620400	0.31310500
H	-12.18956200	-2.07177500	0.18251700
H	-12.73322500	0.59776300	0.15269900

Specie 9b. 7Py-NO_3^- complex

C	-1.13183500	-0.69156600	-0.23132700
C	-0.72285600	-2.02445900	-0.14221700
C	0.68519000	-2.04121600	-0.22913700
C	1.11340500	-0.71820600	-0.36673400
N	-0.00448300	0.08135600	-0.36322700
H	0.00182600	1.11507600	-0.50460900
H	-1.36822000	-2.88357200	-0.00375100
H	1.31933500	-2.91932400	-0.21330300
C	2.45540800	-0.19376400	-0.49118400
C	2.93851900	1.07595600	-0.79992600
N	3.55482200	-1.01039100	-0.29657100
C	4.35114200	1.01171200	-0.76970200
H	2.31866600	1.93530900	-1.02900100
C	4.72520300	-0.28889600	-0.44444000
H	3.50773300	-1.93582500	0.10026300
H	5.02993900	1.82119900	-1.00838400
C	-2.46055000	-0.12412500	-0.19317000
C	-2.90275700	1.18575900	-0.02027500
N	-3.58244500	-0.92099500	-0.31518300
C	-4.31607500	1.15840600	-0.03592200
H	-2.26066900	2.04988300	0.11970900

C	-4.73097400	-0.15913600	-0.21776500
H	-3.56436400	-1.92220100	-0.42804300
H	-4.96903800	2.01892900	0.04384200
C	-6.04545400	-0.74340300	-0.30701900
C	-6.48961300	-1.96944700	-0.79792300
N	-7.16378100	-0.07544600	0.15027800
C	-7.89486400	-2.02957800	-0.61755300
H	-5.87229500	-2.71329200	-1.28430500
C	-8.30135800	-0.84322600	-0.01996300
H	-7.12517700	0.77389200	0.69317100
H	-8.55141200	-2.82506000	-0.94750700
C	6.02051500	-0.89576200	-0.26826700
C	6.43727700	-2.22476900	-0.29617300
N	7.14358000	-0.13633600	-0.00776700
C	7.83145600	-2.25061000	-0.03766200
H	5.81077500	-3.07357300	-0.53661800
C	8.25757300	-0.94118800	0.14626100
H	7.11296800	0.84517200	0.22373100
H	8.47098600	-3.12447600	-0.04890900
N	0.11175300	3.69280300	-0.17817300
O	-0.77674600	3.59113400	0.70359300
O	0.25840800	2.74367400	-1.03472900
O	0.85021900	4.69204200	-0.24846000
C	-9.60695900	-0.37638200	0.39034300
C	-10.12534200	0.90107700	0.56686300
N	-10.62318900	-1.26161600	0.69360300
C	-11.47701800	0.76884500	0.99126700
H	-9.59902900	1.82465500	0.36523500
C	-11.75946200	-0.57808400	1.06453600
H	-10.49504200	-2.26052300	0.74089700

H	-12.16823000	1.57348300	1.20461100
H	-12.66146600	-1.10397100	1.34248700
C	9.56193000	-0.39142400	0.44168400
C	10.11863700	0.86046000	0.20769100
N	10.53247900	-1.14486900	1.07311800
C	11.44619700	0.85029900	0.71944700
H	9.63428800	1.67439900	-0.31539300
C	11.67647500	-0.39980600	1.25190400
H	10.36610400	-2.06670700	1.44597700
H	12.15664300	1.66573600	0.68726700
H	12.54661600	-0.82035400	1.73502800

Specie 10a. 9Py oligomers

C	1.14022900	1.88400400	-0.53213200
C	0.71165800	1.90874200	-1.85480200
C	-0.70496300	1.90420600	-1.85341500
C	-1.13078900	1.87667700	-0.52992300
N	0.00550200	1.87473000	0.25473000
H	0.00704800	1.69961000	1.24830300
H	1.35278800	1.98492500	-2.72311900
H	-1.34823900	1.97618600	-2.72050300
C	2.46319400	1.86912200	0.04563000
C	2.92709100	2.25079800	1.29968700
N	3.55861700	1.42003500	-0.66529100
C	4.32346700	2.01489000	1.33736800
H	2.33152800	2.70770500	2.07901700
C	4.70166900	1.49075800	0.10600900
H	3.50024900	0.93587600	-1.54848900
H	4.99417600	2.25728900	2.15119800
C	-2.45247300	1.85307300	0.05046500
C	-2.91592600	2.22959500	1.30625500

N	-3.54671900	1.39888800	-0.65899400
C	-4.31077600	1.98514800	1.34654600
H	-2.32144600	2.68857800	2.08519500
C	-4.68843800	1.46115300	0.11503000
H	-3.48737300	0.91601400	-1.54284200
H	-4.98124200	2.22187100	2.16223500
C	-5.97049600	1.02857300	-0.38852800
C	-6.45692900	0.89741100	-1.68434200
N	-6.99087700	0.64888600	0.46093600
C	-7.78896200	0.42143400	-1.60273700
H	-5.92822800	1.17474600	-2.58676200
C	-8.10548300	0.26475700	-0.25788000
H	-6.87340500	0.49090100	1.45040900
H	-8.46554200	0.26634800	-2.43299400
C	5.98516600	1.06511600	-0.39955300
C	6.46732000	0.92807200	-1.69652500
N	7.01229000	0.70025000	0.44837200
C	7.80348500	0.46364100	-1.61734000
H	5.93228600	1.19397700	-2.59868400
C	8.12697200	0.32067600	-0.27258500
H	6.90199200	0.55144300	1.44008000
H	8.47973700	0.30832000	-2.44762100
C	-9.30908100	-0.18940600	0.39875400
C	-9.79135100	0.02049800	1.68633800
N	-10.24065400	-0.97368700	-0.25042600
C	-11.03073900	-0.65554500	1.80215400
H	-9.31382200	0.62294900	2.44781500
C	-11.29814300	-1.26974500	0.58368300
H	-10.16256900	-1.28637300	-1.20632200
H	-11.64780200	-0.71853700	2.68885300

C	9.33708700	-0.11973200	0.38073400
C	9.83061900	0.11080000	1.65971900
N	10.26104100	-0.91728600	-0.26534500
C	11.06842000	-0.56974700	1.77725800
H	9.37675200	0.75200000	2.40388900
C	11.31940500	-1.21119900	0.57011600
H	10.09845700	-1.37029400	-1.15207400
H	11.73625200	-0.54450800	2.62840600
C	-12.40716300	-2.08793700	0.14259400
C	-12.50429300	-3.05283000	-0.85246000
N	-13.65116400	-2.00052000	0.73522300
C	-13.83836700	-3.54331600	-0.85487300
H	-11.69024500	-3.39972600	-1.47570300
C	-14.52646600	-2.87350700	0.13434600
H	-13.89459000	-1.31654500	1.43521000
H	-14.24362200	-4.31096000	-1.49999700
H	-15.55411200	-2.94502100	0.45964300
C	12.41778500	-2.04604000	0.13497700
C	12.91971600	-2.32547200	-1.13017800
N	13.19362100	-2.74831400	1.03569400
C	14.01436700	-3.21894400	-0.97642700
H	12.56555500	-1.89314900	-2.05682900
C	14.16019000	-3.46585200	0.37219600
H	13.00405900	-2.79592900	2.02505700
H	14.63386200	-3.62384600	-1.76510300
H	14.86388100	-4.08396500	0.91047100

Specie 10b. 9Py-NO_3^- complex

C	-1.12632500	-0.26940900	-0.62227100
C	-0.72353100	-1.59848300	-0.77557100
C	0.68301900	-1.60407000	-0.88070100

C	1.11687900	-0.27886600	-0.78698000
N	0.00348100	0.51098000	-0.62848300
H	0.01364600	1.55312700	-0.57981300
H	-1.37164800	-2.46650200	-0.78256900
H	1.31228600	-2.47392900	-1.02528900
C	2.45949300	0.25541000	-0.83683100
C	2.94428700	1.56027600	-0.90495600
N	3.55702300	-0.58588700	-0.82950600
C	4.35613700	1.48789300	-0.92092700
H	2.32532500	2.44937400	-0.94864500
C	4.72876500	0.14778400	-0.86260800
H	3.51262100	-1.57157000	-0.62321500
H	5.03448800	2.32688700	-1.01482300
C	-2.45151500	0.28732900	-0.47342500
C	-2.88527600	1.54803900	-0.06763500
N	-3.57816000	-0.46944700	-0.72942200
C	-4.29817500	1.53127400	-0.08169800
H	-2.23763800	2.36941600	0.22295100
C	-4.72189600	0.26911500	-0.49359700
H	-3.56555200	-1.43232800	-1.02651500
H	-4.94557400	2.36710200	0.15395900
C	-6.03997700	-0.28046300	-0.68097700
C	-6.49296800	-1.40466900	-1.37031600
N	-7.15394200	0.31284300	-0.12290900
C	-7.89792800	-1.48173400	-1.20626900
H	-5.88016700	-2.06399200	-1.97081600
C	-8.29778300	-0.40651000	-0.42125500
H	-7.10899700	1.06047800	0.55268900
H	-8.55930700	-2.20735600	-1.66280000
C	6.02343500	-0.48332300	-0.83981800

C	6.43124700	-1.78366000	-1.13315500
N	7.15712500	0.21083100	-0.46917600
C	7.82992400	-1.86100700	-0.92100400
H	5.79344500	-2.56989200	-1.51480800
C	8.27006200	-0.61079600	-0.50158400
H	7.13666900	1.13000700	-0.05390800
H	8.46290500	-2.71826400	-1.11324400
N	0.15352600	4.00883500	0.25198100
O	-0.74323500	3.75641800	1.09405000
O	0.27598300	3.25159000	-0.78164000
O	0.92299100	4.97728600	0.38811300
C	-9.59843700	-0.00165700	0.05281900
C	-10.08441400	1.22566000	0.49334500
N	-10.64626600	-0.89724800	0.14003300
C	-11.44361200	1.05048500	0.85796000
H	-9.53265000	2.15628600	0.49397000
C	-11.77813800	-0.27970200	0.63891200
H	-10.54144900	-1.89588400	0.04403900
H	-12.12489100	1.82539300	1.18580800
C	9.58330900	-0.13067100	-0.14699700
C	10.12177300	1.15164300	-0.10448900
N	10.58664200	-0.99533500	0.24456000
C	11.46712700	1.04482500	0.33091900
H	9.61435300	2.05658900	-0.41109400
C	11.74076100	-0.29895500	0.55168700
H	10.43479900	-1.96727400	0.46769000
H	12.18059500	1.85477900	0.41468500
C	-13.01217800	-1.00549400	0.84387900
C	-13.52216100	-2.15477800	0.25173100
N	-13.94712100	-0.58842300	1.77068700

C	-14.78518200	-2.42818500	0.84645200
H	-13.05494500	-2.70555400	-0.55403600
C	-15.02294600	-1.44630600	1.78413400
H	-13.79553400	0.17505000	2.41175800
H	-15.45063500	-3.24570600	0.60290100
H	-15.85735200	-1.28446000	2.45107800
C	12.93692100	-0.97266700	1.00680100
C	13.39915900	-2.27002000	0.82024300
N	13.87954300	-0.32265200	1.77870100
C	14.64104300	-2.39279100	1.50308500
H	12.91580000	-3.02747400	0.21732600
C	14.91369100	-1.17553400	2.08948200
H	13.75595200	0.60937700	2.14328400
H	15.27019900	-3.27184600	1.54673000
H	15.74685200	-0.84556300	2.69296300