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Supporting Information

Interplay among Electrostatic, Dispersion, and Steric Interactions: Spectroscopy and Quantum Chemical Calculations of π -Hydrogen Bonded Complexes

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Supporting Information

Interplay among electrostatic, dispersion and steric interactions: Spectroscopy and quantum chemical calculations of π -hydrogen bonded complexes

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Figure S1: TOF mass spectrum of indole (ind) in presence of 1,4-dimethylbenzene (2mb) recorded at laser frequency of 34994 cm^{-1} , which corresponds to the band maximum of the ind...2mb dimer. Water is present as an impurity in the sample or the carrier gas.

Figure S2: TOF mass spectrum of indole (ind) in presence of 1,3,5-trimethylbenzene (3mb) recorded at laser frequency of 34986 cm^{-1} , which corresponds to the band maximum of the ind...3mb dimer. Water is present as an impurity in the sample or the carrier gas.

Figure S3: TOF mass spectrum of indole (ind) in presence of hexamethylbenzene (6mb) recorded at laser frequency of 34927 cm^{-1} , which corresponds to the band maximum of the ind...6mb dimer. 3mb and water are present as impurities in the experiment.

Figure S4: 2C-R2PI spectra measured in the mass channels of (a) indole...3-mb and (c) indole...6-mb complexes. The corresponding 1C-R2PI spectra of ind...2-mb and ind...3-mb have been provided in parts (b) and (d), respectively, for comparison.

Figure S5: 1C-R2PI spectra in the (a) indole...6-mb dimer and (b) indole...6-mb...H₂O trimer mass channels. The trimer spectrum is magnified by 3 times as the R2PI signal of indole...6-mb...H₂O trimer is very weak compared to that of the indole...6-mb dimer.

Table S1: SAPT decomposition (SAPT2+/aug-cc-pVDZ) of the different components of the interaction energy (kcal mol^{-1}) of various conformations of the indole...benzene dimer.

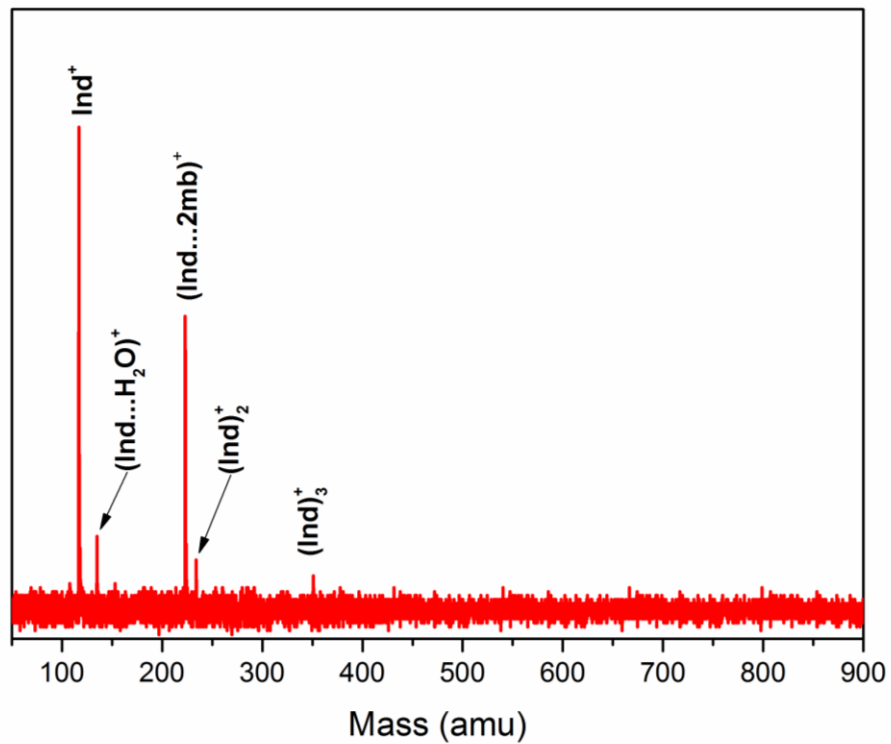


Figure S1: TOF mass spectrum of indole (ind) in the presence of 1,4-dimethylbenzene (2mb) recorded at laser frequency of 34994 cm^{-1} , which corresponds to the band maximum of the ind...2mb dimer. Water is present as an impurity in the sample or the carrier gas.

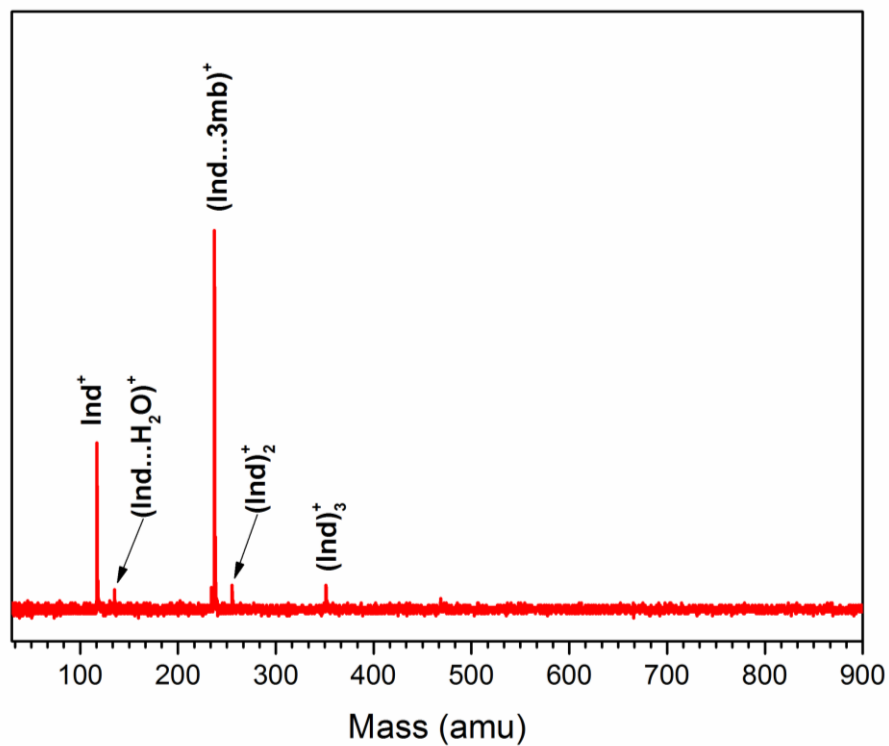


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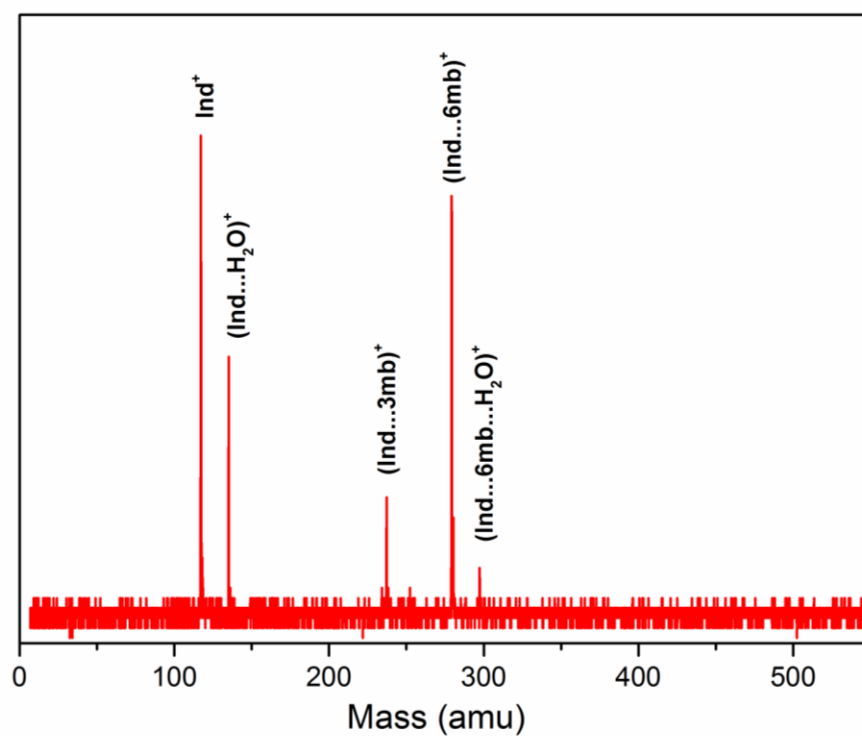


Figure S3: TOF mass spectrum of indole (ind) in the presence of hexamethylbenzene (6mb) recorded at laser frequency of 34927 cm^{-1} , which corresponds to band maximum of the ind...6-mb dimer. 3mb and water are present as impurities in the experiment.

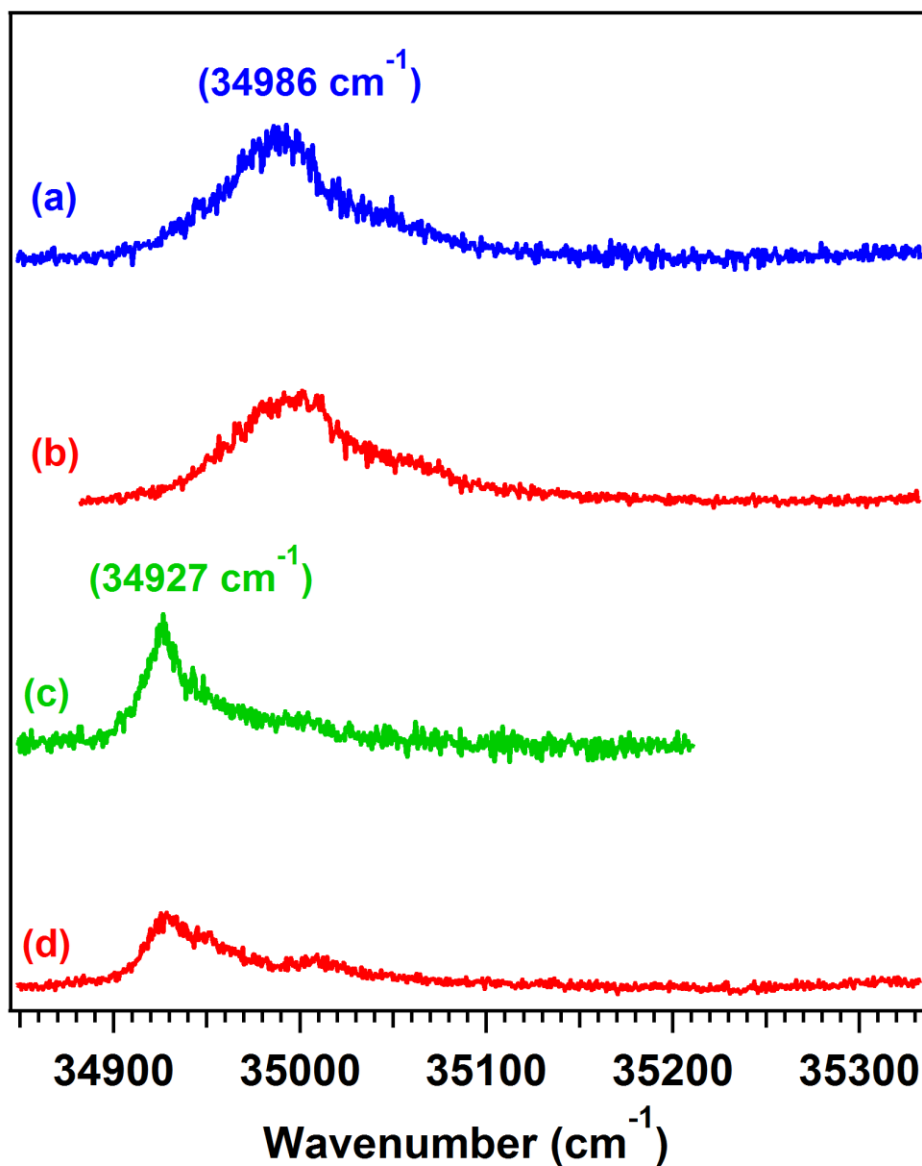


Figure S4: 2C-R2PI spectra measured in the mass channels of (a) indole...3-mb and (c) indole...6-mb complexes. The corresponding 1C-R2PI spectra of ind...2-mb and ind...3-mb have been provided in parts (b) and (d), respectively, for comparison.

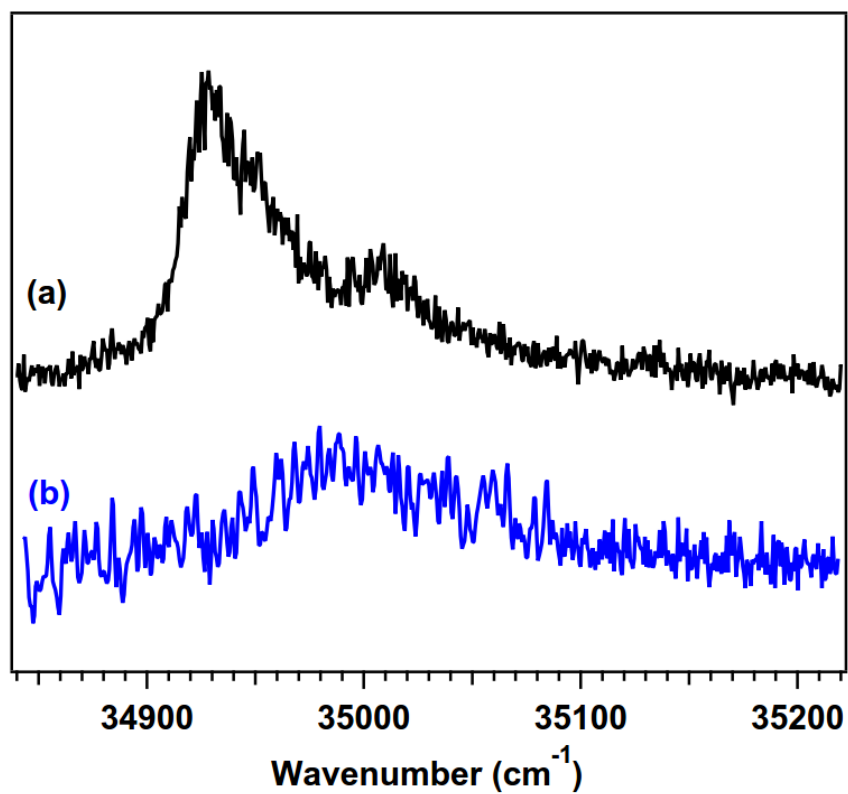


Figure S5: 1C-R2PI spectra in the (a) indole...6-mb dimer and (b) indole...6-mb...H₂O trimer mass channels. The trimer spectrum is magnified by 3 times as the R2PI signal of indole...6-mb...H₂O trimer is very weak compared to that of the indole...6-mb dimer.

Table S1: SAPT decomposition (SAPT2+/aug-cc-pVDZ) of the different components of the interaction energy (kcal/mol) of various conformations of the indole...benzene dimer.

Conformation	Electrostatic	Exchange	Induction	Dispersion
PD	-3.86	10.20	-1.20	-10.50
T-shaped	-4.07	6.36	-1.74	-6.19
Tilted S1	-4.49	7.68	-1.93	-7.07
Tilted S2	-4.83	8.63	-1.85	-7.90

The SAPT decomposition follows the established “chemist’s grouping”, which is assembled from the standard SAPT terms as follows:

$$E_{\text{electrostatic}} = E_{\text{elst}}^{(10)} + E_{\text{elst, resp}}^{(12)}$$

$$E_{\text{exchange}} = E_{\text{exch}}^{(10)} + E_{\text{exch}}^{(11)} + E_{\text{exch}}^{(12)}$$

$$E_{\text{induction}} = E_{\text{ind, resp}}^{(20)} + E_{\text{exch-ind, resp}}^{(20)} + {}^tE_{\text{ind}}^{(22)} + {}^tE_{\text{exch-ind}}^{(22)} + \delta E_{\text{HF}}^{(2)}$$

$$E_{\text{dispersion}} = E_{\text{disp}}^{(20)} + E_{\text{disp}}^{(21)} + E_{\text{disp}}^{(22)} + E_{\text{disp-exch}}^{(20)}$$

Cartesian Coordinates of Tilted S1 Complexes

Ind...1mb

31

DF-SCSN-LMP2/AVTZ,H=VTZ ENERGY=-632.59820296

N	1.0296259107	-0.7846386693	0.5341930072
C	-2.3060141171	-0.0534741173	2.7765925203
C	-1.1267763766	0.6318656672	2.9664597954
C	-0.0297957434	0.3244235001	2.1608746401
C	1.2985020127	0.8206805380	2.0565784472
C	1.8983218695	0.1279837753	1.0479239729
C	-0.1649237182	-0.6851323980	1.1802493838
C	-1.3488540529	-1.3833724574	0.9949086959
C	-2.4158701533	-1.0525437028	1.8017578257
H	-3.1599717304	0.1773496927	3.3894110673
H	-1.0538568615	1.3953313225	3.7226180159
H	1.7562239365	1.5876858809	2.6484872383
H	-3.3501592292	-1.5732002740	1.6824168152
H	-1.4335288469	-2.1537099931	0.2475968416
H	1.1810904038	-1.2979816807	-0.3099803921
H	2.8898187197	0.2184292115	0.6514408323
C	0.5221672850	1.5630883676	-1.7938188414
C	-0.7328753442	0.9736745819	-1.7066039716
C	-0.9093634531	-0.2780646691	-2.2838937880
C	0.1375644705	-0.9304097706	-2.9136513282
C	1.3866857136	-0.3332508094	-2.9849215509
C	1.5721548491	0.9208763924	-2.4271584386
H	0.6790125093	2.5345279977	-1.3546958325
C	-1.8510262970	1.6533116939	-0.9822973493
H	-1.8789581614	-0.7460187796	-2.2373926091
H	2.1989841779	-0.8315495205	-3.4854247167
H	-2.8148488923	1.3149230614	-1.3429487113
H	-1.7984183610	2.7289135422	-1.1041417129
H	-1.8032176125	1.4353477894	0.0810879468
H	-0.0239771244	-1.8972317711	-3.3591287925
H	2.5340442172	1.4004855982	-2.4873490109

Ind...2mb

34

DF-SCSN-LMP2/AVTZ,H=VTZ ENERGY=-671.71941002

N	0.9489351293	-0.7202793077	0.5286515198
C	-2.3248145609	-0.0960585367	2.8908688900
C	-1.1437271343	0.5876947498	3.0746883816
C	-0.0686895459	0.3184343216	2.2272277931
C	1.2529743419	0.8277629951	2.1032435383
C	1.8262670486	0.1791781361	1.0507626369
C	-0.2268635665	-0.6530113157	1.2121555549
C	-1.4125596731	-1.3498811997	1.0324499668
C	-2.4580006583	-1.0565247415	1.8809435925

H	-3.1620994781	0.1056877325	3.5360005050
H	-1.0528960208	1.3211459531	3.8580677690
H	1.7237218099	1.5741660188	2.7110321294
H	-3.3931771271	-1.5767929497	1.7671485913
H	-1.5147494178	-2.0907504897	0.2581192061
H	1.0719781105	-1.1899791568	-0.3455091360
H	2.8043394368	0.2932440359	0.6281352232
C	0.4915202818	1.5954816503	-1.8164337842
C	-0.7642210978	1.0147415640	-1.6991196295
C	-0.9439708032	-0.2460806796	-2.2523004860
C	0.0957625043	-0.9078052792	-2.8842512595
C	1.3531646323	-0.3266615506	-2.9984645171
C	1.5293097788	0.9386235036	-2.4536181553
H	0.6625429806	2.5721346369	-1.3942103664
C	-1.8691477837	1.7036560302	-0.9636743126
H	-1.9102459576	-0.7184938314	-2.1841594279
C	2.4642599156	-1.0176641791	-3.7285789650
H	-2.8392890315	1.3814324530	-1.3226052512
H	-1.8031507660	2.7793727619	-1.0776450332
H	-1.8202713170	1.4769968070	0.0979384007
H	-0.0756993043	-1.8848082654	-3.3074659456
H	2.4923725919	1.4174975763	-2.5297373946
H	2.4734452729	-0.7322502408	-4.7760935251
H	2.3547748815	-2.0944434288	-3.6859743112
H	3.4310545272	-0.7582357736	-3.3135621982

Ind...3mb

37

DF-SCSN-LMP2/AVTZ,H=VTZ ENERGY=-710.84145106

N	1.0039763596	-0.8021959984	0.4975942071
C	-2.2645259549	-0.0103370848	2.8170187521
C	-1.0631488001	0.6395008906	2.9925548826
C	0.0083084780	0.3146315426	2.1598470775
C	1.3484268336	0.7738279159	2.0363151908
C	1.9072183776	0.0801682265	1.0047906796
C	-0.1749390882	-0.6750984681	1.1670622758
C	-1.3816047000	-1.3369420726	0.9952661007
C	-2.4221737705	-0.9903648321	1.8294519473
H	-3.0992033730	0.2345500651	3.4506320196
H	-0.9538767923	1.3886613413	3.7585655228
H	1.8406923430	1.5159156181	2.6323298215
H	-3.3734200696	-1.4817916891	1.7205543560
H	-1.5031740889	-2.0909831917	0.2364859256
H	1.1120702924	-1.2765758823	-0.3763038557
H	2.8936987442	0.1466253889	0.5907640107
C	0.4799144759	1.5641960316	-1.7538856905
C	-0.7644809346	0.9516157167	-1.7360360447
C	-0.8944339827	-0.2953620102	-2.3335150943
C	0.1856304632	-0.9341059399	-2.9261125152
C	1.4214443025	-0.2977881881	-2.9110122502

C	1.5816485105	0.9562620635	-2.3378168832
H	0.5968910735	2.5294136182	-1.2860859510
C	-1.9238897990	1.6013096778	-1.0490396459
H	-1.8583071238	-0.7803755049	-2.3316669537
C	0.0152691763	-2.2605489047	-3.6021072111
H	2.2705596863	-0.7825127102	-3.3685611076
C	2.9092771537	1.6486327974	-2.3562325710
H	3.7186626588	0.9465146784	-2.5177616793
H	3.0895833486	2.1702958310	-1.4230486821
H	2.9505690005	2.3850868903	-3.1528993931
H	0.9314549107	-2.8387422998	-3.5753361573
H	-0.2554907827	-2.1284032536	-4.6452236587
H	-0.7692132342	-2.8441703574	-3.1347764881
H	-2.8664806461	1.2357501069	-1.4384034881
H	-1.8972002820	2.6777787668	-1.1725236393
H	-1.9029527665	1.3874612205	0.0160961909

Ind...4mb

40

DF-SCSN-LMP2/AVTZ,H=VTZ ENERGY=-749.96481688

N	0.9476251364	-0.7351525977	0.4811237217
C	-2.2681301794	-0.0633303581	2.9103348933
C	-1.0570441076	0.5629581919	3.1036942195
C	-0.0053127227	0.2828852719	2.2305516260
C	1.3367631331	0.7376221024	2.1095783148
C	1.8684895526	0.1069104461	1.0245425150
C	-0.2172682897	-0.6399231526	1.1802987369
C	-1.4338308480	-1.2784053850	0.9904201651
C	-2.4545671678	-0.9762483086	1.8653516216
H	-3.0876866793	0.1469515306	3.5753632754
H	-0.9250455060	1.2592573799	3.9147241046
H	1.8480179850	1.4361963058	2.7412539393
H	-3.4124064152	-1.4519803184	1.7448636098
H	-1.5765000326	-1.9820991622	0.1883067630
H	1.0316921563	-1.1512271830	-0.4255106571
H	2.8459458744	0.1944621133	0.5936475641
C	0.4739731483	1.5350196861	-1.8069587674
C	-0.7682354892	0.9000794554	-1.7892335813
C	-0.8812254989	-0.3512683034	-2.3773366355
C	0.1908019132	-1.0045607126	-2.9699325889
C	1.4338710261	-0.3681741289	-2.9878206325
C	1.5430270171	0.8896174840	-2.4112132622
C	0.6553286581	2.8728263347	-1.1657113691
C	-1.9458964004	1.5393835304	-1.1269556520
H	-1.8434868414	-0.8398987414	-2.3679545857
C	0.0089443093	-2.3529460621	-3.5943348593
C	2.6187909166	-1.0150218630	-3.6346059594
H	0.6598062365	-3.0969829086	-3.1443623385
H	0.2430319301	-2.3327454941	-4.6545963262
H	-1.0128819716	-2.6941655611	-3.4857356134

H	-2.8359008966	0.9360264496	-1.2528542565
H	-2.1434842195	2.5262287786	-1.5344887812
H	-1.7758430539	1.6567118859	-0.0598265720
H	2.5025758933	1.3838936386	-2.4274780819
H	1.6783285667	3.2142914117	-1.2637706940
H	0.4157415493	2.8302300442	-0.1073388425
H	0.0064067672	3.6192866945	-1.6141797448
H	2.8327422249	-1.9886157596	-3.2038607356
H	3.5027498484	-0.3994336883	-3.5249835309
H	2.4520124768	-1.1724490466	-4.6962710014

Ind...5mb

43

DF-SCSN-LMP2/AVTZ,H=VTZ ENERGY=-789.08047611

N	0.9722696515	-0.9899394822	0.4212989953
C	-2.1571909410	0.2314521033	2.7451085679
C	-0.9063439541	0.8009068274	2.8377284246
C	0.1134995509	0.3298979992	2.0097372816
C	1.4831691007	0.6642750158	1.8261842309
C	1.9569277905	-0.1502183646	0.8413846372
C	-0.1740026154	-0.7157552463	1.1021925560
C	-1.4290478997	-1.2991139969	1.0177893366
C	-2.4156230838	-0.8110737264	1.8470557512
H	-2.9514242237	0.5870458779	3.3782827930
H	-0.7184457365	1.5951203955	3.5406352816
H	2.0498508932	1.4054149685	2.3535166711
H	-3.4014302499	-1.2411884006	1.8069892541
H	-1.6242025218	-2.1073426639	0.3338123714
H	1.0165932863	-1.5358150326	-0.4152975374
H	2.9358385498	-0.2006241174	0.4077972992
C	0.4019058770	1.5258557016	-1.6902355077
C	-0.8363900651	0.8820490287	-1.7764442065
C	-0.9318107708	-0.3420444140	-2.4380497340
C	0.2160683619	-0.8918054393	-2.9880618193
C	1.4484104138	-0.2561595374	-2.9353948817
C	1.5406996762	0.9766961130	-2.2882194250
C	0.4835362262	2.8251625383	-0.9462609289
C	-2.0404169443	1.5169668773	-1.1503997160
C	-2.2364646144	-1.0663148743	-2.5838137345
C	2.6329745514	-0.9078095971	-3.5873783007
H	-1.9944763131	1.4538040672	-0.0653261434
H	-2.9570154879	1.0387448901	-1.4639071913
H	-2.1106323442	2.5676904461	-1.4101637383
C	2.8470091751	1.7130369675	-2.2330222850
H	1.5004223819	3.0887033563	-0.6972365700
H	-0.0751240278	2.7718739307	-0.0192728568
H	0.0634301080	3.6411095366	-1.5309965824
H	2.3557673730	-1.8741056495	-3.9901379589
H	3.4515188923	-1.0622382895	-2.8913616537
H	3.0199212948	-0.3103915302	-4.4069991971

H	0.1434258510	-1.8393860149	-3.4999929624
H	-2.0813930905	-2.0386207137	-3.0356555501
H	-2.9263277200	-0.5162511006	-3.2170439804
H	-2.7275386670	-1.2125682822	-1.6282756613
H	3.6055047091	1.2308783725	-2.8321502145
H	3.2243035044	1.7798509572	-1.2161033129
H	2.7415640518	2.7292005025	-2.5975818016

Ind...6mb

46

DF-SCSN-LMP2/AVTZ,H=VTZ ENERGY=-828.19313468

N	0.9557417687	-0.8440728167	0.4038949019
C	-2.2150655378	0.0314989848	2.8269503312
C	-0.9842637339	0.6298020753	2.9820805646
C	0.0511212181	0.2795939199	2.1146146018
C	1.4066121610	0.6826937644	1.9662647349
C	1.9076780667	-0.0105464461	0.9052481848
C	-0.1986404797	-0.6802397165	1.1068043749
C	-1.4333965855	-1.2932975907	0.9582718516
C	-2.4371671393	-0.9233209856	1.8271889194
H	-3.0216803837	0.2950199249	3.4888232894
H	-0.8242427452	1.3562924105	3.7609517319
H	1.9463135768	1.3888484734	2.5650214767
H	-3.4081577373	-1.3793234210	1.7388559542
H	-1.6021664097	-2.0321455899	0.1940023447
H	1.0110767036	-1.2802304805	-0.4955263132
H	2.8863790685	0.0214459493	0.4695453565
C	0.4311990376	1.5670979551	-1.7459613831
C	-0.8221720947	0.9542405894	-1.7982001597
C	-0.9657359127	-0.2861182137	-2.4228919127
C	0.1394008589	-0.9002901056	-3.0184780166
C	1.3950270446	-0.2869767424	-2.9626793812
C	1.5299959181	0.9685205222	-2.3650916692
C	0.5897255662	2.8558373273	-0.9913366212
C	-2.0091098152	1.6422856437	-1.1879363805
C	-2.3054954269	-0.9664047837	-2.4506171847
C	2.5995585257	-0.9808562401	-3.5378717062
H	-2.1387237488	1.3602577166	-0.1442535602
H	-2.9234529496	1.3954133845	-1.7099705180
H	-1.9005766242	2.7178016647	-1.2258083018
C	2.8490490989	1.6872669925	-2.4095139168
H	1.6149924071	3.0209316116	-0.6946333357
H	-0.0019258174	2.8413015291	-0.0847654361
H	0.2711227333	3.7144039941	-1.5792329895
H	2.5001546524	-2.0564170731	-3.4843600357
H	3.5002633533	-0.7191945438	-2.9991631833
H	2.7618965522	-0.7228997770	-4.5823548290
C	-0.0381319659	-2.1942161031	-3.7654786076
H	-2.2045763598	-2.0438166688	-2.4451383987
H	-2.8731118504	-0.7011843942	-3.3404646252

H	-2.9015896741	-0.6968327278	-1.5905972281
H	3.4380153737	1.3817184429	-3.2627937038
H	3.4483635901	1.5112265169	-1.5182538240
H	2.7052924139	2.7563723884	-2.4899116321
H	0.6979727194	-2.3029444087	-4.5493741659
H	-1.0108359628	-2.2402825924	-4.2361581445
H	0.0463265459	-3.0649103597	-3.1179314544