Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

A fluorescent probe of *N'*-formyl-rhodamine B hydrazide: structure and spectral properties of protonation behaviour

Jingze Wang, [a] Qiwu Yang,[b] Haibin Song[a]* and Wenqin Zhang[b]*

a: College of Chemistry,Nankai University, Tianjin 300073, P. R. China. Fax: 86 022 2350 5108; Tel: 86 022 2350 5108; E-mail: haibin.song@yahoo.cn;

b: Department of Chemistry, Nankai University, Tianjin, 300072, P. R. China. Fax: +86 022 2740 7999, E-mail: zhangwenqin@mail.tju.edu.cn.

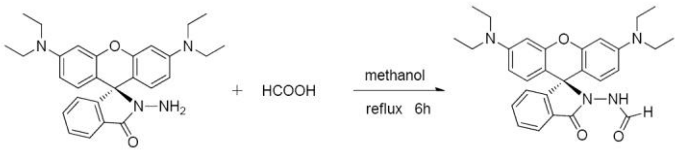
Table of contents Page

Materials and measurements

Unless otherwise stated all chemicals and solvents were obtained commercially and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 400MHz Varian MERCURY-VX 400 apparatus (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Chemical shifts are reported in ppm with tetramethylsilane (TMS) as the internal standard. Absorption spectra were recorded on a Jasco V-560 UV/VIS spectrophotometer. Fluorescence was measured on a Perkin Elmer Luminescence Spectrometer LS50B.

Synthesis of spirolactam *N'*-formyl-rhodamine B hydrazide

A spirolactam form of *N'*-formyl-rhodamine B hydrazide, named **RhBN-Fo**, was synthesized as shown in Scheme S1.



Scheme S1

The **RhBN-Fo** was synthesized from rhodamine B by a two-step reaction in a yield of 65%. The first step was to prepare rhodamine B hydrazide according to the literature method. Then, 0.91 g (2.00 mmol) rhodamine B hydrazide and 0.12 g (2.55 mmol) formic acid were dissolved in 10 mL of methanol. The solution was refluxed under N_2 for 6 h and then cooled. The cooled solution was then poured into 100 mL of ice water and allowed to stir overnight at room temperature. The residue was purified by column chromatography (hexane/CH_2Cl_2 = 10:1) to give 0.63 g of **RhBN-Fo** (65 %) as a colorless solid, mp: 105−107 ˚C. The **RhBN-Fo** probe was characterized by ^{1}H NMR and ^{13}C NMR.^{1}H NMR δ (ppm) (400 MHz, $CDCl_3$) 7.94 (phenyl, 1H), 7.43 (phenyl, 2H), 7.10 (phenyl, 1H), 6.37-6.46 (xanthenes, 4H), 6.27-6.29 (xanthenes, 2H), 3.32-3.34 (N–C*H*$_2$–CH$_3$), 8H), 1.14-1.17 (N–CH$_2$–C*H*$_3$), 12H). ^{13}C NMR δ (ppm) (101 MHz, $CDCl_3$) 166.14, 153.86, 151.57, 148.89, 132.51, 130.04, 128.12, 128.09, 123.84, 122.98, 108.05, 104.60, 98.00, 65.92, 44.38, 25.37, 12.62. MS (ESI-MS): m/z calcd. for $C_{29}H_{33}N_4O_3$ ($M + H^+$): 485.26, found: 485.40.

Single-crystal structure determination

A single-crystal of **RhBN-Fo** was obtained from a CH_2Cl_2-CH_3OH (3:1, v/v) solution after one week of slow evaporation at room temperature. A colorless block of **RhBN-Fo** was epoxied onto the end of a thin glass fiber and then mounted onto the goniometer of an X-ray single-crystal Bruker SMART APEX CCD-based diffractometer. The crystal data was collected using Cu *Kα* radiation (λ = 0.71073 Å) in the θ range of 1.58 to 27.87 with ϕ/ω scan technique at 113 K. The

intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on multiscan techniques. The structure was solved using the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97. [1]

Reference:

1. G. M. Sheldrick, SHELXS-97 and SHELXL-97, Program for X-ray Crystal Structure Determination, University of Göttingen, Germany, 1997.

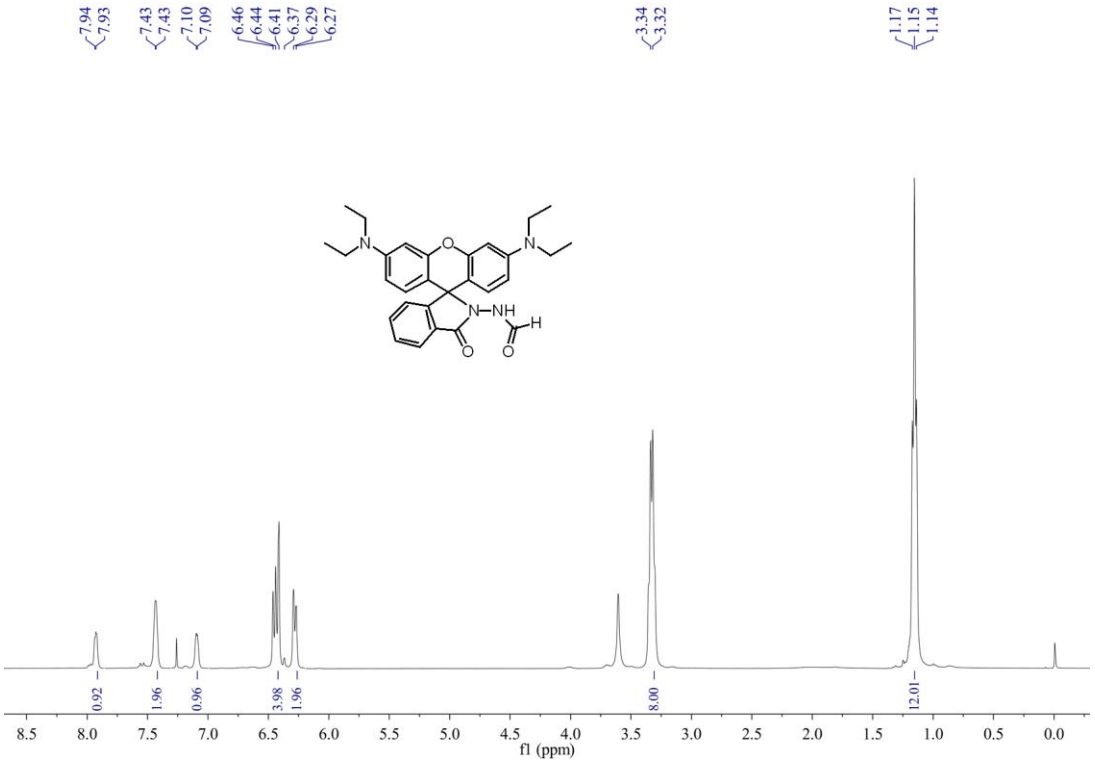
Computational details

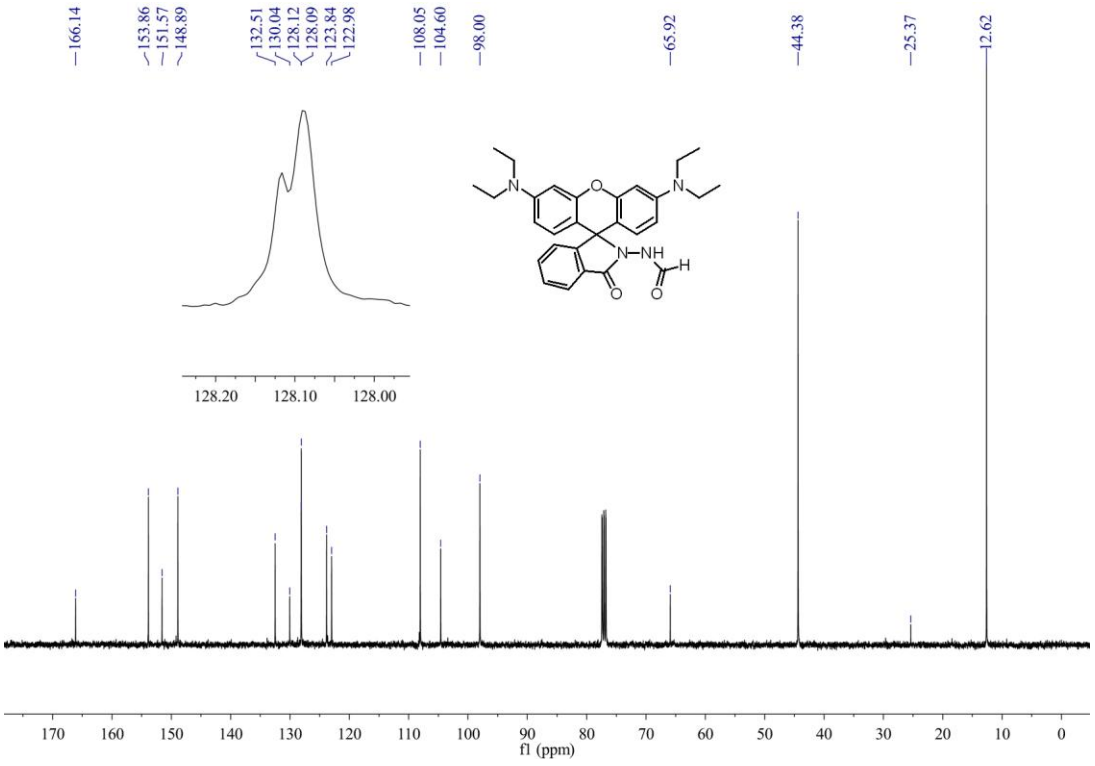
The calculations were carried out with a Gaussian 03 program package. [47] The geometries of the structures were optimized using the B3LYP [48, 49] functional. Frequency calculations at the same level of theory were performed to identify all the stationary points as minima (zero imaginary frequency). The 6-31G(d) basis set was used for C, N, and O atoms, whereas the 6-31G(d,p) was used for H atom.

Refenence:

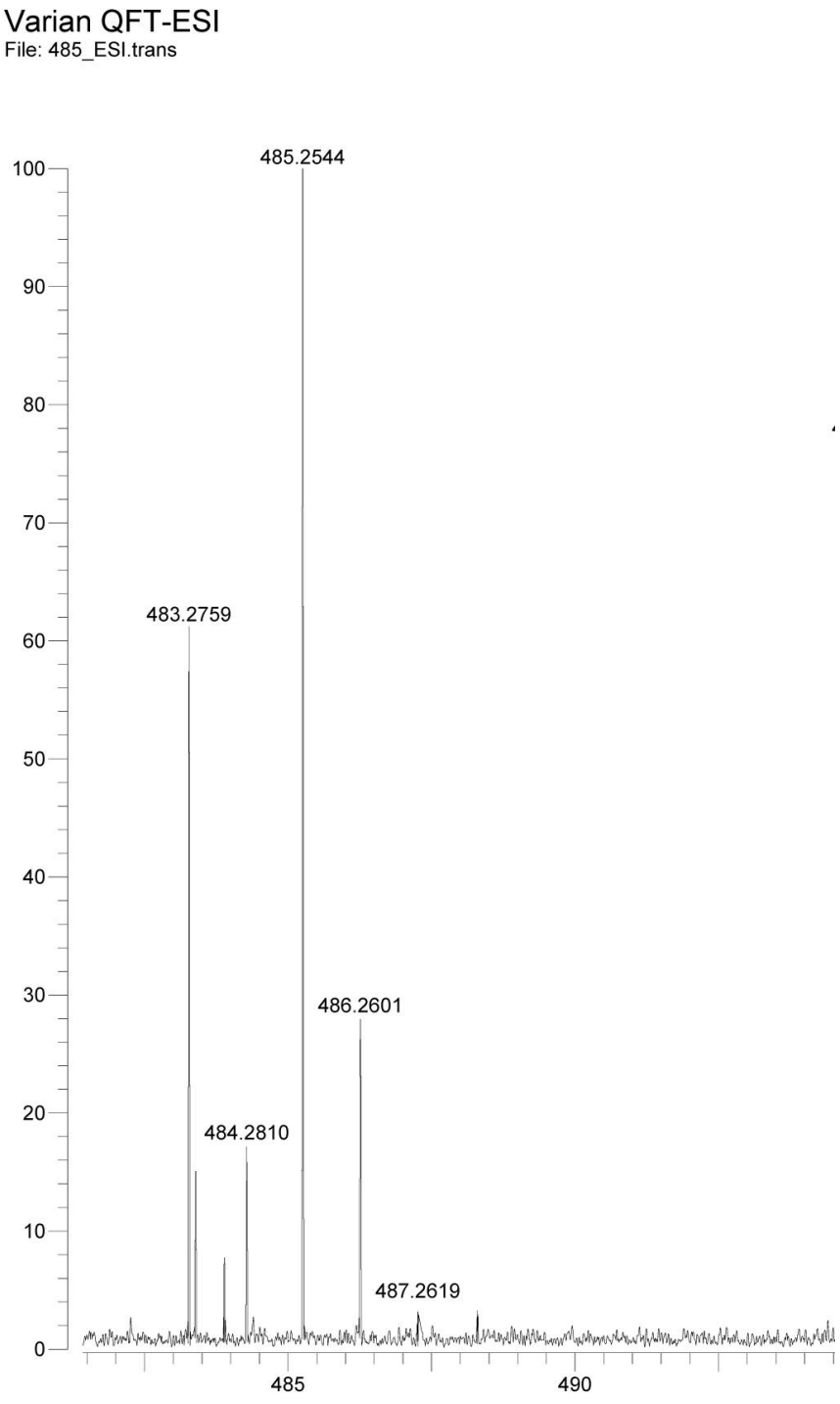
1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, GAUSSIAN 03 (Revision D.01), Gaussian, Inc., Wallingford, CT, 2004.
2. C. Lee, W. Yang,, R. G. Parr, Phys. Rev. B 1988, **37**, 785.
3. A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648.

NMR for RhBN-Fo





MS for RhBN-Fo



The curves change and Boltzmann formula

*Absorption spectra of **RhBN-Fo:***

b in 325 nm:

Model Boltzmann
Equation y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))
Reduced Chi-Sqr 3.5865E-6
Adj. R-Square 0.99955

		Value	Standard Error
B	A1	0.21286	0.00226
B	A2	0.00781	0.00114
B	x0	3.31827	0.01875
B	dx	0.33274	0.01353

c in 556 nm:

Model Boltzmann
Equation y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))
Reduced Chi-Sqr 3.80063E-5
Adj. R-Square 0.99847

		Value	Standard Error
B	A1	0.11361	0.00736
B	A2	0.4834	0.00365
B	x0	3.16938	0.02841
B	dx	0.28971	0.03315

*Fluorescence spectra of **RhBN-Fo:***

Model Boltzmann
Equation y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))
Reduced Chi-Sqr 236.20882
Adj. R-Square 0.99609

		Value	Standard Error
B	A1	599.40661	16.78943
B	A2	55.22728	9.08849
B	x0	3.36444	0.05749
B	dx	0.28566	0.03463

Molecular Geometries and Energies (unit is a.u.):

Closed structure of RhBN-Fo

SCF Done: E(RB+HF-LYP) = -1569.05528920

Sum of electronic and thermal Free Energies= -1568.557778

8	-0.033741000	-1.713741000	-0.144816000
8	-0.192984000	4.174758000	2.059606000
8	0.862039000	0.849973000	4.467319000
7	4.713067000	-2.027060000	-0.425865000
7	-4.787759000	-2.036138000	-0.114814000
7	-0.001411000	1.996569000	1.261012000
7	-0.112981000	1.351895000	2.464325000
6	3.573723000	-1.244805000	-0.346123000
6	2.289360000	-1.818966000	-0.285032000
1	2.133825000	-2.888908000	-0.317464000
6	1.149631000	-1.019217000	-0.196501000
6	-1.218024000	-1.021405000	-0.132184000
6	-2.359852000	-1.823218000	-0.132264000
1	-2.203673000	-2.893514000	-0.119909000
6	-3.646851000	-1.251989000	-0.119657000
6	-3.720022000	0.167176000	-0.117547000
1	-4.677492000	0.671361000	-0.137435000
6	-2.567857000	0.935463000	-0.112182000
1	-2.666691000	2.017650000	-0.111999000
6	-1.281371000	0.374680000	-0.117174000
6	-0.030967000	1.234849000	-0.037078000
6	1.210946000	0.376072000	-0.181058000
6	2.494395000	0.939775000	-0.247348000
1	2.589835000	2.021914000	-0.226474000
6	3.645401000	0.174349000	-0.324203000
1	4.601911000	0.680106000	-0.348357000
6	6.037563000	-1.441280000	-0.614100000
1	5.959856000	-0.572390000	-1.275325000
1	6.646433000	-2.172621000	-1.157693000
6	6.742078000	-1.058116000	0.694099000
1	7.735156000	-0.643302000	0.489422000
1	6.867296000	-1.932972000	1.340197000
1	6.166081000	-0.313092000	1.250087000
6	4.650442000	-3.481740000	-0.320207000
1	3.883718000	-3.758785000	0.410757000
1	5.601490000	-3.823733000	0.103091000

6	4.397857000	-4.192032000	-1.657234000
1	4.370983000	-5.278219000	-1.517396000
1	5.190979000	-3.962726000	-2.376485000
1	3.446981000	-3.878345000	-2.096845000
6	-6.118687000	-1.455788000	0.043421000
1	-6.064484000	-0.599616000	0.723314000
1	-6.743890000	-2.197948000	0.552467000
6	-6.780959000	-1.048624000	-1.279469000
1	-7.780872000	-0.638746000	-1.099692000
1	-6.883360000	-1.911522000	-1.945511000
1	-6.188175000	-0.292290000	-1.801800000
6	-0.060418000	2.414131000	-1.009563000
6	-0.049357000	2.393643000	-2.401370000
1	-0.010548000	1.454327000	-2.944793000
6	-0.090353000	3.613834000	-3.082094000
1	-0.083702000	3.618982000	-4.168465000
6	-0.140492000	4.832340000	-2.388349000
1	-0.171794000	5.764864000	-2.944080000
6	-0.149960000	4.850536000	-0.993685000
1	-0.188311000	5.777931000	-0.430630000
6	-0.108083000	3.628879000	-0.324878000
6	-0.114889000	3.380280000	1.139945000
6	0.954047000	1.265270000	3.331273000
1	1.893716000	1.593710000	2.850930000
1	-1.042951000	1.206300000	2.844631000
6	-4.716527000	-3.491050000	-0.213303000
1	-5.648234000	-3.835916000	-0.675577000
1	-3.919277000	-3.767407000	-0.911226000
6	-4.517917000	-4.198490000	1.134346000
1	-4.483335000	-5.284807000	0.997464000
1	-5.340671000	-3.969828000	1.819608000
1	-3.586863000	-3.882567000	1.612825000

Os1 (opened structure) of RhBN-Fo

SCF Done: E(RB+HF-LYP) = -1569.47106104

Sum of electronic and thermal Free Energies= -1568.961692

8	-0.735417000	-1.897545000	0.071617000
8	-0.415739000	2.182849000	-2.001444000
8	4.789036000	2.320851000	-1.057948000
7	-5.429592000	-1.183781000	-0.144865000
7	3.880923000	-3.041577000	0.148232000
7	1.586768000	3.210470000	-2.268126000
7	2.868765000	3.349605000	-1.767993000

6	-4.175666000	-0.701418000	0.046669000
6	-3.035932000	-1.544250000	-0.021664000
1	-3.116362000	-2.605830000	-0.207411000
6	-1.773765000	-1.020434000	0.166124000
6	0.551036000	-1.488001000	0.244148000
6	1.527167000	-2.455618000	0.116985000
1	1.208568000	-3.458481000	-0.130080000
6	2.896675000	-2.116795000	0.277541000
6	3.204486000	-0.746236000	0.594448000
1	4.229180000	-0.438335000	0.750715000
6	2.218778000	0.193520000	0.721179000
1	2.490622000	1.209995000	0.980918000
6	0.841345000	-0.122482000	0.533818000
6	-0.215049000	0.808833000	0.619158000
6	-1.536456000	0.357315000	0.446259000
6	-2.690202000	1.191760000	0.500547000
1	-2.553759000	2.251835000	0.679706000
6	-3.950199000	0.695062000	0.317317000
1	-4.785867000	1.380499000	0.347318000
6	-6.630884000	-0.346507000	0.014189000
1	-6.479600000	0.347211000	0.844768000
1	-7.440248000	-1.013084000	0.325859000
6	-7.028328000	0.399091000	-1.263600000
1	-7.942638000	0.974727000	-1.090791000
1	-7.219903000	-0.298971000	-2.084028000
1	-6.243757000	1.089561000	-1.585813000
6	-5.674512000	-2.580649000	-0.536171000
1	-4.884851000	-2.904215000	-1.219345000
1	-6.599346000	-2.589136000	-1.120022000
6	-5.799183000	-3.534990000	0.655869000
1	-6.006939000	-4.549295000	0.302044000
1	-6.618146000	-3.234698000	1.316299000
1	-4.880473000	-3.560290000	1.248727000
6	5.310094000	-2.686295000	0.202998000
1	5.458992000	-1.712094000	-0.268748000
1	5.837333000	-3.407878000	-0.427784000
6	5.889779000	-2.707336000	1.620341000
1	6.957078000	-2.468952000	1.589477000
1	5.777633000	-3.694335000	2.079355000
1	5.395179000	-1.976647000	2.266539000
6	0.078438000	2.238825000	0.943238000
6	-0.039848000	2.660421000	2.273981000
1	-0.367260000	1.951961000	3.028934000
6	0.265203000	3.972971000	2.637607000

1	0.163948000	4.281853000	3.673221000
6	0.698040000	4.880597000	1.671487000
1	0.927134000	5.905395000	1.945545000
6	0.829564000	4.469216000	0.346337000
1	1.138982000	5.181881000	-0.411513000
6	0.526035000	3.154856000	-0.032592000
6	0.518667000	2.775214000	-1.486796000
6	3.673364000	2.257995000	-1.527566000
1	3.162762000	1.316745000	-1.805826000
1	3.239322000	4.281831000	-1.627727000
6	3.586771000	-4.466993000	-0.065330000
1	4.413977000	-5.031137000	0.374919000
1	2.697659000	-4.738923000	0.509821000
6	3.423819000	-4.841910000	-1.542021000
1	3.231229000	-5.914910000	-1.635611000
1	4.330753000	-4.612252000	-2.109288000
1	2.591736000	-4.302962000	-2.003742000
1	1.500529000	2.972093000	-3.251951000

Os2 of RhBN-Fo

SCF Done: E(RB+HF-LYP) = -1569.45830248

Sum of electronic and thermal Free Energies= -1568.949084

8	0.305100000	-1.853459000	-0.280411000
8	1.653084000	2.951822000	1.961620000
8	-3.890895000	1.416228000	2.158178000
7	5.047265000	-1.829505000	0.029980000
7	-4.429653000	-2.273404000	-0.235293000
7	-0.505916000	2.332802000	2.280504000
7	-1.801944000	2.262710000	1.838807000
6	3.878745000	-1.162621000	-0.152146000
6	2.628646000	-1.834132000	-0.131450000
1	2.551853000	-2.903057000	0.008358000
6	1.457851000	-1.128679000	-0.318115000
6	-0.907611000	-1.262112000	-0.462556000
6	-2.013749000	-2.073138000	-0.320305000
1	-1.845971000	-3.109379000	-0.062543000
6	-3.319171000	-1.526229000	-0.438219000
6	-3.423214000	-0.132872000	-0.788557000
1	-4.395036000	0.316365000	-0.933423000
6	-2.313226000	0.645904000	-0.940870000
1	-2.431911000	1.687989000	-1.214563000

6	-0.994771000	0.133845000	-0.749980000
6	0.177751000	0.913060000	-0.754513000
6	1.421846000	0.279535000	-0.540826000
6	2.685170000	0.939483000	-0.552357000
1	2.710807000	2.012045000	-0.703393000
6	3.858328000	0.259900000	-0.369769000
1	4.783463000	0.819525000	-0.373637000
6	6.359822000	-1.173004000	-0.089214000
1	6.318838000	-0.424110000	-0.883716000
1	7.062948000	-1.936119000	-0.435303000
6	6.856712000	-0.559912000	1.223458000
1	7.850503000	-0.125184000	1.080312000
1	6.930537000	-1.317773000	2.009240000
1	6.186141000	0.228252000	1.577655000
6	5.081463000	-3.265016000	0.351302000
1	4.247009000	-3.503011000	1.016248000
1	5.989956000	-3.438370000	0.935196000
6	5.074252000	-4.166610000	-0.887753000
1	5.125901000	-5.217049000	-0.586037000
1	5.934412000	-3.958129000	-1.530850000
1	4.167023000	-4.024297000	-1.481454000
6	-5.774726000	-1.673536000	-0.154083000
1	-5.697020000	-0.688248000	0.311584000
1	-6.349276000	-2.289590000	0.543645000
6	-6.494931000	-1.606310000	-1.503980000
1	-7.496152000	-1.186050000	-1.370191000
1	-6.604072000	-2.601849000	-1.944876000
1	-5.954290000	-0.979745000	-2.219252000
6	0.105275000	2.390274000	-0.979787000
6	-0.059437000	2.886396000	-2.280646000
1	-0.143375000	2.189336000	-3.109012000
6	-0.098449000	4.260802000	-2.518213000
1	-0.222946000	4.627635000	-3.532191000
6	0.028715000	5.157796000	-1.457099000
1	0.002550000	6.227473000	-1.638306000
6	0.191531000	4.677322000	-0.158199000
1	0.293269000	5.369832000	0.671542000
6	0.223167000	3.299234000	0.094136000
6	0.386155000	2.816740000	1.499682000
6	-2.744178000	1.560659000	2.543507000
1	-2.332025000	1.146199000	3.479654000
1	-2.088628000	2.708879000	0.972288000
6	-4.363011000	-3.723703000	0.001071000
1	-5.294942000	-4.148915000	-0.382913000

1	-3.563011000	-4.147552000	-0.611510000
6	-4.185929000	-4.096570000	1.476864000
1	-4.181253000	-5.185118000	1.587126000
1	-5.004333000	-3.700047000	2.084888000
1	-3.247546000	-3.706702000	1.880984000
1	1.651861000	2.672775000	2.893077000

Os1 of acrylic carbonyl

SCF Done: E(RB+HF-LYP) = -1646.87412876

Sum of electronic and thermal Free Energies= -1646.334477

8	1.271622000	1.949108000	-0.055252000
8	0.005574000	-1.888679000	-1.661070000
8	-5.213545000	-3.711656000	-1.152643000
7	5.789064000	0.509167000	-0.372997000
7	-3.077078000	3.845027000	0.226299000
7	-1.791148000	-3.220776000	-1.859280000
7	-2.970461000	-3.756926000	-1.377105000
6	4.485179000	0.238571000	-0.107532000
6	3.482772000	1.236922000	-0.208510000
1	3.711890000	2.257157000	-0.481781000
6	2.165838000	0.929101000	0.066488000
6	-0.050014000	1.759262000	0.205462000
6	-0.863711000	2.867199000	0.073424000
1	-0.402544000	3.790552000	-0.247365000
6	-2.253733000	2.769487000	0.335898000
6	-2.759106000	1.482426000	0.734877000
1	-3.807290000	1.360891000	0.970972000
6	-1.933465000	0.397448000	0.857269000
1	-2.349900000	-0.551420000	1.176040000
6	-0.535908000	0.477874000	0.594563000
6	0.367764000	-0.600692000	0.710902000
6	1.735902000	-0.368277000	0.467080000
6	2.752815000	-1.362366000	0.550584000
1	2.468682000	-2.372193000	0.822910000
6	4.063921000	-1.081662000	0.282706000
1	4.786838000	-1.883606000	0.341058000
6	6.859552000	-0.481371000	-0.172442000
1	6.629898000	-1.088181000	0.706753000
1	7.764368000	0.079351000	0.080121000
6	7.114713000	-1.362007000	-1.399602000
1	7.942994000	-2.048772000	-1.200802000
1	7.381347000	-0.756443000	-2.271052000

1	6.232652000	-1.954378000	-1.659134000
6	6.223018000	1.820538000	-0.878475000
1	5.467917000	2.204770000	-1.569458000
1	7.120466000	1.648578000	-1.479598000
6	6.522763000	2.833673000	0.231227000
1	6.861007000	3.777816000	-0.206268000
1	7.312275000	2.468688000	0.895128000
1	5.637380000	3.035780000	0.840476000
6	-4.534218000	3.745870000	0.408097000
1	-4.885686000	2.795383000	-0.001309000
1	-4.983953000	4.523780000	-0.215807000
6	-4.982059000	3.917181000	1.862926000
1	-6.073083000	3.865348000	1.927749000
1	-4.667021000	4.886723000	2.260160000
1	-4.563118000	3.137769000	2.505664000
6	-0.098832000	-1.934252000	1.203953000
6	0.075577000	-2.211030000	2.566105000
1	0.529308000	-1.460144000	3.205836000
6	-0.321571000	-3.435018000	3.105335000
1	-0.176268000	-3.630666000	4.163119000
6	-0.891948000	-4.402884000	2.280640000
1	-1.185332000	-5.365869000	2.685836000
6	-1.082330000	-4.134629000	0.926550000
1	-1.509335000	-4.900334000	0.292751000
6	-0.707079000	-2.902936000	0.371713000
6	-0.802228000	-2.619568000	-1.099155000
6	-4.192536000	-3.074611000	-1.347286000
1	-3.073952000	-4.763748000	-1.449612000
6	-2.563138000	5.189815000	-0.075626000
1	-3.247740000	5.904491000	0.390323000
1	-1.600913000	5.326347000	0.425256000
6	-2.448498000	5.476134000	-1.576356000
1	-2.080074000	6.493990000	-1.735895000
1	-3.421627000	5.389848000	-2.069205000
1	-1.760044000	4.781631000	-2.065906000
1	-1.737722000	-2.982259000	-2.845841000
6	-4.152355000	-1.597370000	-1.534572000
1	-3.195568000	-1.102764000	-1.663329000
6	-5.298229000	-0.911226000	-1.560354000
1	-6.246228000	-1.426855000	-1.439057000
1	-5.314615000	0.163506000	-1.710764000

Os1 of oxalic carbonyl

SCF Done: E(RB+HF-LYP) = -1722.10990456

Sum of electronic and thermal Free Energies= -1721.568633

8	1.011412000	2.029696000	0.063584000
8	0.868044000	-2.438434000	-1.357811000
8	-4.559566000	-2.905171000	-1.014228000
7	5.640510000	1.069991000	-0.408338000
7	-3.516054000	3.433523000	0.411690000
7	-1.094024000	-3.558875000	-1.554763000
7	-2.411664000	-3.617665000	-1.104832000
6	4.388351000	0.673469000	-0.070662000
6	3.280082000	1.555799000	-0.161715000
1	3.387385000	2.583019000	-0.479410000
6	2.017560000	1.118443000	0.178166000
6	-0.272799000	1.703705000	0.371528000
6	-1.210505000	2.706613000	0.225717000
1	-0.865240000	3.663936000	-0.137976000
6	-2.574086000	2.462305000	0.530674000
6	-2.920590000	1.138459000	0.979491000
1	-3.942608000	0.907665000	1.247791000
6	-1.973269000	0.158412000	1.114636000
1	-2.270427000	-0.822113000	1.469730000
6	-0.598692000	0.390471000	0.819524000
6	0.428759000	-0.570254000	0.956334000
6	1.747820000	-0.204212000	0.639355000
6	2.871913000	-1.077676000	0.723297000
1	2.707916000	-2.100625000	1.039387000
6	4.131124000	-0.667235000	0.390976000
1	4.939833000	-1.382396000	0.449420000
6	6.818990000	0.201913000	-0.241492000
1	6.703404000	-0.393313000	0.667128000
1	7.672238000	0.861773000	-0.059248000
6	7.094071000	-0.689674000	-1.456042000
1	7.998134000	-1.282164000	-1.286598000
1	7.248484000	-0.090435000	-2.358402000
1	6.264097000	-1.376010000	-1.646075000
6	5.908159000	2.399140000	-0.980763000
1	5.083692000	2.676685000	-1.642579000
1	6.787833000	2.296880000	-1.622483000
6	6.154410000	3.478389000	0.078564000
1	6.375159000	4.434028000	-0.406344000
1	7.006079000	3.218384000	0.714166000
1	5.281728000	3.614432000	0.723436000
6	-4.948507000	3.179056000	0.638539000
1	-5.202492000	2.181845000	0.270758000
1	-5.497636000	3.879607000	0.002775000

6	-5.375345000	3.352382000	2.099333000
1	-6.452333000	3.185913000	2.196508000
1	-5.157162000	4.363527000	2.455731000
1	-4.859072000	2.645363000	2.754907000
6	0.111420000	-1.925526000	1.508178000
6	0.095081000	-2.078263000	2.901700000
1	0.326617000	-1.224773000	3.531957000
6	-0.208091000	-3.309346000	3.484081000
1	-0.205743000	-3.408697000	4.564956000
6	-0.508034000	-4.405833000	2.676231000
1	-0.732328000	-5.370057000	3.121048000
6	-0.513046000	-4.260433000	1.290388000
1	-0.717866000	-5.119729000	0.658776000
6	-0.209146000	-3.029710000	0.691492000
6	-0.099888000	-2.936566000	-0.805521000
6	-3.433993000	-2.775558000	-1.469959000
1	-2.690766000	-4.441029000	-0.584784000
6	-3.165076000	4.816732000	0.053148000
1	-3.913675000	5.465129000	0.517339000
1	-2.211783000	5.076611000	0.520839000
6	-3.123619000	5.063116000	-1.458537000
1	-2.880864000	6.110787000	-1.659854000
1	-4.092631000	4.848025000	-1.918867000
1	-2.371749000	4.437227000	-1.947369000
1	-1.011139000	-3.393811000	-2.554675000
6	-3.162159000	-1.718231000	-2.567430000
6	-4.134086000	-0.571609000	-2.595395000
1	-4.032971000	0.013764000	-1.673875000
1	-3.934259000	0.056206000	-3.463741000
8	-2.271620000	-1.876100000	-3.381578000
1	-5.158232000	-0.954084000	-2.613411000

Os1 of benzoyl carbonyl

SCF Done: E(RB+HF-LYP) = -1800.52861830

Sum of electronic and thermal Free Energies= -1799.944742

8	-1.362328000	-1.905748000	0.350039000
8	-0.695225000	2.214254000	-1.627459000
8	4.658606000	2.948672000	-0.468277000
7	-5.954896000	-1.096832000	-0.570652000
7	3.160275000	-3.146895000	1.135201000
7	1.319004000	3.252618000	-1.584978000
7	2.516547000	3.380846000	-0.899782000
6	-4.731716000	-0.637212000	-0.202409000
6	-3.613024000	-1.503843000	-0.097415000

1	-3.686834000	-2.564838000	-0.289411000
6	-2.382887000	-1.005829000	0.279717000
6	-0.108120000	-1.521810000	0.714327000
6	0.853193000	-2.511495000	0.742387000
1	0.553431000	-3.509344000	0.455056000
6	2.188371000	-2.200270000	1.109284000
6	2.474276000	-0.835487000	1.465769000
1	3.469945000	-0.556027000	1.780557000
6	1.506012000	0.128918000	1.431261000
1	1.758662000	1.145012000	1.712181000
6	0.165680000	-0.160914000	1.040357000
6	-0.873105000	0.790317000	0.969493000
6	-2.161083000	0.367011000	0.591421000
6	-3.289814000	1.226828000	0.463711000
1	-3.156999000	2.285108000	0.655366000
6	-4.517587000	0.756675000	0.089655000
1	-5.331140000	1.461340000	-0.013729000
6	-7.150432000	-0.237613000	-0.588785000
1	-7.099545000	0.469380000	0.242638000
1	-8.006469000	-0.885074000	-0.377650000
6	-7.359455000	0.489918000	-1.920434000
1	-8.279132000	1.081497000	-1.882278000
1	-7.450120000	-0.220086000	-2.748001000
1	-6.527524000	1.163445000	-2.144846000
6	-6.170866000	-2.494710000	-0.974823000
1	-5.303217000	-2.841060000	-1.542732000
1	-7.009711000	-2.496715000	-1.676652000
6	-6.469183000	-3.430106000	0.201686000
1	-6.639410000	-4.447436000	-0.163366000
1	-7.366362000	-3.111478000	0.740912000
1	-5.639527000	-3.455276000	0.913619000
6	4.574081000	-2.817724000	1.387021000
1	4.807227000	-1.855759000	0.924038000
1	5.169998000	-3.559907000	0.847923000
6	4.948327000	-2.828064000	2.872171000
1	6.014479000	-2.612259000	2.989978000
1	4.750652000	-3.805875000	3.321742000
1	4.384046000	-2.078916000	3.434773000
6	-0.610984000	2.209617000	1.359766000
6	-0.900620000	2.600563000	2.673774000
1	-1.327699000	1.876865000	3.361511000
6	-0.640904000	3.901861000	3.105797000
1	-0.876123000	4.187169000	4.126339000
6	-0.083254000	4.829180000	2.226216000

1	0.110884000	5.846063000	2.551879000
6	0.219777000	4.447081000	0.920844000
1	0.627161000	5.175739000	0.227208000
6	-0.034172000	3.143366000	0.473937000
6	0.159665000	2.798553000	-0.975048000
6	3.629085000	2.539600000	-0.987607000
1	2.781548000	4.320050000	-0.624608000
6	2.871861000	-4.565668000	0.878106000
1	3.609420000	-5.147151000	1.438823000
1	1.899707000	-4.817316000	1.310138000
6	2.928864000	-4.939612000	-0.606893000
1	2.726482000	-6.007580000	-0.732173000
1	3.918084000	-4.732418000	-1.025803000
1	2.192431000	-4.378947000	-1.189405000
1	1.363579000	3.093077000	-2.587022000
6	3.590844000	1.217404000	-1.705565000
6	2.452665000	0.507216000	-2.127731000
6	4.860811000	0.663677000	-1.954287000
6	2.593378000	-0.714816000	-2.789075000
1	1.450063000	0.868536000	-1.947658000
6	4.994983000	-0.551459000	-2.618298000
1	5.731504000	1.216021000	-1.619879000
6	3.858240000	-1.245151000	-3.042213000
1	1.704117000	-1.247289000	-3.113038000
1	5.985162000	-0.951702000	-2.814763000
1	3.958872000	-2.188440000	-3.571317000

Os1 of picolinic carbonyl

SCF Done: E(RB+HF-LYP) = -1816.56981461

Sum of electronic and thermal Free Energies= -1815.997746

8	-1.451222000	1.924167000	-0.268998000
8	-0.535340000	-2.298059000	1.528998000
8	4.422230000	-1.980877000	-0.509681000
7	-6.009705000	1.021418000	0.729327000
7	3.025706000	3.266017000	-1.142082000
7	1.551692000	-3.166465000	1.243232000
7	2.682861000	-3.069658000	0.417715000
6	-4.790795000	0.592551000	0.312825000
6	-3.684961000	1.476389000	0.217007000
1	-3.766400000	2.527554000	0.454530000
6	-2.458658000	1.009334000	-0.209061000
6	-0.199728000	1.568201000	-0.668697000
6	0.745985000	2.573842000	-0.691455000
1	0.435807000	3.559541000	-0.374760000

6	2.076437000	2.295033000	-1.097681000
6	2.382573000	0.939669000	-1.471781000
1	3.379432000	0.669502000	-1.791455000
6	1.425940000	-0.037889000	-1.452259000
1	1.696240000	-1.040913000	-1.760160000
6	0.085679000	0.223035000	-1.043210000
6	-0.945007000	-0.740345000	-1.003648000
6	-2.229145000	-0.346857000	-0.583069000
6	-3.345107000	-1.225044000	-0.464059000
1	-3.205152000	-2.273395000	-0.699950000
6	-4.568295000	-0.785504000	-0.041098000
1	-5.370465000	-1.504115000	0.055003000
6	-7.195168000	0.148225000	0.737426000
1	-7.153734000	-0.524208000	-0.122677000
1	-8.062648000	0.793377000	0.570106000
6	-7.368051000	-0.634670000	2.042539000
1	-8.281584000	-1.235372000	1.999433000
1	-7.449319000	0.040422000	2.899748000
1	-6.524006000	-1.306455000	2.222565000
6	-6.231138000	2.397670000	1.199261000
1	-5.353330000	2.729901000	1.759995000
1	-7.052018000	2.358937000	1.921076000
6	-6.570012000	3.379492000	0.072628000
1	-6.745251000	4.377173000	0.486352000
1	-7.475455000	3.071825000	-0.459109000
1	-5.758158000	3.448280000	-0.656785000
6	4.430647000	2.979530000	-1.476135000
1	4.714045000	2.015925000	-1.045848000
1	5.036699000	3.729369000	-0.959035000
6	4.721492000	3.017528000	-2.979560000
1	5.784152000	2.829549000	-3.159808000
1	4.474959000	3.995440000	-3.403952000
1	4.144346000	2.260395000	-3.517571000
6	-0.681583000	-2.135452000	-1.467582000
6	-1.072943000	-2.496883000	-2.763693000
1	-1.579162000	-1.767659000	-3.389146000
6	-0.808624000	-3.774724000	-3.258979000
1	-1.120772000	-4.037255000	-4.264862000
6	-0.147281000	-4.707498000	-2.460739000
1	0.050213000	-5.707061000	-2.834797000
6	0.252028000	-4.355243000	-1.171592000
1	0.735060000	-5.089826000	-0.533275000
6	-0.004792000	-3.074292000	-0.663867000
6	0.307364000	-2.763411000	0.776544000

6	3.653976000	-2.095302000	0.441686000
1	2.737266000	-3.712561000	-0.360694000
6	2.708846000	4.676559000	-0.872681000
1	3.411683000	5.278159000	-1.456291000
1	1.716479000	4.903283000	-1.271362000
6	2.805093000	5.051282000	0.610014000
1	2.582452000	6.114329000	0.742756000
1	3.812133000	4.867743000	0.996542000
1	2.100512000	4.474963000	1.216265000
1	1.771966000	-2.858233000	2.193027000
6	3.834718000	-1.254571000	1.683741000
6	4.812976000	-0.255646000	1.644787000
6	5.046590000	0.493439000	2.795408000
1	5.379104000	-0.114867000	0.731768000
6	3.350878000	-0.803912000	3.887852000
6	4.299975000	0.218458000	3.940784000
1	5.805564000	1.269967000	2.803384000
1	2.755737000	-1.055956000	4.761992000
1	4.451822000	0.773382000	4.860613000
7	3.120447000	-1.528589000	2.788080000

Os1 of coumarin carbonyl

SCF Done: E(RB+HF-LYP) = -2065.30083131

Sum of electronic and thermal Free Energies= -2064.693910

8	1.140764000	-2.041826000	-0.722136000
8	1.845477000	2.567641000	1.106964000
8	-3.177347000	2.914345000	-0.430128000
7	5.637367000	-1.939281000	0.806941000
7	-3.305428000	-2.642112000	-2.298904000
7	-0.100950000	3.742213000	1.072073000
7	-1.342749000	3.874682000	0.463667000
6	4.566008000	-1.304614000	0.270241000
6	3.341485000	-1.983928000	0.035291000
1	3.218636000	-3.037195000	0.243599000
6	2.268703000	-1.308460000	-0.506217000
6	0.028767000	-1.479839000	-1.269248000
6	-1.045922000	-2.323682000	-1.473629000
1	-0.933998000	-3.356250000	-1.174392000
6	-2.244192000	-1.828449000	-2.048417000
6	-2.294729000	-0.424111000	-2.355442000
1	-3.189807000	0.008696000	-2.780588000
6	-1.216457000	0.394081000	-2.145279000
1	-1.298999000	1.446115000	-2.391439000
6	0.008869000	-0.096149000	-1.607534000

6	1.173840000	0.683676000	-1.410804000
6	2.312712000	0.074902000	-0.856202000
6	3.552432000	0.740316000	-0.617054000
1	3.621786000	1.797159000	-0.839247000
6	4.628156000	0.090240000	-0.084080000
1	5.531308000	0.654831000	0.101386000
6	6.947637000	-1.284874000	0.966935000
1	7.123817000	-0.617868000	0.119983000
1	7.703112000	-2.072188000	0.889249000
6	7.098486000	-0.541164000	2.297286000
1	8.102276000	-0.112355000	2.372511000
1	6.956853000	-1.217475000	3.145689000
1	6.371189000	0.270457000	2.388551000
6	5.563652000	-3.333122000	1.272317000
1	4.582676000	-3.508559000	1.721712000
1	6.289563000	-3.435623000	2.083930000
6	5.858506000	-4.358041000	0.172104000
1	5.813447000	-5.371012000	0.583226000
1	6.858052000	-4.209020000	-0.247081000
1	5.136295000	-4.286953000	-0.646008000
6	-4.579227000	-2.135714000	-2.837461000
1	-4.804354000	-1.166127000	-2.386135000
1	-5.361241000	-2.816664000	-2.488972000
6	-4.605852000	-2.047756000	-4.366583000
1	-5.587478000	-1.701795000	-4.703889000
1	-4.418462000	-3.025343000	-4.820913000
1	-3.850553000	-1.351157000	-4.741045000
6	1.197674000	2.100395000	-1.891336000
6	1.356116000	2.309457000	-3.270422000
1	1.478210000	1.451427000	-3.924775000
6	1.366034000	3.596340000	-3.806351000
1	1.504167000	3.734530000	-4.874033000
6	1.195504000	4.697748000	-2.967747000
1	1.205022000	5.704209000	-3.373946000
6	1.014141000	4.500966000	-1.600421000
1	0.895694000	5.356048000	-0.940855000
6	1.017458000	3.212019000	-1.045520000
6	0.951564000	3.091029000	0.458295000
6	-2.333971000	2.915518000	0.460286000
1	-1.437028000	4.586092000	-0.249819000
6	-3.229948000	-4.097754000	-2.105080000
1	-3.894463000	-4.554149000	-2.844538000
1	-2.222644000	-4.441078000	-2.354390000
6	-3.629822000	-4.547433000	-0.695861000

1	-3.556489000	-5.636182000	-0.614290000
1	-4.663580000	-4.264588000	-0.473021000
1	-2.983853000	-4.101696000	0.066145000
1	-0.142468000	3.733387000	2.091218000
6	-2.406653000	1.909444000	1.580305000
6	-3.081855000	0.753836000	1.311040000
6	-1.971257000	2.188255000	2.955418000
6	-3.322484000	-0.240136000	2.309104000
1	-3.454726000	0.604990000	0.301972000
6	-3.997132000	-1.456638000	2.071284000
6	-2.870067000	0.035127000	3.613391000
6	-4.201213000	-2.356144000	3.104709000
1	-4.356788000	-1.670014000	1.068896000
6	-3.070363000	-0.864788000	4.661851000
6	-3.735783000	-2.056342000	4.398051000
1	-4.725880000	-3.288267000	2.922991000
1	-2.710472000	-0.613871000	5.653309000
1	-3.901614000	-2.762239000	5.205879000
8	-1.430706000	3.193948000	3.369345000
8	-2.225661000	1.200383000	3.893374000

Table 1 Crystallographic data for RhBN-Fo

crystal data	**RhBN-Fo**
CCDC no.	CCDC-861458
Formula	$C_{29}H_{32}N_4O_3$
formula weight	484.59
temperature, K	113(2)
wavelength, Å	0.71073
crystal system	triclinic
space group	*P*-1
a (Å)	9.0438(8)
b (Å)	12.1015(12)
c (Å)	14.1578(14)
α, °	98.54(5)
β, °	108.13(4)
γ, °	110.06(3)
V, Å^3	1325.5(7)
Z	2
crystal size (mm^3)	0.20 × 0.18 × 0.12
D(calcd), Mg m^{-3}	1.214
μ, mm^{-1}	0.080
F(000)	516
θ range, °	1.58 to 27.87
h, *k*, *l* range	$-11 \le h \le 11$
	$-15 \le k \le 15$
	$-18 \le l \le 18$
Reflections collected/unique	17076 / 6292
Data/restraints/parameters	6292 / 128 / 367
R and w*R2*	0.0424 and 0.1037
Goodness-of-fit on F^2	0.94
Max. res. peak and hole (e Å^{-3})	0.263 and –0.189

Figures

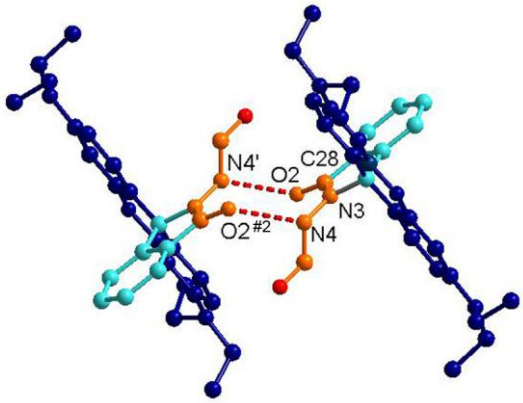


Figure S1: A dimer of two **RhBN-Fo** molecules. Two reciprocal hydrogen bonds occur through N4–H4···O2 interactions showing the R_2^2 (8) in a chair conformation (orange colored). [N4–H4 ··O2 $^{\#2}$: 2.931 (9) Å, N4–H4 ··O2 $^{\#2}$ angle 162.710 (7) °, #2 = 2 – x, 2 – y, 1 – z].