Electronic Supporting Information

Synthesis and chemistry of a very stable but reactive diisocyanate, trioxabicyclo[3.3.1]nonadiene diisocyanate

Ralph Smounig,[a] Sabine Leber,[a,b] David Kvaskoff,[b] Gert Kollenz[a]* and Curt Wentrup[b]*

Contents:

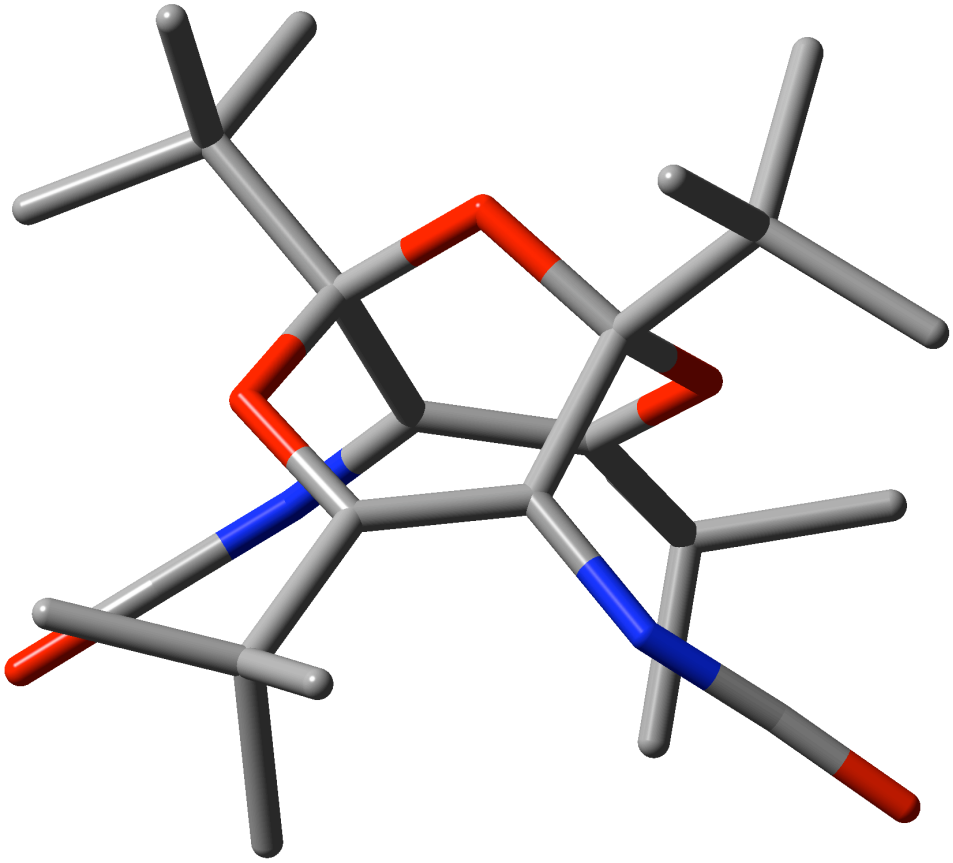


Figure S1. Another view of the structure of diisocyanate **5** calculated at the B3LYP/6-31G** level. Both NCO groups are *endo* with respect to the bicyclic system (hydrogen atoms omitted for clarity). A C2 symmetry axis passes through the central oxygen. The C=C double bonds are twisted by an angle 11.6^{o}.

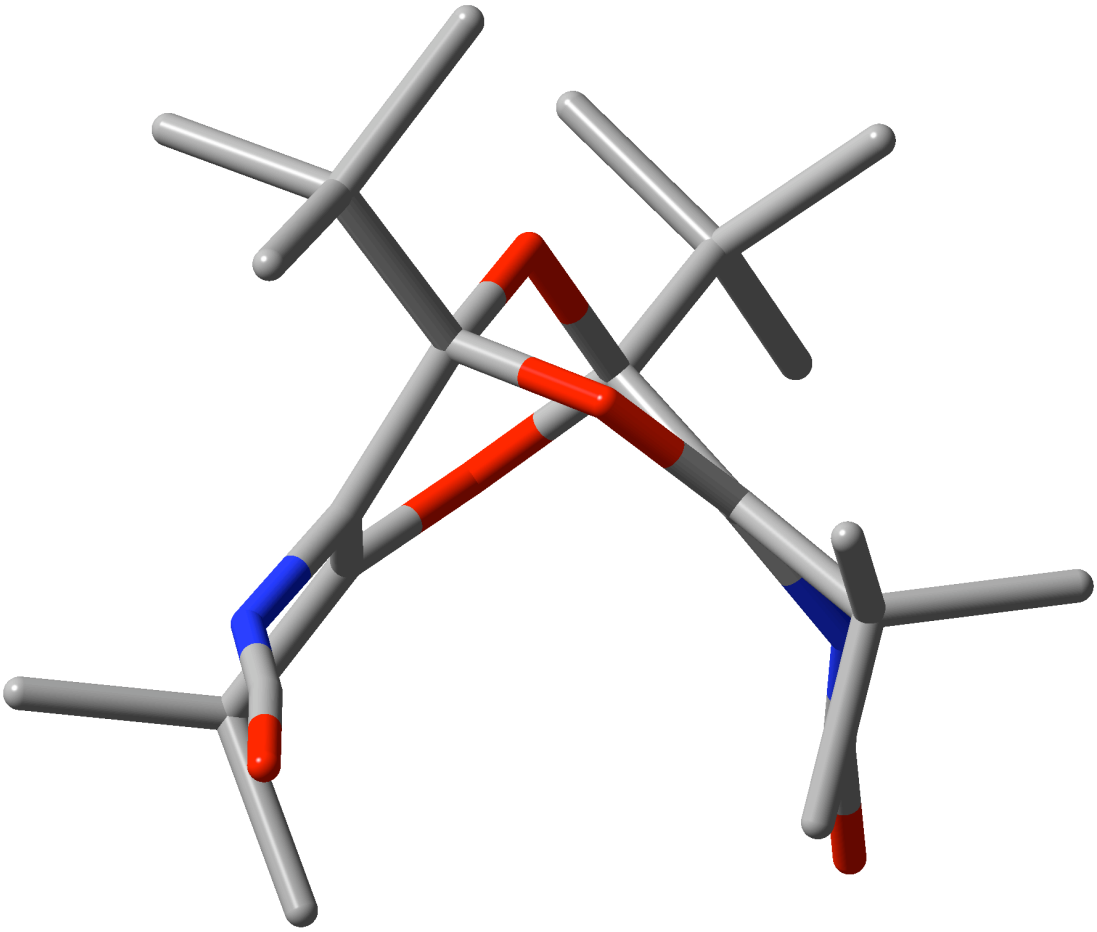


Figure S2. Another view of the structure of diisocyanate **5** calculated at the B3LYP/6-31G** level. The C=C double bonds are twisted by an angle 11.6°. The concave angle between the two rings is 110°.

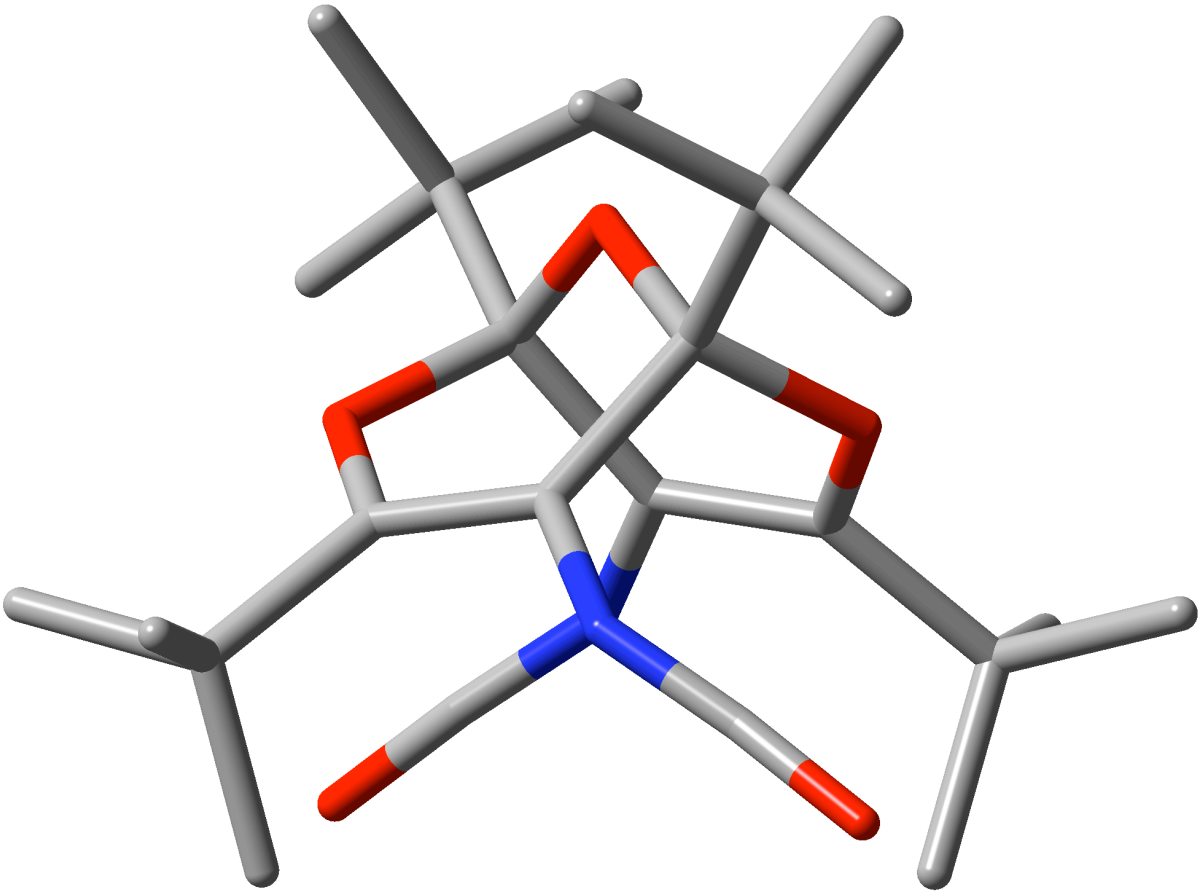


Figure S3. Another view of the structure of diisocyanate **5** calculated at the B3LYP/6-31G** level. The C=C double bonds are twisted by an angle 11.6°. The concave angle between the two rings is 110°. The angle between the two C-NCO moieties is 112°.

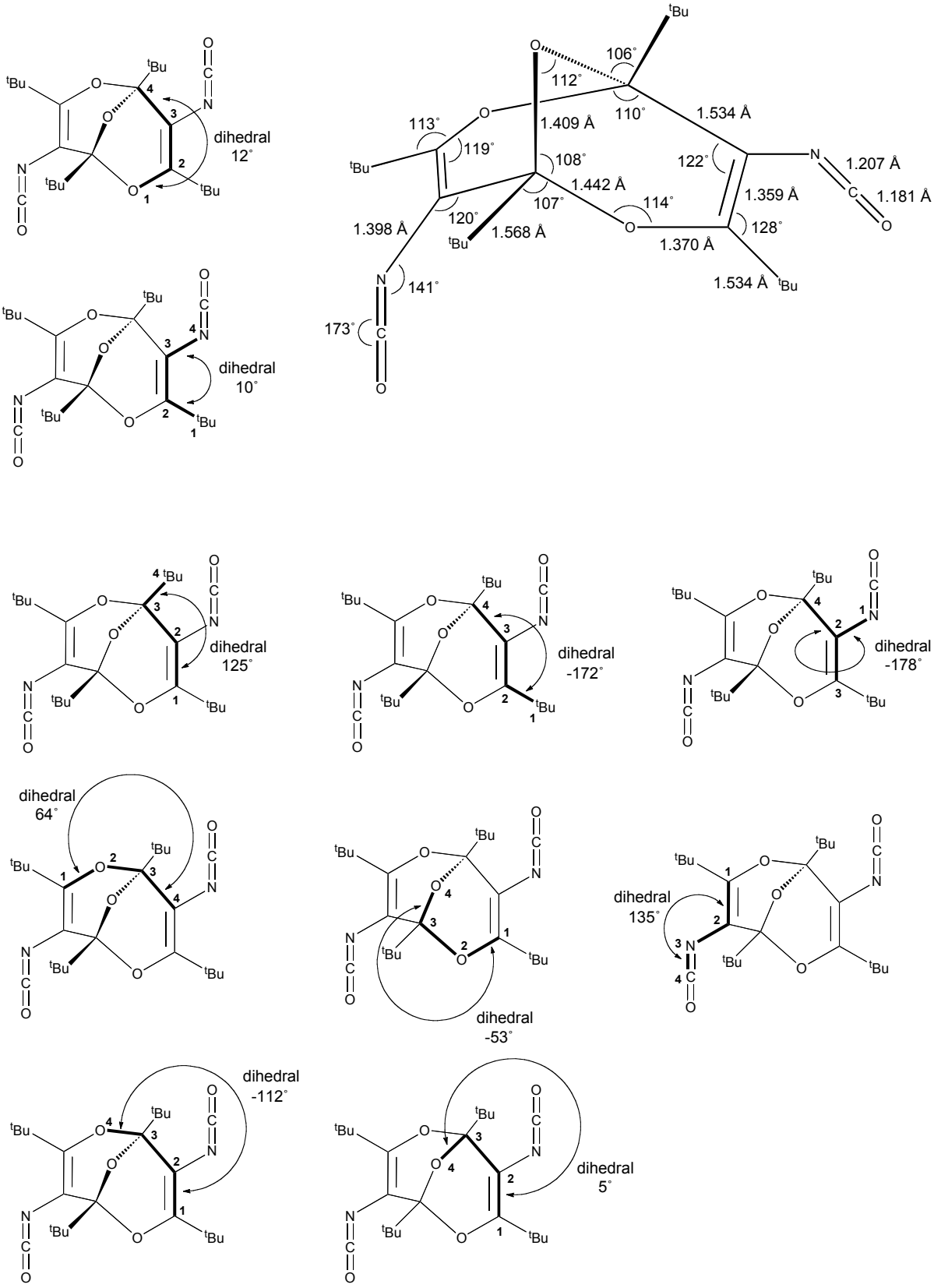


Figure S4. Additional bond lengths (Å) and angles (degrees) for diisocyanate **5** calculated at the B3LYP/6-31G** level.

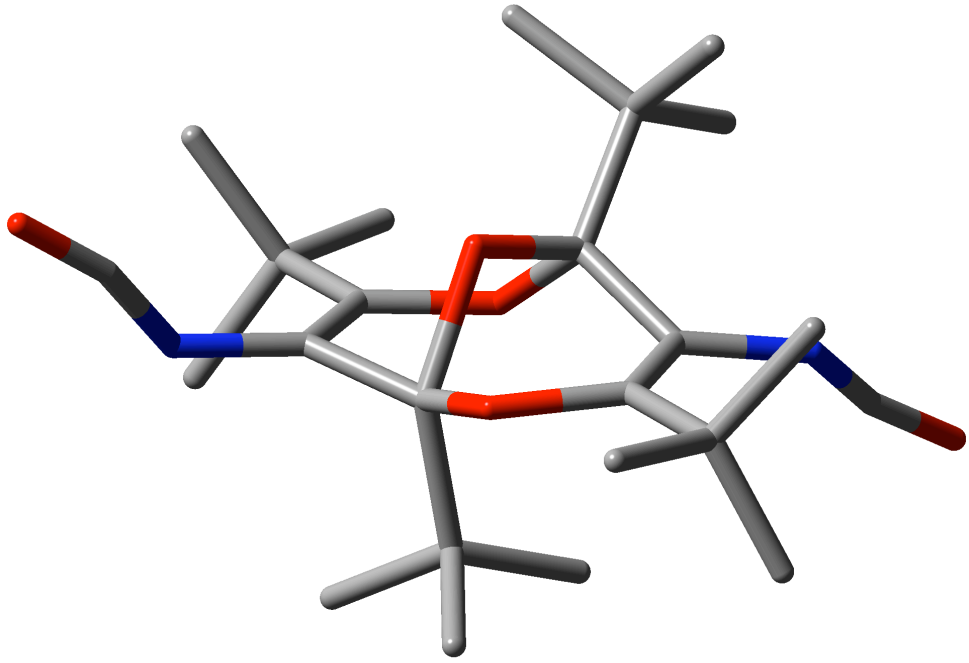
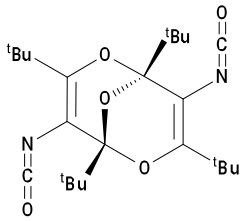


Figure S5. Non-obserevd *exo,endo*-isomer of **5** at the PM6 level. The *exo,endo* and *exo,exo* isomers are considerably more strained than the *endo,endo* isomer (Figure S1), and neither forms a stable minimum; attempted optimization at the B3LYP level leads to ring opening.

Calculated Energies and Cartesian Coordinates (B3LYP/6-31G**)

Calculations were carried out at the B3LYP/6-31G** level using the Gaussian suite of programs.[1] The temperature used was 298.15 K, and calculated wavenumbers were scaled by a factor 0.9613.[2]

(*endo,endo*)-Trioxabicyclo[3.3.1]nonadiene diisocyanate 5



Atom Type	Coordinates (Angstroms) X	Y	Z
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C	-1.15325796	0.17296775	0.97078181
C	2.30894501	-0.53536807	1.96601571
C	-2.30894501	0.53536807	1.96601571
C	-0.82217331	1.18739170	-0.13073040
C	0.82217331	-1.18739170	-0.13073040
C	-0.43165727	-1.68263707	-0.29297564
C	-0.87783883	-2.81572997	-1.22577760
O	-1.47548870	-1.10135130	0.37822991
C	0.43165727	1.68263707	-0.29297564
O	1.47548870	1.10135130	0.37822991
N	-1.84733791	1.57215692	-0.99996800
N	1.84733791	-1.57215692	-0.99996800
C	0.87783883	2.81572997	-1.22577760
C	0.83677880	2.32144815	-2.69243060
H	-0.17035527	2.02142031	-2.98999430
H	1.16259535	3.12563188	-3.36110159
H	1.51153675	1.47246717	-2.84170700
C	2.32547252	3.24203494	-0.89690394
H	2.42247643	3.58027970	0.13864914
H	3.03699765	2.42931812	-1.05680594
H	2.60492781	4.07229454	-1.55282684
C	-0.03620637	4.04988089	-1.05751329
H	-1.07426667	3.83143088	-1.31211021
H	-0.00563499	4.41952766	-0.02742998
H	0.31236045	4.85402675	-1.71403149
C	3.69660741	-0.54431760	1.29169483
H	3.84174176	-1.41298857	0.64771307
H	3.87421731	0.36327858	0.70945425
H	4.46418092	-0.59248440	2.07070458
C	2.02872182	-1.92052928	2.57982994
H	2.79789979	-2.15280124	3.32326016
H	1.05581888	-1.94676373	3.07682821
H	2.04787742	-2.70871455	1.82158766
C	2.33327154	0.52894533	3.08751026
H	2.51302397	1.52706240	2.68001980
H	1.39663812	0.55002652	3.64692616
H	3.14283870	0.29539962	3.78624123
C	-2.02872182	1.92052928	2.57982994

H	-2.79789979	2.15280124	3.32326016
H	-1.05581888	1.94676373	3.07682821
H	-2.04787742	2.70871455	1.82158766
C	-2.33327154	-0.52894533	3.08751026
H	-2.51302397	-1.52706240	2.68001980
H	-1.39663812	-0.55002652	3.64692616
H	-3.14283870	-0.29539962	3.78624123
C	-3.69660741	0.54431760	1.29169483
H	-3.84174176	1.41298857	0.64771307
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H	-4.46418092	0.59248440	2.07070458
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C	-2.75674703	1.10026671	-1.63812967
O	-3.68187676	0.77872677	-2.29801609
O	3.68187676	-0.77872677	-2.29801609
C	0.03620637	-4.04988089	-1.05751329
H	-0.31236045	-4.85402675	-1.71403149
H	1.07426667	-3.83143088	-1.31211021
H	0.00563499	-4.41952766	-0.02742998
C	-2.32547252	-3.24203494	-0.89690394
H	-2.42247643	-3.58027970	0.13864914
H	-3.03699765	-2.42931812	-1.05680594
H	-2.60492781	-4.07229454	-1.55282684
C	-0.83677880	-2.32144815	-2.69243060
H	0.17035527	-2.02142031	-2.98999430
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H	-1.51153675	-1.47246717	-2.84170700

State= 1-A
Point Group: C2
HF= -1421.8904123
RMSD=5.471e-09\RMSF=1.658e-05
Zero-point correction= 0.570795 (Hartree/Particle)
Sum of electronic and zero-point Energies= -1421.319618

Vibrational Frequencies (scaled by 0.9613):

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1	B	26.8	0.6	0
2	A	31.4	0.0	0
3	A	36.6	0.2	0
4	A	44.4	0.0	0
5	B	45.2	0.0	0
6	A	50.3	0.0	0
7	B	50.7	1.2	0
8	A	59.8	0.1	0
9	B	63.0	0.1	0
10	B	81.8	0.9	0
11	A	97.8	0.5	0
12	A	119.1	0.0	0
13	B	126.9	0.1	0
14	A	143.9	2.0	0
15	B	156.8	1.3	0
16	B	178.7	1.0	0
17	A	193.8	0.4	0
18	A	207.4	0.0	0
19	B	210.7	0.9	0
20	A	216.1	0.0	0
21	B	219.8	0.2	0
22	A	227.0	0.1	0

23	B	238.1	0.3	0
24	A	239.9	0.0	0
25	A	242.0	0.2	0
26	B	249.0	1.3	0
27	B	253.0	0.7	0
28	A	258.2	0.1	0
29	B	261.2	0.0	0
30	A	262.6	0.0	0
31	B	262.8	0.2	0
32	A	274.0	1.9	0
33	B	276.0	0.0	0
34	B	290.3	0.5	0
35	A	290.7	0.8	0
36	A	303.3	0.4	0
37	B	303.4	6.5	0
38	A	306.2	0.7	0
39	B	309.8	0.5	0
40	B	324.2	0.8	0
41	A	339.7	0.6	0
42	A	344.6	4.9	0
43	B	358.8	2.7	0
44	B	373.3	0.4	0
45	A	376.6	0.6	0
46	B	379.7	0.3	0
47	A	390.9	4.5	0
48	A	393.1	2.1	0
49	B	404.1	0.1	0
50	A	405.9	0.0	0
51	B	420.7	3.5	0
52	A	453.7	0.4	0
53	B	465.8	3.9	0
54	B	491.5	3.8	0
55	A	500.3	0.4	0
56	B	507.6	12.3	1
57	A	514.4	20.4	1
58	B	535.6	7.7	0
59	A	537.8	0.3	0
60	A	560.2	1.6	0
61	B	571.9	15.4	1
62	A	582.1	3.3	0
63	A	610.6	4.3	0
64	B	610.9	24.6	2
65	B	633.5	1.1	0
66	B	667.6	20.2	1
67	A	681.5	0.3	0
68	A	690.5	1.5	0
69	B	701.4	9.8	1
70	A	731.5	0.6	0
71	B	782.4	1.1	0
72	A	798.1	0.5	0
73	B	807.1	3.2	0
74	A	857.1	0.8	0
75	B	867.2	82.9	5
76	A	903.0	1.8	0
77	B	903.5	3.7	0
78	A	904.6	0.0	0
79	B	904.8	0.3	0
80	A	906.2	1.7	0
81	B	909.3	9.9	1
82	B	913.0	15.8	1
83	A	913.4	0.6	0

84	B	934.0	15.9	1
85	A	934.3	0.2	0
86	B	935.3	52.8	3
87	A	935.4	0.7	0
88	B	935.9	30.0	2
89	A	941.1	41.6	3
90	B	988.8	21.2	1
91	A	991.9	21.5	1
92	B	1009.5	11.1	1
93	A	1010.1	9.0	1
94	B	1014.9	2.1	0
95	A	1017.4	3.9	0
96	B	1017.5	11.8	1
97	A	1017.8	5.2	0
98	B	1025.3	34.5	2
99	A	1033.1	39.8	3
100	B	1071.4	80.1	5
101	B	1085.8	227.7	15
102	A	1109.3	14.9	1
103	A	1134.3	41.3	3
104	A	1169.4	41.7	3
105	B	1180.1	97.2	6
106	B	1184.7	56.3	4
107	A	1184.9	1.4	0
108	B	1200.8	0.5	0
109	A	1201.2	0.0	0
110	B	1206.4	47.3	3
111	B	1211.4	1.5	0
112	A	1212.4	22.4	1
113	A	1219.6	4.7	0
114	B	1225.0	10.5	1
115	A	1244.9	7.9	1
116	A	1267.1	11.7	1
117	B	1277.3	99.9	6
118	B	1353.8	1.6	0
119	A	1354.7	0.4	0
120	B	1355.0	4.1	0
121	A	1355.6	5.3	0
122	B	1357.1	8.7	1
123	A	1357.3	2.1	0
124	A	1358.7	0.5	0
125	B	1358.8	7.1	0
126	B	1385.7	24.1	2
127	A	1387.5	21.0	1
128	B	1389.6	16.9	1
129	A	1390.2	0.7	0
130	A	1434.4	0.5	0
131	B	1435.3	0.2	0
132	B	1435.7	0.6	0
133	A	1436.2	0.0	0
134	B	1440.9	1.0	0
135	A	1442.7	0.5	0
136	A	1446.2	0.1	0
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139	B	1447.4	4.2	0
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141	B	1449.6	9.7	1
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143	A	1453.6	0.5	0
144	B	1456.8	0.7	0

145	A	1458.0	2.9	0
146	A	1459.0	1.7	0
147	B	1459.9	1.7	0
148	B	1461.3	5.3	0
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150	B	1466.5	5.6	0
151	A	1467.4	0.3	0
152	B	1478.7	17.2	1
153	A	1479.8	11.8	1
154	B	1484.3	23.7	2
155	A	1484.8	18.0	1
156	A	1604.7	5.2	0
157	B	1613.1	35.2	2
158	B	2289.5	1562.5	100
159	A	2289.8	550.5	35
160	B	2928.8	13.9	1
161	A	2929.1	31.3	2
162	B	2931.4	21.0	1
163	A	2931.4	5.7	0
164	B	2933.3	32.8	2
165	A	2933.3	1.8	0
166	B	2938.6	5.9	0
167	A	2938.7	22.1	1
168	B	2938.8	66.4	4
169	A	2939.0	0.0	0
170	B	2945.1	53.0	3
171	A	2945.4	15.6	1
172	B	2992.2	8.7	1
173	A	2992.4	12.4	1
174	B	2994.3	32.3	2
175	A	2994.6	12.2	1
176	A	2999.0	13.5	1
177	B	2999.0	13.0	1
178	B	3003.2	6.2	0
179	A	3003.2	11.6	1
180	B	3004.7	29.3	2
181	A	3004.8	79.2	5
182	B	3008.9	46.0	3
183	A	3009.0	54.7	4
184	B	3016.3	24.1	2
185	A	3016.6	3.4	0
186	B	3020.3	23.7	2
187	A	3020.4	1.1	0
188	A	3021.7	1.5	0
189	B	3021.8	42.0	3
190	B	3031.7	13.6	1
191	A	3032.0	0.2	0
192	A	3032.0	9.9	1
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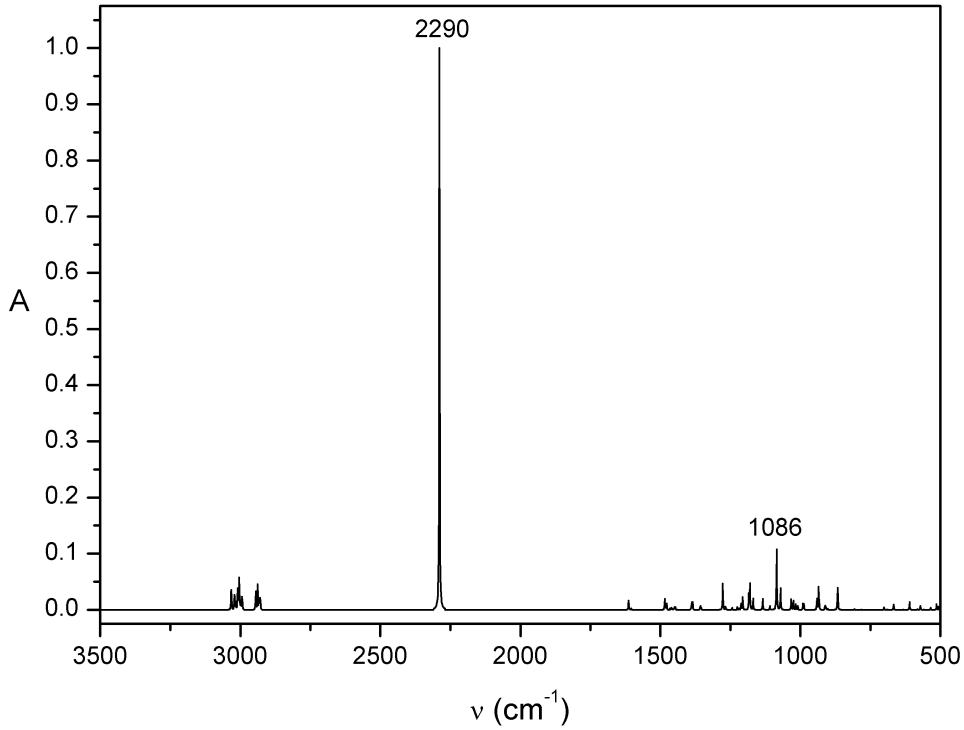

Figure S6. Calculated IR spectrum of diisocyanate **5**.

References

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[2] M. W. Wong, *Chem. Phys. Lett.* **1996**, *256*, 391.