Direct Observation of Carbene and Diazo Fromation from Phenyldiazirines by Ultrafast Infrared Spectroscopy

Yunlong Zhang[a], Gotard Burdzinski[b], Jacek Kubicki[b], and Matthew S. Platz[a]*

[a] *Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio, 43210, U.S.A.*

[b] *Quantum Electronics Laboratory, Faculty of Physics, Adam Mickiewicz University, 85 Umultowska, Poznan 61-614, Poland*

RECEIVED DATE (automatically inserted by publisher); platz.1@osu.edu

Ultrafast IR pump-probe absorption measurements were performed using the home-built spectrometer at the Ohio State University described elsewhere.[1] Solution concentrations were adjusted to absorption of unity in a 1 mm cell. Sample solutions were excited in a stainless steel flow cell equipped with 2 mm thick BaF$_2$ windows. After passing the sample reference and probe beam were spectrally dispersed with a polychromator and independently imaged on a liquid-nitrogen cooled HgCdTe detector (2 x 32 pixels). The pump pulse energy was about 4 μJ at the sample position. The entire set of pump-probe delay positions (cycle) is repeated at least three times, to observe data reproducibility from cycle to cycle. To avoid rotational diffusion effects, the angle between polarizations of the pump beam and the probe beam was set to the magic angle (54.7°). Kinetic traces are analyzed by fitting to a sum of exponential terms. The Band Integrals (BI) of transient species are calculated by trapezoidal rule. All experiments were performed at room temperature.

DFT calculations were performed using the Gaussian 03 suite of programs[2] at The Ohio Supercomputer Center. Geometries were optimized at the B3LYP/6-31G(d) level of theory. Vibrational frequency analyses at the B3LYP/6-31G(d) level were utilized to verify that stationary points obtained corresponded to energy minima. The calculated frequencies were scaled by factor 0.9614.[3] The absolute energies of optimized structures are in Hartrees.

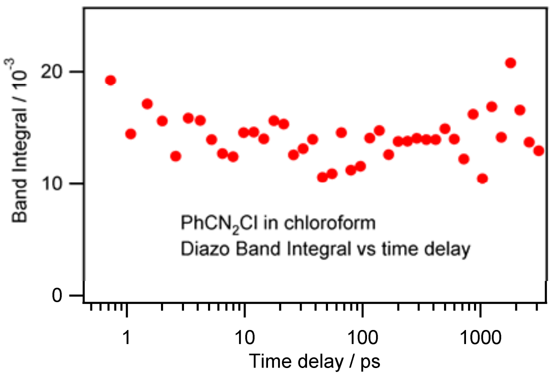
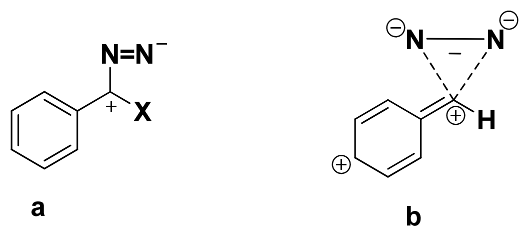


Figure S1. Ultrafast IR (λ_{ex} = 270 nm) on chlorophenyldiazirine in chloroform. The band integrals of the diazo band versus time delay.



Scheme S1. The structure of the zwitterion proposed in reference **4** (a) and another possible zwitterionic structure (b).

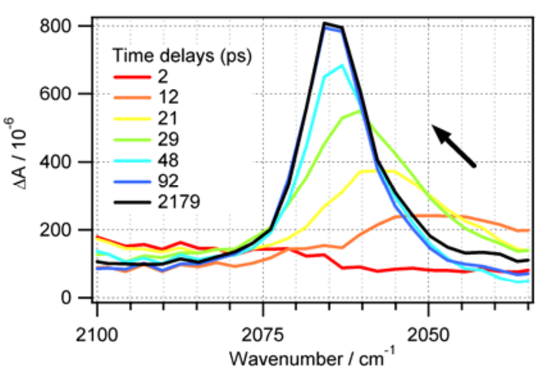


Figure S2. Transient IR spectra of phenyldiazirine (λ_{ex} = 270 nm) in acetonitrile. Spectra of diazo formation at selected time delays.

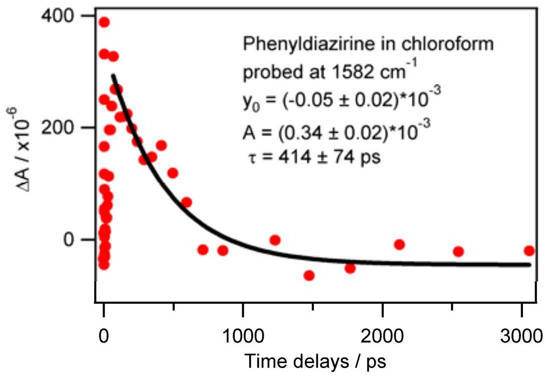


Figure S3. Ultrafast IR on phenyldazirine (λ_{ex} = 270 nm) in chloroform. The decay of phenylcarbene by fitting at 1582 cm^{-1}.

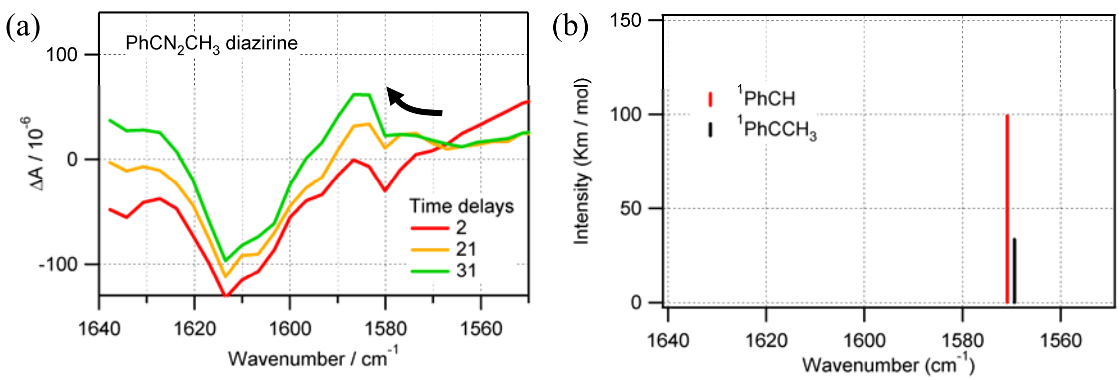


Figure S4. Transient IR spectra of phenylmethyldiazirine (λ_{ex} = 270 nm). (a) Spectra of carbene formation in chloroform at selected time delays, (b) Computed IR frequencies (scaled by 0.9614) of ^{1}PhCH and ^{3}PhCCH$_3$ by B3LYP/6-31+G(d).

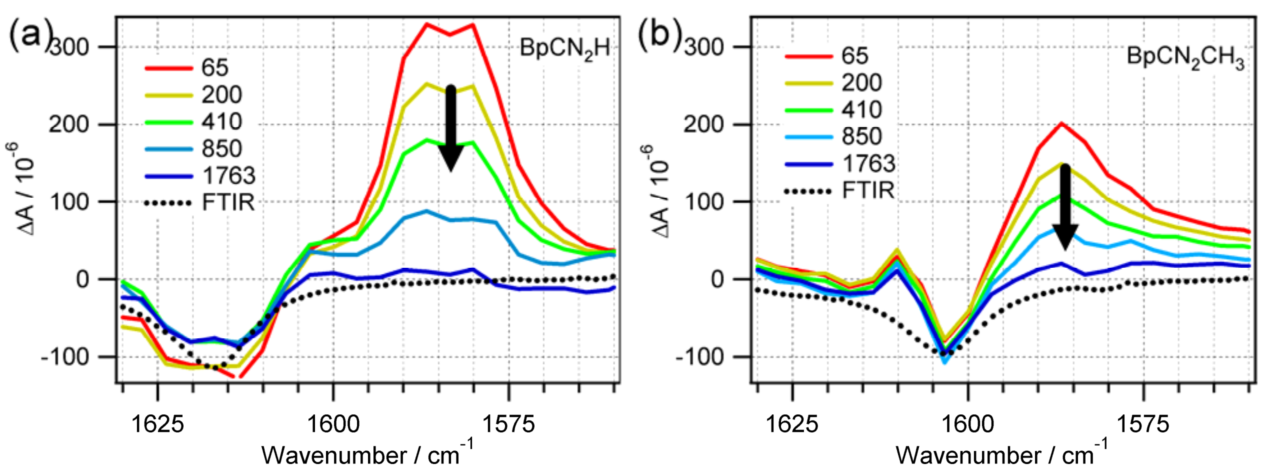


Figure S5. Transient IR spectra of *p*-biphenyldiazirine and *p*-biphenylmethyldiazirine (λ_{ex} = 270 nm) in chloroform. (a) spectra of ^{1}BpCH carbene at selected time delays. (b) spectra of ^{1}BpCCH$_3$ carbene at selected time delays.

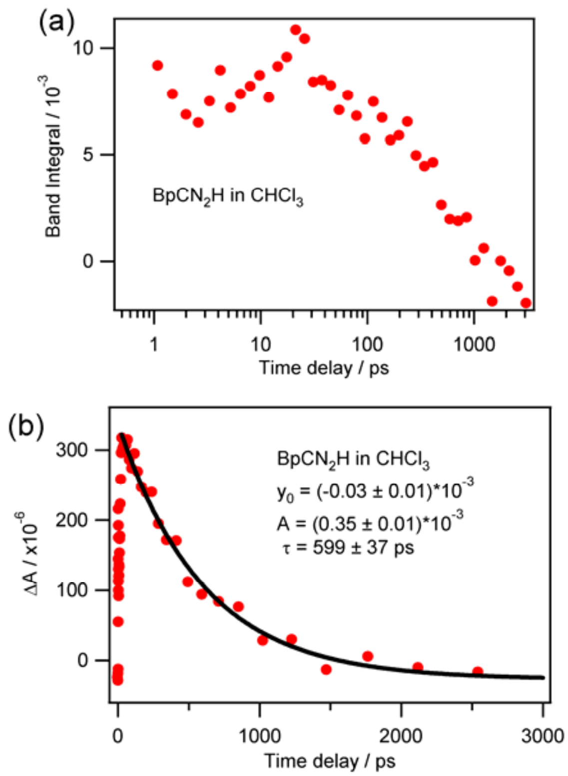


Figure S6. Transient IR spectra of *p*-biphenyldiazirine (λ_{ex} = 270 nm) in chloroform. (a) The kinetic trace of ^{1}BpCH carbene band integration versus time delay. (b) The kinetic trace of ^{1}BpCH carbene band at 1585 cm^{-1} by fitting into exponential function.

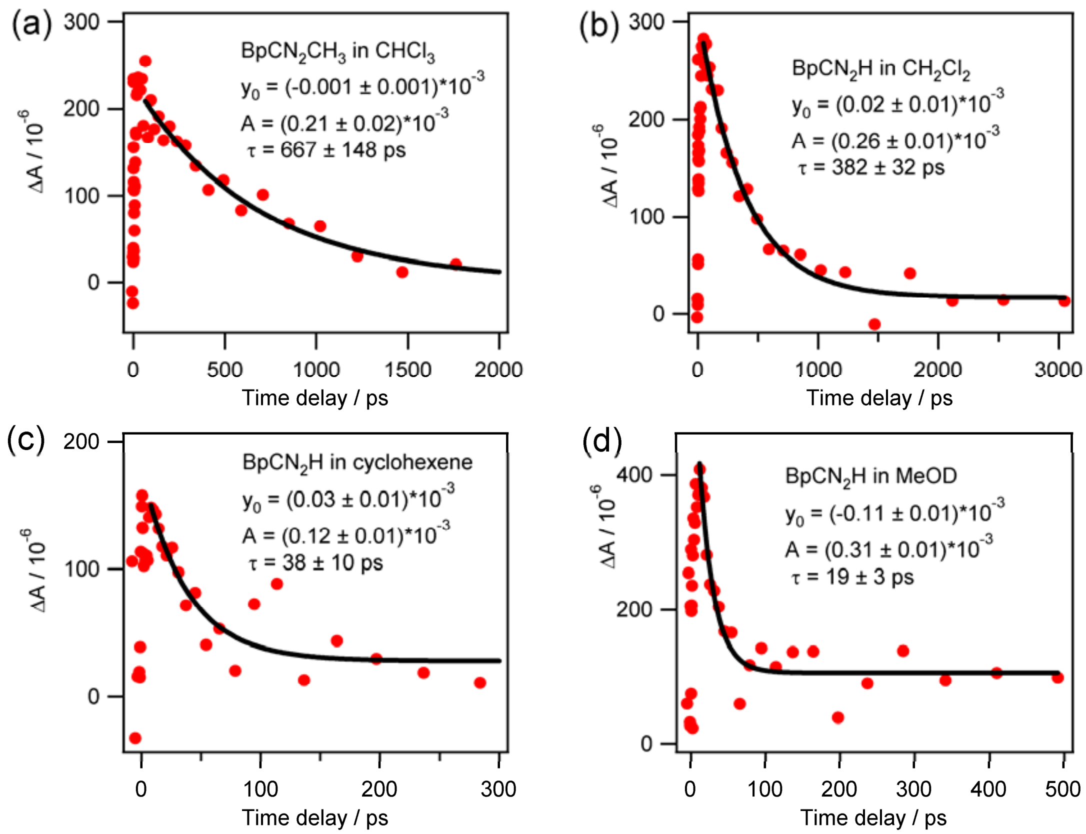


Figure S7. The decay of carbene bands (λ_{ex} = 270 nm) by fitting at the maximum absorption. (a) $BpCN_2CH_3$ diazirine in $CHCl_3$, (b) $BpCN_2H$ diazirine in $CHCl_3$, (c) $BpCN_2H$ diazirine in cyclohexene, (d) $BpCN_2H$ diazirine in methanol-O-*d*.

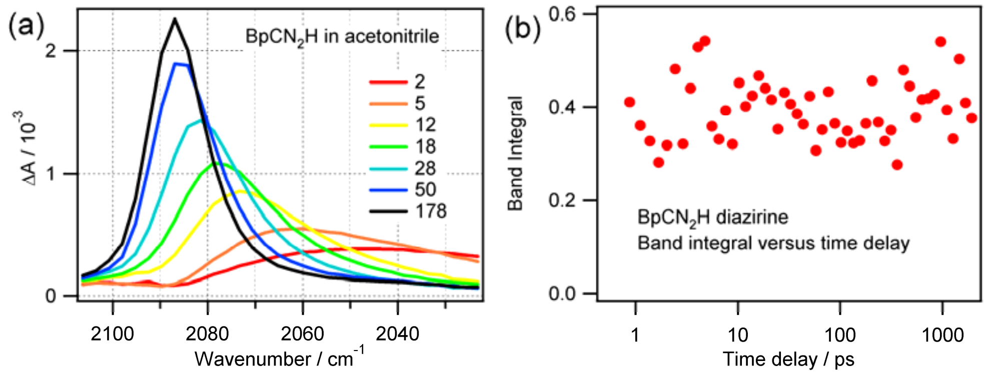


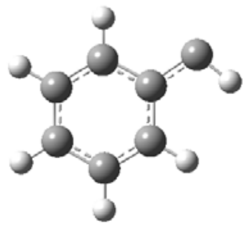
Figure S8. Ultrafast IR (λ_{ex} = 270 nm) on *p*-biphenyldiazirine in acetonitrile. (a) Spectra of diazo formation at selected time delays, (b) The diazo band integrals versus time delays.

Table S1. B3LYP/6-31G(d) calculated IR frequencies and intensities for singlet phenylcarbene ^{1}PhCH, triplet phenylcarbene ^{3}PhCH, singlet *p*-biphenylcarbene ^{1}BpCH, triplet *p*-biphenylcarbene ^{3}BpCH, and chloro benzyl radical PhCHCl.

^{1}PhCH		^{3}PhCH		PhCHCl		^{1}BpCH		^{3}BpCH	
Freq (cm^{-1})	Intensity km/mol	Freq (cm^{-1})	Intensity km/mol	Freq (cm^{-1})	Intensity km/mol	Freq (cm^{-1})	Intensity km/mol	Freq (cm^{-1})	Intensity km/mol
177	5.3	194	1.5	103	0.0	67	2.2	68	0.1
290	35.2	331	3.4	169	0.3	70	0.8	69	0.1
376	10.7	388	0.4	219	1.1	111	1.5	112	0.1
444	0.2	437	36.3	344	1.5	174	7.1	185	0.0
519	2.2	486	1.6	395	1.2	273	25.0	283	0.4
522	43.1	513	0.1	455	21.1	284	1.4	288	0.5
601	0.4	599	0.1	547	15.5	289	8.3	333	1.8
659	45.8	653	35.3	554	2.9	346	4.1	391	1.8
749	51.4	722	58.3	600	0.6	401	4.3	397	2.3
802	0.2	795	1.2	655	31.9	402	1.7	403	0.2
827	0.3	796	0.0	731	60.6	489	3.9	469	29.8
937	2.6	853	15.4	754	42.5	506	31.2	494	1.6
964	0.1	862	3.0	801	0.1	547	2.6	534	1.1
974	0.8	932	0.0	865	49.7	555	2.2	550	7.8
984	0.0	950	0.0	867	4.1	607	0.2	606	0.1
1004	2.5	951	0.5	937	0.0	624	0.6	622	0.5
1040	18.1	1000	3.5	954	0.0	684	19.6	684	18.7
1108	7.1	1067	3.8	955	0.8	700	5.3	698	1.9
1147	3.1	1139	0.1	1003	1.8	718	17.3	699	7.6
1155	18.9	1148	0.5	1071	4.2	755	35.4	747	47.1
1239	144.2	1255	0.9	1141	0.2	814	1.0	794	3.8
1294	6.1	1267	0.3	1150	1.0	821	9.0	805	9.2
1315	15.3	1306	0.1	1193	0.9	829	2.8	808	21.0
1425	26.4	1409	3.2	1287	6.6	837	24.5	826	0.9
1458	13.1	1441	5.5	1310	6.0	902	1.0	864	19.4
1545	1.9	1518	1.2	1326	37.0	937	1.1	891	1.6
1571	99.3	1543	0.2	1426	15.0	950	0.0	922	0.7
2818	121.5	3056	2.9	1455	3.8	963	0.0	932	0.2
3060	0.1	3063	2.9	1529	1.9	969	0.1	934	0.1
3068	3.9	3074	17.4	1550	0.2	978	3.3	956	0.1
3078	17.3	3080	30.1	3056	4.8	983	2.8	965	2.4
3085	18.3	3087	12.8	3064	0.8	999	0.9	977	0.1
3096	7.2	3125	1.3	3073	26.4	1027	0.7	997	0.5
				3085	23.2	1064	19.6	1027	1.8
				3095	5.4	1074	2.5	1072	3.0
				3116	6.5	1121	1.4	1105	2.8
						1149	0.0	1147	0.0
						1161	41.8	1153	1.4
						1173	24.3	1172	0.2
						1244	209.2	1246	4.5
						1263	40.2	1263	0.1
						1266	1.9	1271	0.5
						1291	3.9	1282	0.9
						1307	3.0	1295	0.1
						1321	3.2	1317	0.3
						1395	31.0	1399	5.0
						1436	2.3	1430	2.2
						1467	3.7	1454	13.1
						1491	11.0	1486	5.0
						1516	9.6	1490	5.1

	1573	0.8	1555	8.2
	1580	344.3	1570	1.9
	1597	4.3	1595	10.0
	2787	190.9	3057	7.3
	3062	8.9	3062	3.2
	3063	1.9	3064	11.6
	3069	4.5	3068	7.4
	3076	11.9	3074	9.8
	3079	5.6	3079	9.5
	3082	4.3	3082	40.6
	3085	33.0	3086	23.0
	3091	19.3	3088	13.5
	3096	6.3	3127	3.1

Singlet phenylcarbene



E = -270.2337355 Hartree

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C	0.35063500	1.20022800	-0.00063000
C	0.27770600	-1.23568400	-0.00055300
C	-1.03849800	1.24341700	0.00010500
H	0.92708900	2.12264600	-0.00112100
C	-1.11314100	-1.19610300	-0.00003600
H	0.81836000	-2.17776500	-0.00080000
C	-1.76628000	0.04339100	0.00050400
H	-1.56290800	2.19535100	0.00016300
H	-1.69277100	-2.11512400	0.00040100
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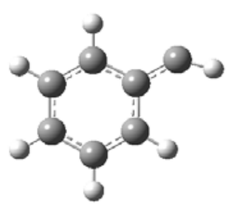
H	2.90326200	0.85582600	0.00132900

Triplet phenylcarbene



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C	0.24760900	-1.25411400	-0.00002300
C	-1.01162200	1.25123200	-0.00004400
H	0.96332600	2.10376500	-0.00000200
C	-1.13779500	-1.17118300	0.00003000
H	0.74159200	-2.22160600	-0.00005200
C	-1.78030100	0.07694300	0.00002300
H	-1.50379200	2.22090300	-0.00004300
H	-1.72895500	-2.08367400	-0.00000200
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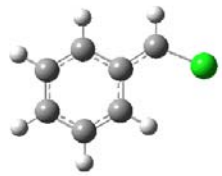
H	3.24828100	0.58423400	0.00031300

Chloro benzyl radical



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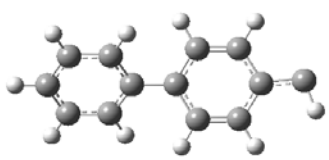
C	1.00363400	1.31705100	0.00011600
C	2.33508600	0.92727800	-0.00021400
C	2.67716200	-0.43421400	-0.00029300
H	1.91993900	-2.45709200	0.00008500
H	-0.45428200	-1.78456600	0.00078400
H	0.74620500	2.37363800	0.00026900
H	3.11589600	1.68363000	-0.00041900
H	3.72077100	-0.73632300	-0.00062500
C	-1.38019800	0.80596100	0.00036800
H	-1.63528800	1.85854600	-0.00007300
Cl	-2.75690700	-0.24416800	-0.00026500

p-Biphenylcarbene singlet



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C	-2.48964500	-1.16509800	-0.37156100
C	-1.10384200	-1.16577200	-0.36824300
C	-0.38839400	-0.00681200	-0.00213000
H	-0.57205100	2.03812000	0.67672900
H	-3.04241600	2.03558400	0.66374100
H	-3.05349900	-2.04554500	-0.66516700
H	-0.55884000	-2.05134500	-0.68100900
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H	-5.06609700	0.87018800	0.30510100
C	1.09277400	-0.00059600	-0.00042500
C	1.81011900	1.14986900	-0.37407900
C	1.81785000	-1.14568100	0.37482700
C	3.20334200	1.15332800	-0.37654700

H	1.27154900	2.03675900	-0.69496400
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H	1.28499300	-2.03650000	0.69424100
C	3.90939800	0.00988500	0.00250200
H	3.73831500	2.04877200	-0.68083700
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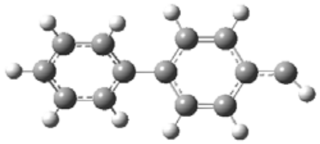
p-Biphenylcarbene Triplet



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C	-1.10826500	1.17237800	0.35316100
C	-0.38320000	0.01123600	0.00345900
H	-0.59795400	-2.04018800	-0.64612600
H	-3.04858600	-2.03858700	-0.63076900
H	-3.02149500	2.09483700	0.64543600
H	-0.56703500	2.06519900	0.65336400
C	-4.63660600	0.04197600	0.01068400
H	-5.40322500	-0.69133800	-0.20750700
C	1.09587000	0.00053300	0.00066300
C	1.81457500	-1.15606800	0.35626600
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H	1.27474000	-2.04624100	0.66650500
C	3.22287400	1.13686700	-0.36021600
H	1.30123700	2.04465900	-0.66552800
C	3.92002200	-0.01965200	-0.00497800
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H	3.76559700	2.03296700	-0.64982500
H	5.00656900	-0.02739300	-0.00711700

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(2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian 03, Revision C.02 ed.; Gaussian, Inc.: Wallingford CT, 2004.
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