SUPPORTING INFORMATION

The Trichloromethide and Bromodichloromethide Carbanions

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1. Figures S-1 – S-4

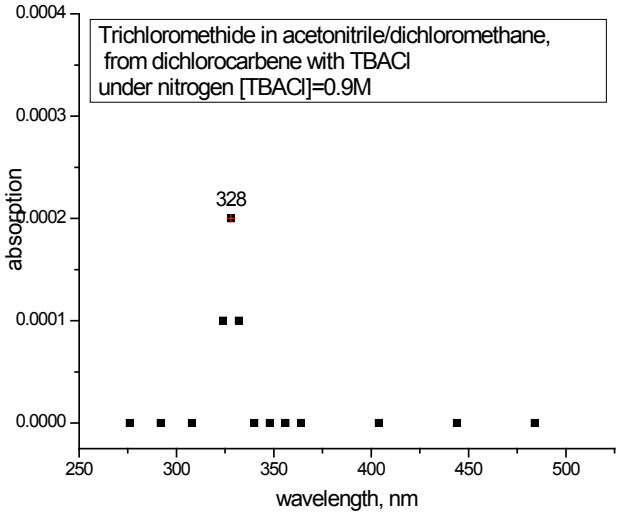


Figure S-1. UV-vis spectrum acquired 100 ns after LFP of dichlorodiazirine (A = 0.37) with 0.9 M TBACl in 1:1 CH_2Cl_2-MeCN under N_2. Absorption from CCl_3^- at 328 nm.

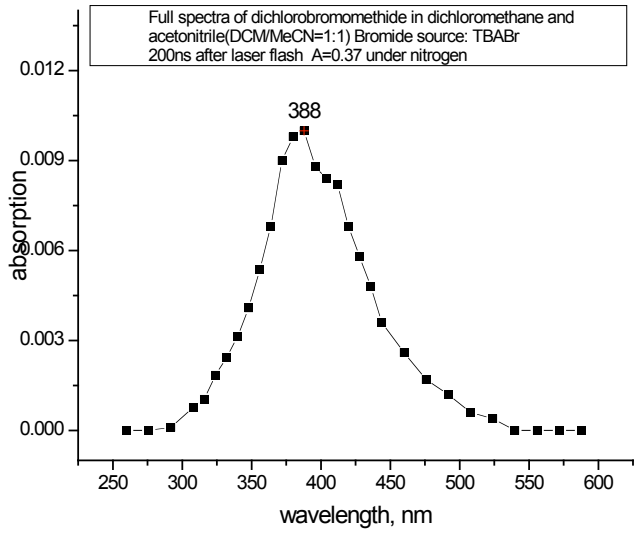


Figure S-2. UV-vis spectrum acquired 200 ns after LFP of dichlorodiazirine (A = 0.37) with 0.6 M TBABr in 1:1 CH_2Cl_2-MeCN under N_2. Absorption from CCl_2Br^- at 388 nm. The shoulder at 404 nm is assigned to $CClBr_2^-$.

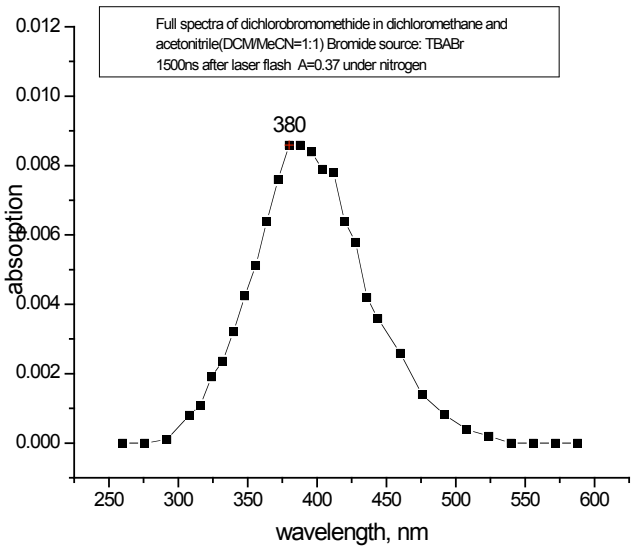


Figure S-3. Same as Figure S-2, but 1500 ns after the laser flash.

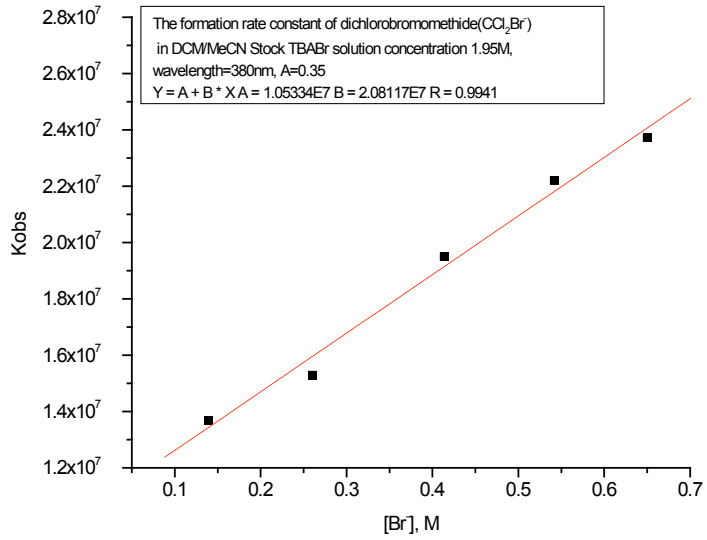
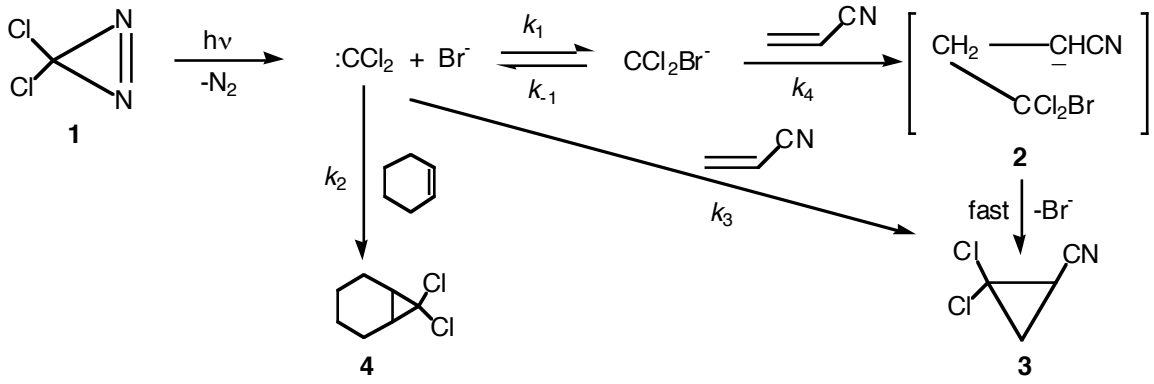


Figure S-4. Rate constant for the formation of CCl_2Br^- measured at 380 nm (A dichlorodiazirine = 0.35): k_{obs} (s^{-1}) vs [Br^-] (M).
$k_2 = 2.08 \times 10^7$ M^{-1} s^{-1}, $r = 0.994$.

2. Estimation of K and k_1/k_{-1} in Scheme 1

Scheme 1



Measured values: $k_1 = 2.1 \times 10^7\ M^{-1}\ s^{-1}$; $k_2 = 6.4 \times 10^7\ M^{-1}\ s^{-1}$; $k_3 = 4.9 \times 10^5\ M^{-1}\ s^{-1}$; $k_4 = 4.1 \times 10^6\ M^{-1}\ s^{-1}$

From the equilibrium between ($CCl_2 + Br^-$) and CCl_2Br^-, we have,

$$K = k_1/k_{-1} = [CCl_2Br^-]/[CCl_2][Br^-]$$

$$[CCl_2Br^-] = (k_1/k_{-1})[CCl_2][Br^-] \quad (1)$$

The formation of cyclopropane **4** can be represented as

$$[\mathbf{4}] = k_2[\text{cyclohex}][CCl_2] \quad (2)$$

The formation of cyclopropane **3** can be represented as

$$[\mathbf{3}] = k_3[CCl_2][ACN] + k_4[CCl_2Br^-][ACN]$$

In light of eq. (1),

$$[\mathbf{3}] = k_3[CCl_2][ACN] + (k_4k_1/k_{-1})[CCl_2][Br^-][ACN]$$

$$[\mathbf{3}] = \{k_3 + (k_4k_1/k_{-1})[Br^-]\}[CCl_2][ACN] \quad (3)$$

Dividing eq. (3) by eq. (2) gives

$$[\mathbf{3}]/[\mathbf{4}] = \{k_3 + (k_4k_1/k_{-1})[Br^-]\}(1/k_2)[ACN]/[\text{cyclohex}]$$

$$[\mathbf{3}]/[\mathbf{4}] = \{k_3/k_2 + (k_4k_1/k_2k_{-1})[Br^-]\}[ACN]/[\text{cyclohex}] \quad (4)$$

From experiment, we know that in the presence of 0.28 M Br^-,

$$[\mathbf{3}]/[\mathbf{4}] = 0.184[ACN]/[\text{cyclohex}] \quad (5)$$

From eq. (5) and eq. (4), we obtain

$$0.184 = k_3/k_2 + (k_4k_1/k_2k_{-1})[Br^-] \quad (6)$$

From eq. (6) and the measured values of $k_1 - k_4$, we calculate

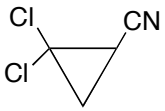
$k_{-1} = 2.1 \times 10^6\ s^{-1}$

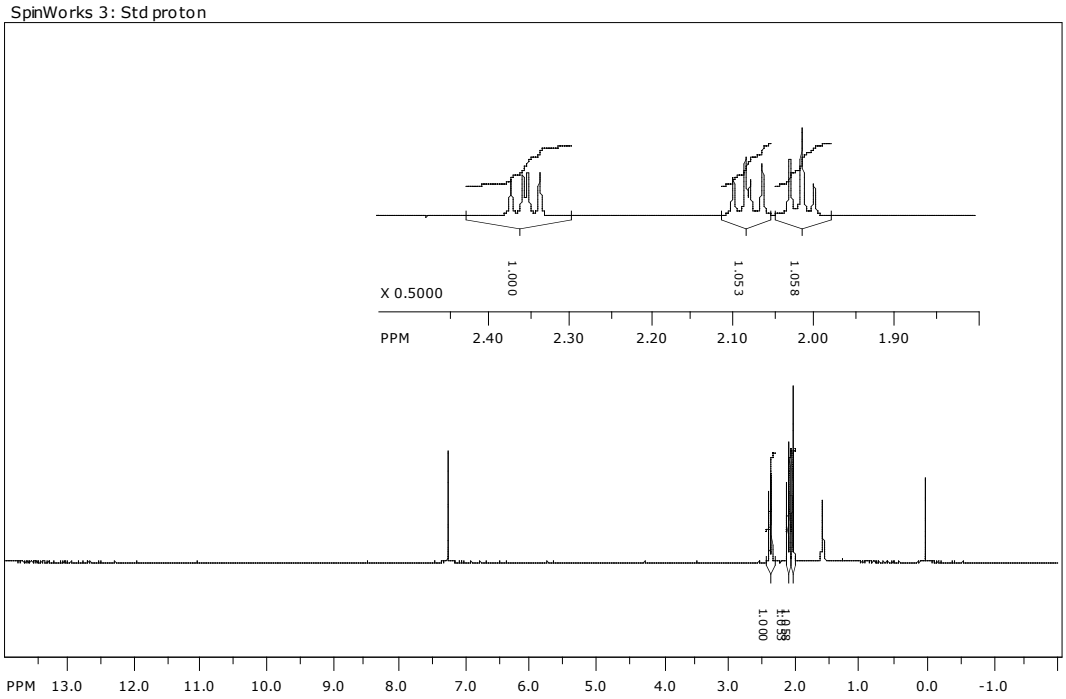
and hence

$K = k_1/k_{-1} = 10\ M^{-1}$.

3. ^{1}H and ^{13}C NMR Spectra of Cyclopropanes 3 and 4

1,1-Dichloro-2-cyanocyclopropane (**3**): ^{1}H NMR spectrum





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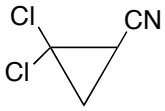
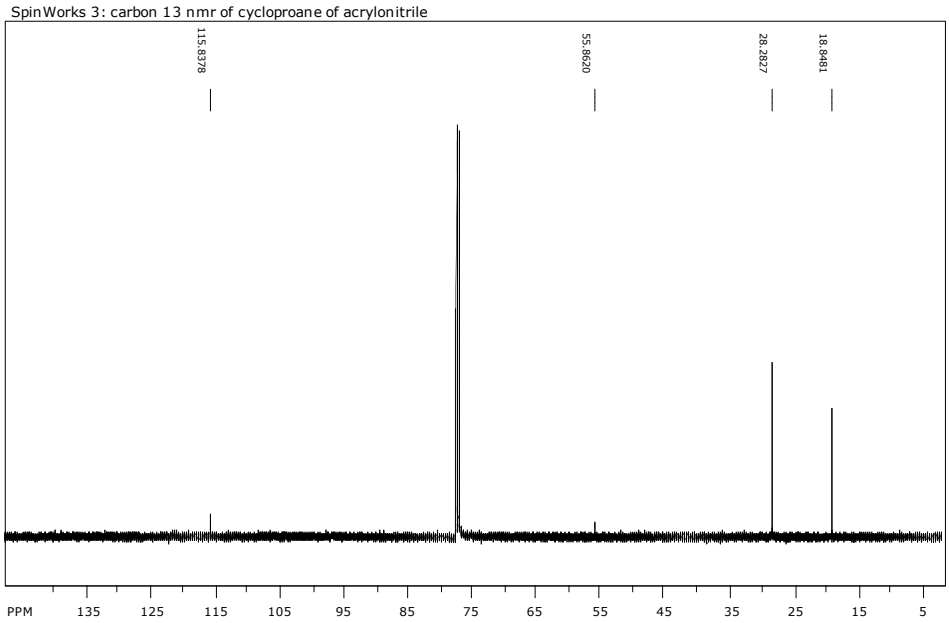
number of scans: 16

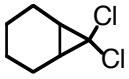
freq. of 0 ppm: 499.769125 MHz
processed size: 65536 complex points
LB: 0.200 GF: 0.0000
Hz/cm: 320.513 ppm/cm: 0.64132

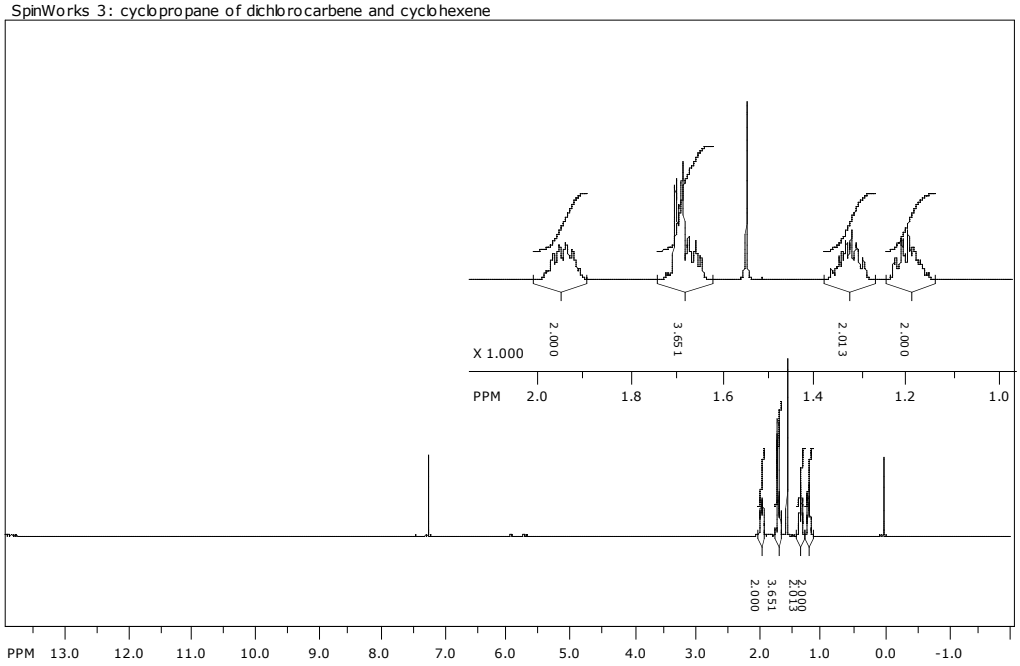
1,1-Dichloro-2-cyanocyclopropane (**3**): ^{13}C NMR spectrum





7,7-Dichloronorcarane (**4**): ^{1}H NMR spectrum





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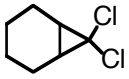
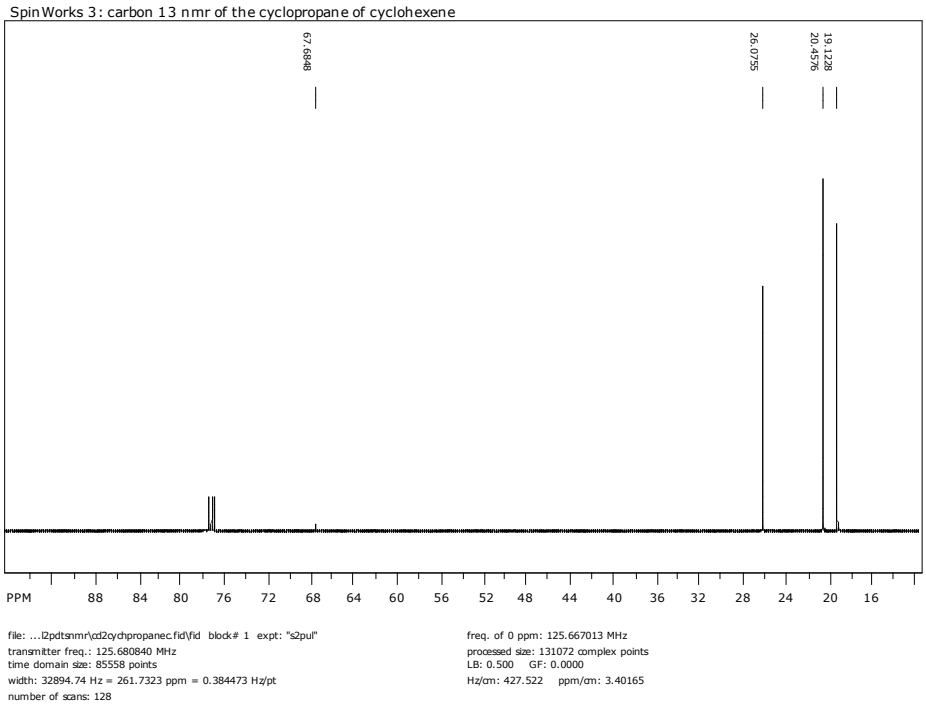
LB: 0.200 GF: 0.0000
Hz/cm: 320.513 ppm/cm: 0.64132

7,7-Dichloronorcarane (**4**): ^{13}C NMR spectrum





4. Computational Details

Electronic structure calculations based on density functional theory (DFT) made use of the PBE[1] and B3LYP[2] exchange-correlation functionals and 6-311+G(d) basis sets.[3] Ground state geometry optimizations were carried out using the PBE functionals (PBE /6-311+G(d)). The polarizable conductor self-consistent reaction field model (CPCM) was used to incorporate general polar solvent effects;[4] default parameters for acetonitrile were applied, except that we chose to use Pauling atomic radii with explicit hydrogens. Stationary points were characterized further by normal

mode analysis, and the (unscaled) vibrational frequencies formed the basis for the calculation of vibrational zero-point energy (ZPE) corrections. Standard statistical mechanical expressions (based on harmonic oscillator/rigid rotor approximations and ideal gas behavior) were then used to evaluate the thermodynamic corrections necessary to convert from purely electronic energies to standard enthalpies (*H*; T = 298.15 K) and Gibbs free energies (*G*; T = 298.15 K, P = 1 atm).[5] The differential free energies presented in Table 1 have been corrected to a reference state of 1 M concentration for each species participating in the reaction by subtracting 1.89 kcal/mol from the Gibbs free energies at P = 1 atm (T = 298.15 K).

Calculations of electronically excited state properties (transition wavelengths (λ) and oscillator strengths (*f*)) were performed at the optimized ground state geometries using the time-dependent DFT formalism,[6] the CPCM model of (acetonitrile) solvation, B3LYP functionals, and 6-311+G(d) basis sets (TD-B3LYP/6-311+G(d)//PBE/6-311+G(d)). The character of a particular electronic transition was assigned by consideration of the largest transition amplitude(s) for the contributing MOs.

The computational scheme outlined above has provided useful information in our previous investigations of e.g. carbene-solvent interactions (see e.g. ref.7). All electronic structure calculations were carried out with the Gaussian03 suite of programs.[8]

(1) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(2) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5468. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(3) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 721. (b) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209. (c) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (d) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (e) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comp. Chem.* **1983**,

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(4) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.

(5) McQuarrie, D. A. *Statistical Thermodynamics*; Harper and Row: New York, 1973.

(6) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439.

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(8) Gaussian 03, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., 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.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

5. **Optimized Geometries, Absolute Energies, Electronic Excitation Energies and Oscillator Strengths for All Species Relevant to Table 1.**

Halides

---
chloride, Cl-

Charge = -1 Multiplicity = 1
Cl

Sum of electronic and zero-point Energies=	-460.208353
Sum of electronic and thermal Energies=	-460.206936
Sum of electronic and thermal Enthalpies=	-460.205992
Sum of electronic and thermal Free Energies=	-460.223375

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bromide, Br-

Charge = -1 Multiplicity = 1
Br

Sum of electronic and zero-point Energies=	-2573.922843
Sum of electronic and thermal Energies=	-2573.921427
Sum of electronic and thermal Enthalpies=	-2573.920483
Sum of electronic and thermal Free Energies=	-2573.939019

Carbenes

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dichlorocarbene, CCl_2

Charge = 0 Multiplicity = 1
C,0,0.,0.,0.8418049875
Cl,0,0.,1.4264642454,-0.1476735235
Cl,0,0.,-1.4264642454,-0.1476735235

Sum of electronic and zero-point Energies=	-958.009911
Sum of electronic and thermal Energies=	-958.006441
Sum of electronic and thermal Enthalpies=	-958.005496
Sum of electronic and thermal Free Energies=	-958.035676

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fluorochlorocarbene, CFCl

Charge = 0 Multiplicity = 1
C,0,0.0137236729,0.,0.0323497583
F,0,-0.0759877397,0.,1.3388696223
Cl,0,1.7364372469,0.,-0.3664212826

Sum of electronic and zero-point Energies=	-597.774679
Sum of electronic and thermal Energies=	-597.771394
Sum of electronic and thermal Enthalpies=	-597.770450
Sum of electronic and thermal Free Energies=	-597.800005

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difluorocarbene, CF_2

Charge = 0 Multiplicity = 1
C,0,0.0096338795,0.,-0.0023167541
F,0,-0.0273870176,0.,1.3155092154
F,0,1.2919263181,0.,-0.3083943634

Sum of electronic and zero-point Energies=	-237.544982
Sum of electronic and thermal Energies=	-237.541938
Sum of electronic and thermal Enthalpies=	-237.540994
Sum of electronic and thermal Free Energies=	-237.569082

Methide Carbanions

CCl_3 minus

Charge = -1 Multiplicity = 1
C,0,-0.0000340296,-0.0000106711,0.7226979914
Cl,0,-0.0001236405,1.7374854159,-0.0814949594
Cl,0,1.5053719707,-0.8688546886,-0.081508789
Cl,0,-1.5052143006,-0.8686200562,-0.0814904458

Sum of electronic and zero-point Energies= -1418.231000
Sum of electronic and thermal Energies= -1418.225840
Sum of electronic and thermal Enthalpies= -1418.224896
Sum of electronic and thermal Free Energies= -1418.260856

Excitation energies and oscillator strengths:
Excited State 1: Singlet-A 3.6076 eV 343.67 nm f=0.0246
29 -> 30 0.68126
Excited State 2: Singlet-A 5.1458 eV 240.94 nm f=0.1063
27 -> 30 0.14328
29 -> 31 0.64925
Excited State 3: Singlet-A 5.1471 eV 240.88 nm f=0.1062
26 -> 30 -0.14333
29 -> 32 0.64925

CCl_2Br minus

Charge = -1 Multiplicity = 1
C,0,0.0049768206,0.0086201061,6.9611204929
Cl,0,1.7300564584,0.0035776599,7.7486431617
Cl,0,-0.8619298848,1.5000616729,7.7486431617
Br,0,-0.9643068712,-1.670228495,7.8445980885

Sum of electronic and zero-point Energies= -3531.944549
Sum of electronic and thermal Energies= -3531.939199
Sum of electronic and thermal Enthalpies= -3531.938255
Sum of electronic and thermal Free Energies= -3531.975635

Excitation energies and oscillator strengths:
Excited State 1: Singlet-A' 3.2998 eV 375.74 nm f=0.0362
38 -> 39 0.66647
Excited State 2: Singlet-A' 4.6954 eV 264.05 nm f=0.0536
36 -> 39 0.33411
38 -> 40 0.58810
Excited State 3: Singlet-A" 4.7159 eV 262.91 nm f=0.0009
37 -> 39 0.68902

CBr_2Cl minus

Charge = -1 Multiplicity = 1
C,0,-0.0197917508,-0.0001320589,7.0232658489
Cl,0,1.7005675084,0.0000688895,7.7786407549
Br,0,-0.9763189622,1.6623260887,7.8986296107
Br,0,-0.9763491314,-1.6622629193,7.8985660952

Sum of electronic and zero-point Energies= -5645.658298
Sum of electronic and thermal Energies= -5645.652762
Sum of electronic and thermal Enthalpies= -5645.651818
Sum of electronic and thermal Free Energies= -5645.690547

Excitation energies and oscillator strengths:
Excited State 1: Singlet-A 3.0941 eV 400.71 nm f=0.0257
47 -> 48 0.66871
Excited State 2: Singlet-A 4.3278 eV 286.48 nm f=0.0193
46 -> 48 0.51212
47 -> 49 -0.44434
Excited State 3: Singlet-A 4.4442 eV 278.98 nm f=0.0517
45 -> 48 -0.36542
46 -> 48 0.42767
47 -> 49 0.38341

CCl_2F minus

Charge = -1 Multiplicity = 1
C,0,-0.0304993633,-0.0528264469,6.9181961633
Cl,0,1.7645840126,-0.0412021461,7.7794431045
Cl,0,-0.9179741115,1.507573509,7.7794431045
F,0,-0.6406695817,-1.1096722664,7.5738054632

Sum of electronic and zero-point Energies= -1057.990928
Sum of electronic and thermal Energies= -1057.985993
Sum of electronic and thermal Enthalpies= -1057.985048
Sum of electronic and thermal Free Energies= -1058.020003

Excitation energies and oscillator strengths:
Excited State 1: Singlet-A' 4.2677 eV 290.52 nm f=0.0826
25 -> 26 0.66229
Excited State 2: Singlet-A" 5.2284 eV 237.14 nm f=0.1636
24 -> 26 0.19718
25 -> 27 0.63168
Excited State 3: Singlet-A" 5.8409 eV 212.27 nm f=0.0972
23 -> 26 0.17481
24 -> 26 0.63504
25 -> 27 -0.14824

CFClBr minus

Charge = -1 Multiplicity = 1
C,0,0.183876702,0.0252202728,6.9758097872
F,0,1.3623913789,0.0136332395,7.6794118696
Cl,0,-0.7565484827,1.539455807,7.7708347674
Br,0,-0.8809230752,-1.7362783753,7.8769484806

Sum of electronic and zero-point Energies= -3171.704838
Sum of electronic and thermal Energies= -3171.699717
Sum of electronic and thermal Enthalpies= -3171.698773
Sum of electronic and thermal Free Energies= -3171.735264
Excitation energies and oscillator strengths:
Excited State 1: Singlet-A 3.8233 eV 324.29 nm f=0.1133
34 -> 35 0.63857
Excited State 2: Singlet-A 4.7505 eV 260.99 nm f=0.0062
33 -> 35 0.64686
34 -> 36 -0.21632
Excited State 3: Singlet-A 4.9068 eV 252.68 nm f=0.0059
32 -> 35 0.65918
34 -> 36 -0.19805

CF_2Cl minus

Charge = -1 Multiplicity = 1
C,0,-0.9718906949,0.1423414783,0.
F,0,-0.9558155975,-0.7069280895,1.0634729074
F,0,-0.9558155975,-0.7069280895,-1.0634729074
Cl,0,1.4200388667,0.7256511269,0.

Sum of electronic and zero-point Energies= -697.753847
Sum of electronic and thermal Energies= -697.748990
Sum of electronic and thermal Enthalpies= -697.748045
Sum of electronic and thermal Free Energies= -697.782985

Excitation energies and oscillator strengths:
Excited State 1: Singlet-A' 4.2076 eV 294.67 nm f=0.0682
19 -> 22 0.55710
21 -> 22 -0.38068
Excited State 2: Singlet-A" 4.2644 eV 290.74 nm f=0.0003
20 -> 22 0.69657
Excited State 3: Singlet-A' 4.4236 eV 280.28 nm f=0.2471
19 -> 22 0.41586
21 -> 22 0.47759

CF_2Br minus

Charge = -1 Multiplicity = 1
C,0,0.0783266856,0.135665799,6.9129536867
F,0,1.2616170793,0.0588938307,7.5805635662
F,0,-0.5798049861,1.1220393559,7.5805635662
Br,0,-1.1154322975,-1.9319854117,8.004802945

Sum of electronic and zero-point Energies= -2811.468765
Sum of electronic and thermal Energies= -2811.463890
Sum of electronic and thermal Enthalpies= -2811.462946
Sum of electronic and thermal Free Energies= -2811.498833

Excitation energies and oscillator strengths:
Excited State 1: Singlet-A' 4.0883 eV 303.26 nm f=0.2566
27 -> 31 0.10530
28 -> 31 0.27230
30 -> 31 0.57238
Excited State 2: Singlet-A" 4.2282 eV 293.23 nm f=0.0001
29 -> 31 0.69849

Excited State 3: Singlet-A' 4.2834 eV 289.45 nm f=0.1138
28 -> 31 0.64038
30 -> 31 -0.21460