Photoselection of Carbene Stereoisomers with Surprisingly Different Electronic Spectra: 3-Furylchlorocarbene

Tania Khasanova and Robert S. Sheridan

Department of Chemistry, University of Nevada, Reno, Nevada 89557

rss@chem.unr.edu

Supporting Material

Preparation of 3-furylchlorodiazirine.

200 mg of 3-furyl amidine hydrochloride was dissolved in 50 mL DMSO in a 250-mL, one-neck flask with side arm. A solution of 3 g of NaCl in 60 mL NaOCl was added dropwise, while stirring and cooling the reaction mixture in an ice bath. The rate of addition was such that the temperature of the reaction mixture didn't exceed 20^{o}C. After all bleach solution was added, the reaction mixture was stirred for another hour and then 3-furylchlorodiazirine was vacuum distilled at room temperature (3 torr) into a 77K trap. Two U-traps were used between one-neck flask and 77K trap: one filled with $CaCl_2$ at -5 to -7^{o}C and an empty one at -20 to -25^{o}C. Diazirine collected in the 77K trap within one hour, but distillation was usually carried out for 3 hours to ensure complete collection of diazirine.

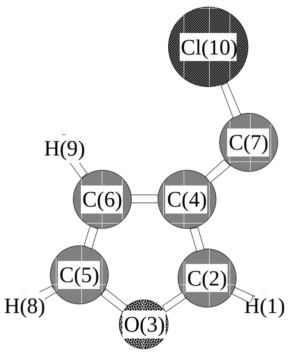
Yield: 45%.

UV/Vis (N_2, 10 K): 394, 373, 355 nm.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (dd, 2H), 6.04 (m, 1H) ppm.

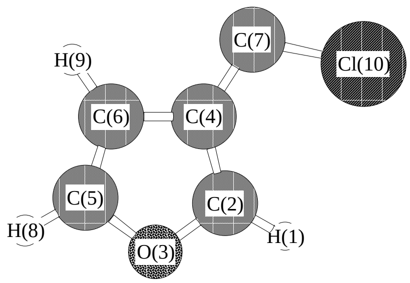
IR (N_2, 10 K): 1572, 1564, 1586, 1507, 1511, 1376, 1311, 1172, 1091, 1055, 1021, 1011, 993, 978, 878, 842, 794, 746, 735, 648, 644, 601, 598 cm^{-1}.

B3LYP/6-31G** Calculated Geometry for 2a



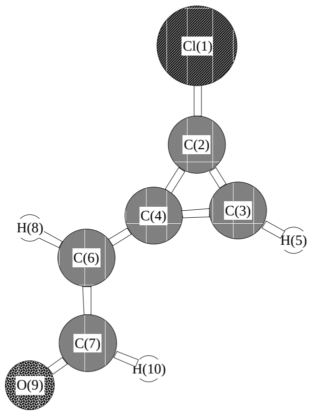
C(2)-O(3)	1.333
C(2)-C(4)	1.388
O(3)-C(5)	1.390
C(4)-C(6)	1.457
C(4)-C(7)	1.430
C(5)-C(6)	1.348
C(5)-H(8)	1.078
C(6)-H(9)	1.080
C(7)-Cl(10)	1.769
H(1)-C(2)	1.080
O(3)-C(2)-C(4)	111.407
H(1)-C(2)-O(3)	117.564
H(1)-C(2)-C(4)	131.026
C(2)-O(3)-C(5)	106.950
C(2)-C(4)-C(6)	104.744
C(2)-C(4)-C(7)	117.737
C(6)-C(4)-C(7)	137.520
O(3)-C(5)-C(6)	110.607
O(3)-C(5)-H(8)	114.829
C(6)-C(5)-H(8)	134.563
C(4)-C(6)-C(5)	106.291
C(4)-C(6)-H(9)	126.487
C(5)-C(6)-H(9)	127.221
C(4)-C(7)-Cl(10)	109.960
C(4)-C(2)-O(3)-C(5)	0.000
H(1)-C(2)-O(3)-C(5)	180.000
O(3)-C(2)-C(4)-C(6)	0.000
O(3)-C(2)-C(4)-C(7)	180.000
H(1)-C(2)-C(4)-C(6)	-180.000
H(1)-C(2)-C(4)-C(7)	0.000
C(2)-O(3)-C(5)-C(6)	0.000
C(2)-O(3)-C(5)-H(8)	180.000
C(2)-C(4)-C(6)-C(5)	0.000
C(2)-C(4)-C(6)-H(9)	-180.000
C(7)-C(4)-C(6)-C(5)	180.000
C(7)-C(4)-C(6)-H(9)	0.000
C(2)-C(4)-C(7)-Cl(10)	180.000
C(6)-C(4)-C(7)-Cl(10)	0.000
O(3)-C(5)-C(6)-C(4)	0.000
O(3)-C(5)-C(6)-H(9)	180.000
H(8)-C(5)-C(6)-C(4)	180.000
H(8)-C(5)-C(6)-H(9)	0.000

B3LYP/6-31G** Calculated Geometry for 2b



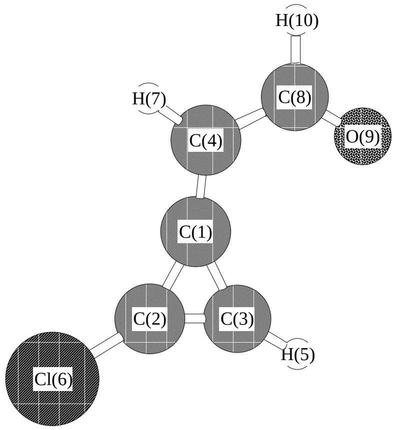
C(2)-O(3)	1.333
C(2)-C(4)	1.390
O(3)-C(5)	1.388
C(4)-C(6)	1.455
C(4)-C(7)	1.435
C(5)-C(6)	1.349
C(5)-H(8)	1.078
C(6)-H(9)	1.080
C(7)-Cl(10)	1.777
H(1)-C(2)	1.079
O(3)-C(2)-C(4)	111.042
H(1)-C(2)-O(3)	116.758
H(1)-C(2)-C(4)	132.201
C(2)-O(3)-C(5)	107.592
C(2)-C(4)-C(6)	104.595
C(2)-C(4)-C(7)	133.483
C(6)-C(4)-C(7)	121.920
O(3)-C(5)-C(6)	109.974
O(3)-C(5)-H(8)	115.029
C(6)-C(5)-H(8)	134.999
C(4)-C(6)-C(5)	106.795
C(4)-C(6)-H(9)	125.403
C(5)-C(6)-H(9)	127.803
C(4)-C(7)-Cl(10)	110.220
C(4)-C(2)-O(3)-C(5)	0.000
H(1)-C(2)-O(3)-C(5)	180.000
O(3)-C(2)-C(4)-C(6)	0.000
O(3)-C(2)-C(4)-C(7)	180.000
H(1)-C(2)-C(4)-C(6)	180.000
H(1)-C(2)-C(4)-C(7)	0.000
C(2)-O(3)-C(5)-C(6)	0.000
C(2)-O(3)-C(5)-H(8)	-180.000
C(2)-C(4)-C(6)-C(5)	0.000
C(2)-C(4)-C(6)-H(9)	180.000
C(7)-C(4)-C(6)-C(5)	180.000
C(7)-C(4)-C(6)-H(9)	0.000
C(2)-C(4)-C(7)-Cl(10)	0.000
C(6)-C(4)-C(7)-Cl(10)	180.000
O(3)-C(5)-C(6)-C(4)	0.000
O(3)-C(5)-C(6)-H(9)	180.000
H(8)-C(5)-C(6)-C(4)	180.000
H(8)-C(5)-C(6)-H(9)	0.000

*B3LYP/6-31G** Geometric Parameters for s-trans 5*



Cl(1)-C(2)	1.694
C(2)-C(3)	1.322
C(2)-C(4)	1.423
C(3)-C(4)	1.451
C(3)-H(5)	1.079
C(4)-C(6)	1.345
C(6)-C(7)	1.454
C(6)-H(8)	1.086
C(7)-O(9)	1.221
C(7)-H(10)	1.116
Cl(1)-C(2)-C(3)	148.078
Cl(1)-C(2)-C(4)	148.242
C(3)-C(2)-C(4)	63.680
C(2)-C(3)-C(4)	61.555
C(2)-C(3)-H(5)	149.889
C(4)-C(3)-H(5)	148.557
C(2)-C(4)-C(3)	54.764
C(2)-C(4)-C(6)	153.816
C(3)-C(4)-C(6)	151.417
C(4)-C(6)-C(7)	120.799
C(4)-C(6)-H(8)	120.454
C(7)-C(6)-H(8)	118.746
C(6)-C(7)-O(9)	125.112
C(6)-C(7)-H(10)	114.310
O(9)-C(7)-H(10)	120.577
Cl(1)-C(2)-C(3)-C(4)	-180.000
Cl(1)-C(2)-C(3)-H(5)	0.316
C(4)-C(2)-C(3)-H(5)	-179.684
Cl(1)-C(2)-C(4)-C(3)	180.000
Cl(1)-C(2)-C(4)-C(6)	-0.316
C(3)-C(2)-C(4)-C(6)	179.684
C(2)-C(3)-C(4)-C(6)	180.000
H(5)-C(3)-C(4)-C(2)	180.000
H(5)-C(3)-C(4)-C(6)	0.000
C(2)-C(4)-C(6)-C(7)	-180.000
C(2)-C(4)-C(6)-H(8)	0.316
C(3)-C(4)-C(6)-C(7)	0.000
C(3)-C(4)-C(6)-H(8)	180.000
C(4)-C(6)-C(7)-O(9)	180.000
C(4)-C(6)-C(7)-H(10)	0.000
H(8)-C(6)-C(7)-O(9)	0.000
H(8)-C(6)-C(7)-H(10)	180.000

*B3LYP/6-31G** Geometric Parameters for s-cis 5*



C(1)-C(2)	1.420
C(1)-C(3)	1.441
C(1)-C(4)	1.347
C(2)-C(3)	1.325
C(2)-Cl(6)	1.696
C(3)-H(5)	1.078
C(4)-C(8)	1.457
C(4)-H(7)	1.085
C(8)-O(9)	1.226
C(8)-H(10)	1.113
C(2)-C(1)-C(3)	55.173
C(2)-C(1)-C(4)	156.462
C(3)-C(1)-C(4)	148.368
C(1)-C(2)-C(3)	63.222
C(1)-C(2)-Cl(6)	148.380
C(3)-C(2)-Cl(6)	148.398
C(1)-C(3)-C(2)	61.604
C(1)-C(3)-H(5)	147.193
C(2)-C(3)-H(5)	151.202
C(1)-C(4)-C(8)	119.244
C(1)-C(4)-H(7)	120.745
H(7)-C(4)-C(8)	120.012
C(4)-C(8)-O(9)	125.252
C(4)-C(8)-H(10)	114.518
O(9)-C(8)-H(10)	120.231
C(3)-C(1)-C(2)-Cl(6)	-180.000
C(4)-C(1)-C(2)-C(3)	179.553
C(4)-C(1)-C(2)-Cl(6)	0.000
C(2)-C(1)-C(3)-H(5)	-180.000
C(4)-C(1)-C(3)-C(2)	-180.000
C(4)-C(1)-C(3)-H(5)	0.000
C(2)-C(1)-C(4)-C(8)	180.000
C(2)-C(1)-C(4)-H(7)	0.000
C(3)-C(1)-C(4)-C(8)	0.000
C(3)-C(1)-C(4)-H(7)	180.000
C(1)-C(2)-C(3)-H(5)	180.000
Cl(6)-C(2)-C(3)-C(1)	180.000
Cl(6)-C(2)-C(3)-H(5)	0.000
C(1)-C(4)-C(8)-O(9)	0.000
C(1)-C(4)-C(8)-H(10)	-180.000
H(7)-C(4)-C(8)-O(9)	-180.000
H(7)-C(4)-C(8)-H(10)	0.000

Experimental and theoretical (B3LYP/6-31G**) IR spectra of two isomers of 3-furylchlorocarbene

#	Experimental carbene bands		Calculated carbene bands **2b** (SYN)		Calculated carbene bands **2a** (ANTI)	
	Wavenumber	Intensity in % to biggest peak	Wavenumber (x0.95)	Intensity in % to biggest peak	Wavenumber (x0.95)	Intensity in % to biggest peak
1	3160	2.5	3146	0.04	3141	0.2
2	3145	7.5	3131	2.1	3128	1.6
3	3136	2.3	3118	1.1	3119	1.0
4	1540a	16.0			1513	2.5
5	1531s	13.3	1489	7.5		
6	1504a	91.4			1459	100
7	1496s	84.3	1457	100		
8	1487a	80.2				
9	1321s	37.0	1312	7.0		
10	1319a	65			1340	1.1
11	1221a	7.8			1285	13.2
12	1210s	4.2	1282	2.8		
13	1198a,s	14.0	1188	6.9	1183	0.3
14	1161s	100	1140	86.5		
15	1154a	100			1139	89.9
16	1097a	14.8			1068	4.5
17	1091s	24.5	1059	9.7		
18	1027a,s	13.9	979	2.8	963	10.1
19	1021a,s	17.6	944	5.5	939	0.3
20	985a,s	28.4	851	3.3	850	2.8
21	975s	24.5	833	8.0		
22	970a	22.3			831	14.8
23	876a	22.5			827	8.6
24	873s	13.6	822	6.5		
25	872a	26.1			728	12.8
26	864s	47.5	720	14.3		
27	861a	32.2			706	98.9
28	860s	42.7	696	87.1		
29	770a	40.7			669	6.9
30	766s	43.4	668	11.3		
31	763a	38.2			603	0.8
32	758s	37.6	595	2.7		
33	752a	87.0			587	8.9
34	748s	85.1	587	6.9		
35	698a	8.3			357	4.1
36	695s	8.1	353	8.5		
37	611s	12.1	213	3.4	288	2.4
38	620a	13.8	174	0.5	167	0.1
39	600a,s	53.3	92	1.4	100	0.1

*Experimental and theoretical (B3LYP/6-31G**) IR spectra of (γ-chloro-α-formyl)methylecyclopropenes (5)*

#	Experimental bands		Calculated bands for s-cis-5 (unscaled)		Calculated bands for s-trans-5 (unscaled)	
#	Wavenumber	Intensity in % to biggest peak	Wavenumber	Intensity in % to biggest peak	Wavenumber	Intensity in % to biggest peak
1	2830	7.9	3313	2.5	3298	2.63
2	2758	5.9	3208	0.8	3209	0.29
3	2730	8.0	2900	31.0	2857	24.3
4	1807	17.7	1865	21.3		
5	1792	31.2			1860	22.0
6	1691	97.4			1782	78.8
7	1670	37.6	1755	19.6		
8	1558	58.9			1631	100
9	1552	52.3				
10	1529	100	1599	100		
11	1468	49.0				
12	1411	10.8			1442	3.9
13	1405	15.2	1437	1.1		
14	1360	16.4	1378	2.0	1305	0.8
15	1146	25.2			1161	25.3
16	1109	29.9	1130	26.0		
17	1100	10.4	1057	3.1		
18	1071	11.0			1108	15.8
19	1051	46.5			1045	7.6
20	1045	42.2	1026	0.4		
21	979	63.2	995	1.9	1018	0.3
22	968	33.1	859	1.4	864	14.9
23	851	12.3			827	8.9
24	841	10.9	820	4.6		
25	806	12.3	800	5.2		
26	798	15.7			798	4.0
27	723	28.6	781	3.8	674	1.1
28	700	16.7	580	0.05	559	0.06
29	622	37.8	559	7.6	505	3.5
30	599	58.4	463	0.1	472	1.9
31			354	0.03	340	0.38
32			218	2.4	242	0.63
33			208	0.06	220	1.1
34			108	1.1	108	0.6
35			98	0.5	105	0.1