

SUPPORTING INFORMATION

Hyperaromatic Stabilization of Arenium ions: Cylohexa- and Cyclohepta-dienyl cations - Experimental and Calculated Stabilities and Magnetic Ring Currents.

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Table **S1** Rate constants for acid-catalysed dehydration of 2,4-cycloheptadienol **6** at different concentrations of HClO₄ and X_o values at 25°

[HClO ₄] (M)	2.00	3.00	4.00	5.00	6.00
k_{obs} (sec ⁻¹)	0.56	2.81	8.24	45.0	250.0
X_o	0.49	0.75	1.08	1.50	2.01

Table S2. Percentages of 2,4-cycloheptadienyl trifluoroethyl ether in mixtures with 2,4-cycloheptadienol **6** measured as a function of time for equilibration in aqueous-TFE containing 30%, 50% or 70% TFE and acid concentration 0.1M HClO₄ at 25° C.

30% TFE		50% TFE		70% TFE	
Time	% Cycloheptadienyl trifluoroethyl ether	Time	% Cycloheptadienyl trifluoroethyl ether	Time	% Cycloheptadienyl trifluoroethyl ether
10 mins	1.02	10 mins	1.06	10 mins	5.74
20	2.10	20	2.0	20	16.7
40	3.74	30	2.26	40	24.0
60	2.79	40	4.14	60	29.8
90	4.01	60	5.75	90	35.0
120	6.54	80	7.33	120	39.0
150	6.69	100	8.76	150	40.7
180	8.13	120	11.7	180	44.6
210	8.13	150	14.8	210	42.7
240	6.01	180	16.0	240	44.4
		210	16.7	300	43.1
		240	16.3	360	40.5
		300	12.1		

Table S3. Percentages of 2,4-cycloheptadienyl trifluoroethyl ether in mixtures with 2,4-cycloheptadienol **6** measured as a function of time for equilibration in aqueous-TFE containing 30%, 50% or 70% TFE and acid concentration 1.0 M HClO₄ at 25° C.

30% TFE		50% TFE		70% TFE	
Time	%Cycloheptadienyl trifluoroethyl ether	Time	%Cycloheptadienyl trifluoroethyl ether	Time	%Cycloheptadienyl trifluoroethyl ether
1.0 mins	1.1	1.0 mins	6.8	1.0 mins	42.9
5.0	7.1	5.0	24.8	5.0	56.8
10.0	11.1	10.0	32.0	10.0	56.8
15.0	16.4	15.0	34.9	15.0	57.0
20.0	16.6	20.0	34.5	20.0	56.2
30.0	16.7	30.0	36.4	30.0	53.3
40.0	16.6	35.0	36.4	40.0	53.2
		50.0	35.8		
		70.0	35.5		

Table S4. Percentages of 2,4-cycloheptadienol **6** formed as function of time in the hydrolysis of the 2,4-cycloheptadienol dichloroacetate ester **8** in water at 25° C.

Time	% Cycloheptadienol	Time	% Cycloheptadienol
1.0 mins	26.2	1.0 mins	20.8
2.0	52.2	2.0	49.0
4.0	81.8	4.0	70.4
6.5	89.9	6.0	84.0
10.0	92.7	8.0	87.4
15.0	94.4	10.0	89.2
20.0	94.8	12.0	90.7
25.0	95.5	15.0	91.5
40.0	95.7	18.0	91.9
60.0	96.3	25.0	92.6

Table S5 Products from solvolysis of 2,4-cycloheptadienyl dichloroacetate **8** in 50% (v/v) aqueous trifluoroethanol in the presence of sodium azide at 25°

[NaN ₃] (molar)	% ROH ^a	% RN ₃ ^a	% ROTFE ^a	$\frac{[\text{ROH}]^a}{[\text{ROTFE}]}$	$\frac{[\text{ROH}]^a}{[\text{RN}_3]}$
0.02	86.7	6.5	6.9	12.6	3.4
0.04	79.1	14.5	6.4	12.3	5.45
0.05	75.0	18.9	6.1	12.3	4.0
0.10	62.8	32.2	5.0	12.5	1.95
0.20	51.0	44.9	4.1	12.4	1.14
0.30	44.0	52.6	3.4	12.8	0.84
0.40	38.6	58.3	3.2	12.2	0.66
0.50	34.2	63.1	2.8	12.3	0.54

^aR

^adenotes 2,4-cycloheptadienyl.

Table S6. Free energies of formation (kcal mol⁻¹) of seven-membered ring hydrocarbons in aqueous solution at 25° C.

Compound	log c _w ^a	p ^b	log c _g ^c	log γ ^d	ΔG _t ^e	ΔG ^o _{f(g)}	ΔG ^o _{f(aq)}
Cycloheptane						15.33	18.03
Cycloheptene	-3.16	25.0	-2.87	-0.29	2.29	32.86	33.2
1,3-Cycloheptadiene	-2.60	22.8	-2.91	0.31	1.47	48.11	49.6
1,4-Cycloheptadiene	-2.60	25.7	-2.86	0.26	1.54	54.1	55.6
Cycloheptatriene					0.91	60.79	61.70

^ac_w is the solubility in water estimated from correlation with molecular volume for cyclic dienes. ^bp is the vapour pressure at 25 °C. ^clog p – 4.269. ^dg = c_w/c_g. ^eMolar free energy of transfer from the gas phase to aqueous solution at 25 °C.

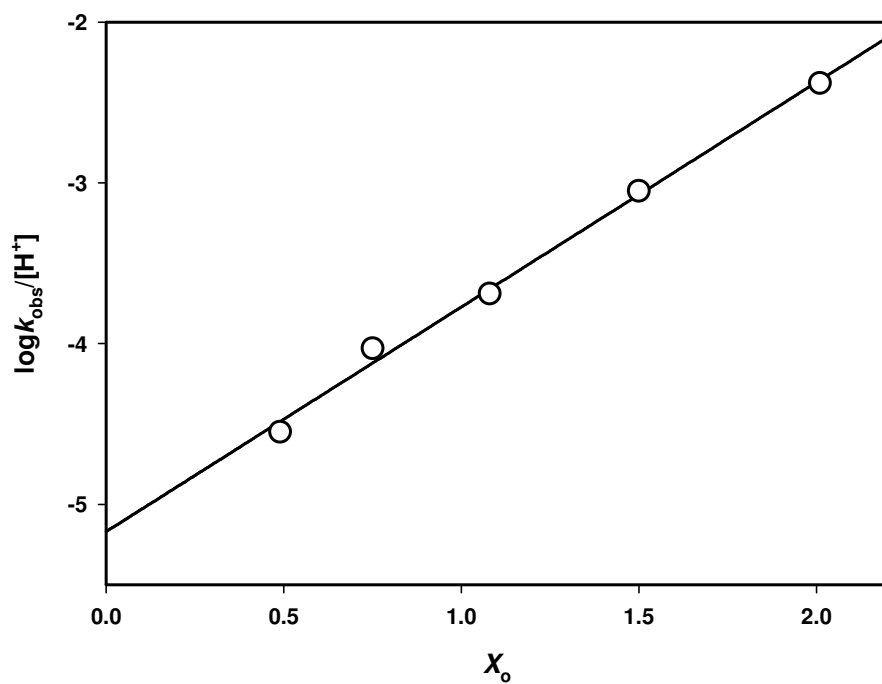


Figure S1 Plot of $\log(k_{\text{obs}}/[\text{H}^+])$ versus X_o for the dehydration of 2,4-cycloheptadienol in aqueous HClO_4 at 25°C .

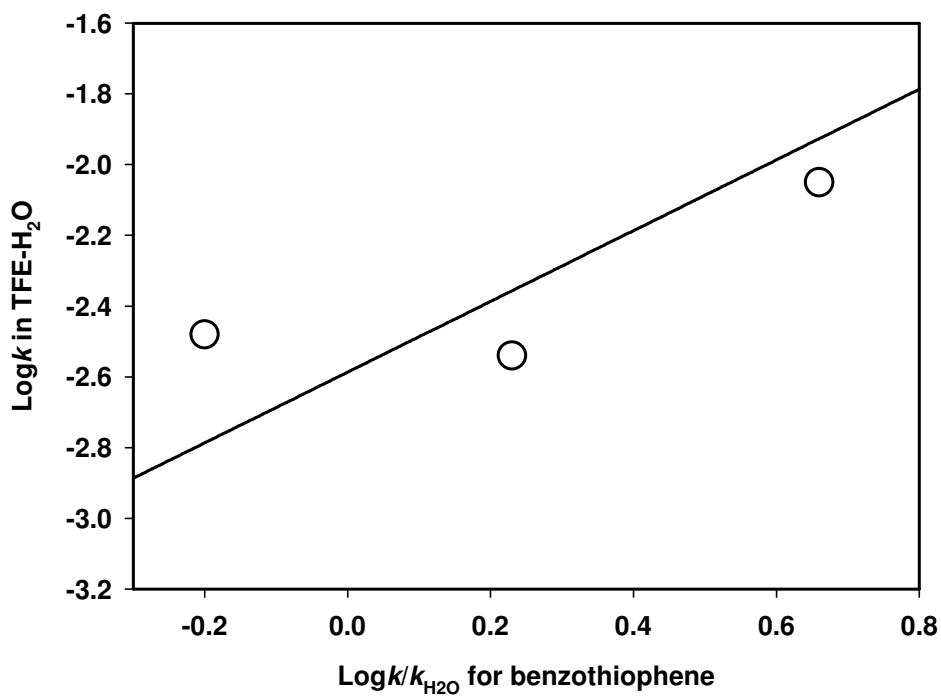


Figure S2 Plot of $\log k_{\text{H}}$ for acid-catalysed reaction of 2,4-cycloheptadienol to form the cycloheptadienyl cation in TFE- H_2O mixtures against $\log(k/k_{\text{H}_2\text{O}})$ for acid-catalyzed dehydration of benzothiophene hydrate in the same mixtures.

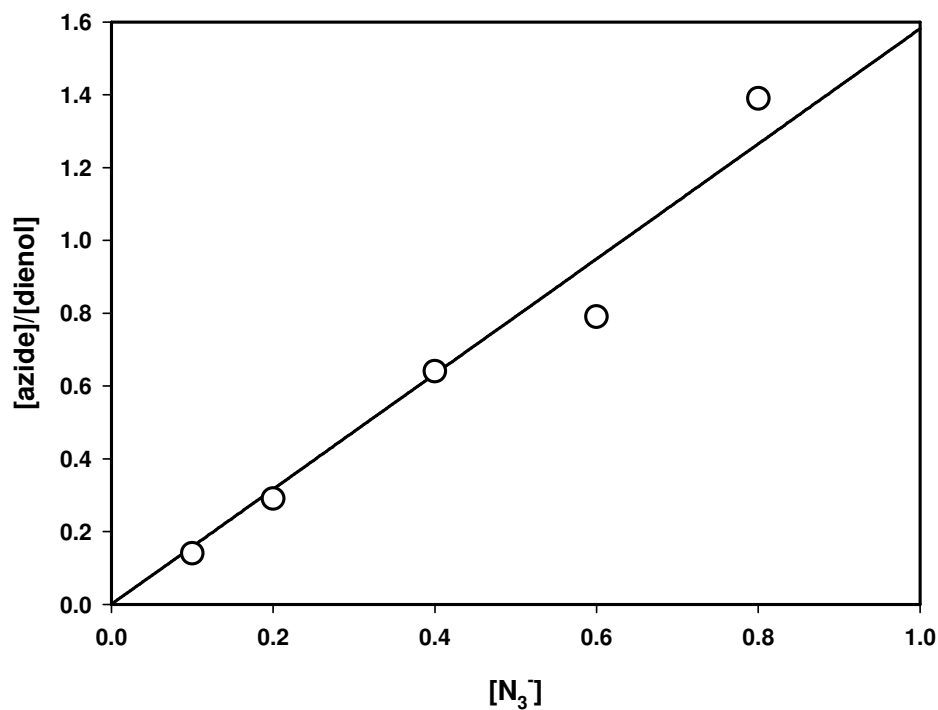


Figure S3 Ratios of 2,4-cycloheptadienol to 2,4-cycloheptadienyl azide formed from solvolysis of 2,4-cycloheptadienyl dichloroacetate at different concentrations of aqueous NaN₃ at 25 °C.

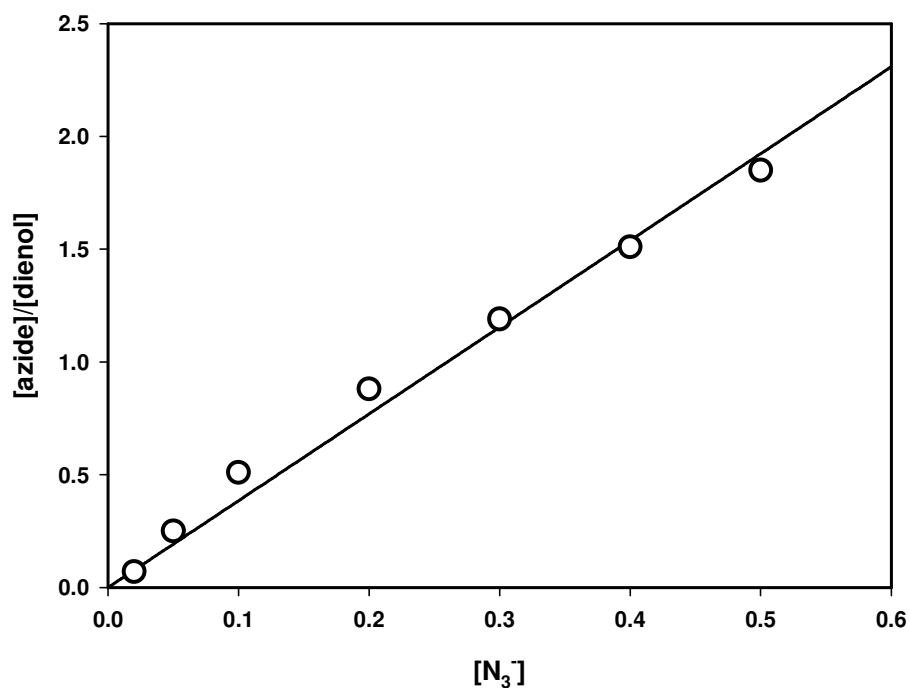


Figure S4 Ratios of 2,4-cycloheptadienol to 2,4-cycloheptadienyl azide formed from solvolysis of the dichloroacetate ester of 2,4-cycloheptadienol at different concentrations of sodium azide in 50:50 v/v aqueous trifluoroethanol at 25° C.

Thermodynamic data for seven-membered ring hydrocarbons. Free energies of formation for seven-membered ring hydrocarbons in the gas phase $\Delta G_f^\circ(\text{g})$ and aqueous solution $\Delta G_f^\circ(\text{aq})$ at 25 °C are listed in Table S6. Values for cycloheptane and cycloheptatriene are taken from the compilation by Guthrie.¹ Values of $\Delta G_f^\circ(\text{g})$ for cycloheptene and 1,3-cycloheptadiene are from the Texas Thermodynamic Research Center publication by Frenkel et al.² For the 1,4-cycloheptadiene $\Delta G_f^\circ(\text{g})$ was obtained from the value for its 1,3-isomer and the difference in heats of hydrogenation of the two isomers.³ Values of ΔG_t , the free energy of transfer from the gas phase to aqueous solution required to convert the free energies of formation for the gas phase to aqueous solution were evaluated in the manner described for cyclohexadienes⁴ using Hine's relationship⁵, $\Delta G_t = -1.364(\log \gamma - 1.39)$, where $\gamma = c_w/c_g$, c_w is the aqueous solubility and $\log c_g = \log p - 4.269$ where p is the vapour pressure at 25 °C. Aqueous solubilities were estimated from correlations of solubilities of cyclic hydrocarbons with molar volume (molecular weight/density).⁶ For the 1,4-diene the molar volume was assumed to be the same as for its 1,4- isomer. For cycloheptene the vapour pressure at 25 °C is 25.0 mm.⁷ For 1,3 cycloheptadiene the vapour pressure was estimated from the b.p. (121° at 724 mm)⁸ as described previously⁴ using the expression of Benson and Mendenhall⁹ with ΔC_{vap} taken -12 cal and ΔH_v estimated as 9.1 kcal mol⁻¹ from the value for 1,3-cyclohexadiene (7.91)¹⁰ plus an increment C-(H₂)(C₂) = 1.19 for the extra methylene group.¹¹ For the 1,4-cycloheptadiene the vapour pressure at 25 °C was also estimated from the b.p.⁸ assuming that ΔH_v is the same as for the 1,3-isomer.

Computations

Minimum energy structures of β -hydroxycarbocations derived from dihydrodiols of benzene, naphthalene (1,2), phenanthrene (9,10) and 1,3-cyclohexadiene were built and optimised at the *ab initio* HF/3-21G or HF/6-31G* levels of theory using Spartan or MacSpartan software packages.¹² Geometry optimizations were then completed at the HF/6-31G* level and single point energies calculated at the MP2/6-311+G** or MP2/6-31G* levels using Gaussian 2003. In the minimum energy conformations the relationship between the β -hydroxyl group and the 'empty' p-orbital at the formal charge centre of the carbocations was pseudoequatorial. Further calculations were carried out for conformations in which the hydroxyl was constrained to a pseudoaxial position. These did not correspond to energy minima except in the case of the 6-hydroxy-2,3-cyclohexenyl cation. For all other ions the dihedral angle (HO-C $_{\beta}$ -C $_{\alpha}^+$ -H) was set at 80°. Conformational energies in hartrees and geometric information are shown in Table S6. Also shown are zero point vibrational energies (zpve) in kcal mol⁻¹ based on harmonic frequencies calculated at the Hartree Fock limit; these energies require scaling by 0.9135.¹³

The following geometric parameters were computed for the **cycloheptadienyl cation** (symmetry C₂)

Bond lengths: d(1-2) = d(4-5) = 1.378 Å d(2-3) = d(3-4) = 1.415 Å d(1-7) = d(5-6) = 1.488 Å
d(6-7) = 1.525 Å

Bond angles: 1,2,3 = 3,4,5 = 124.9° 2,3,4 = 130.9° 2,1,7 = 4,5,6 = 125.7° 5,6,7 =
1,7,6 = 112.9°

Ring dihedral angles: 1,2,3,4 = 2,3,4,5 = 17.5° 1,2,4,5 = 29.1°

Table S7. Electronic Energies (hartrees), Zero-point Energies, Enthalpies and Free Energies (kcal/mol) for Carbocations and Related Compounds Used in this Work.^a

Compound ^b	Energy (MP2/6-311+G**)	ZPVE (HF/6-311+G**)	Enthalpy (G3MP2)	Free Energy (G3MP2)
<u>Sigma Complexes</u>				
cyclohexadienyl+ (C _{2v})	-231.8707539	73.57	-232.103032	-232.136479
cyclohexa-1,4-diene (D _{2h})	-232.7358158	81.57	-232.976477	-233.011170
cyclohexa-1,3-diene (C ₂)	-232.7391585	81.64	-232.976695	-233.010494
cyclohexa-2,4-dienol, eq	-307.8169109	85.10	-308.120293	-308.157424
cyclohexenyl+ (C _s)	-233.0609229	89.23	-233.287367	-233.365422
cyclohexene (C ₂)	-233.9534602	97.37	-234.183153	-234.217667
	*	*	*	
6-methylcyclohexadienyl+ (C _s)	-271.0720399	92.60	-271.339165	-271.376804
6-methylcyclohexa-1,3-diene, ax	-271.9386609	100.32	-272.212131	-272.249741
6-methylcyclohexa-1,3-diene, eq	-271.9383192	100.17		
6-methylcyclohex-1-enyl+	-272.2619062	107.83		
6-methylcyclohex-1-ene, ax	-273.1519062	116.03		
6-methylcyclohex-1-ene, eq	-273.1527929	115.9		
	*	*	*	

Table S7. Electronic Energies (hartrees), Zero-point Energies, Enthalpies and Free Energies (kcal/mol) for Carbocations and Related Compounds Used in this Work.^a

Compound ^b	Energy (MP2/6-311+G**)	ZPVE (HF/6-311+G**)	Enthalpy (G3MP2)	Free Energy (G3MP2)
6,6-dimethylcyclohexadienyl+ (C _{2v})	-310.2754351	111.31	-310.577328	-310.617208
6,6-dimethylcyclohexa-1,3-diene	-311.140513	118.61	-311.450117	-311.490463
6,6-dimethylcyclohex-1-enyl+	-311.4653691	126.44		
6,6-dimethylcyclohex-1-ene	-312.353763	134.36		
	*	*	*	
spiro[2.5]octa-4,6-dienyl+ (/C _{2v}) ^f	-309.0820187	97.03	-309.383355	-309.421655
spiro[2.5]octa-4,6-diene	-309.9129575	104.15	-310.225925	-310.264568
spiro[2.5]octa-4-enyl+	-319.2550761	112.15	-310.555532	-310.594946
sprio[2.5]octa-4-ene	-311.1277119	119.90	-311.432950	-311.472218
	*	*	*	
6-aminocyclohexadienyl+, eq (C _s)	-287.0909525	85.23	-287.371268	-287.408769
6-aminocyclohexa-1,3-diene, ax	-287.9618937	93.38		
6-aminocyclohexa-1,3-diene, eq	-287.9630375	93.35	-288.250726	-288.288137

Table S7. Electronic Energies (hartrees), Zero-point Energies, Enthalpies and Free Energies (kcal/mol) for Carbocations and Related Compounds Used in this Work.^a

Compound ^b	Energy (MP2/6-311+G**) ZPVE (HF/6-311+G**) Enthalpy (G3MP2) Free Energy (G3MP2)
6-aminocyclohex-1-enyl+, ax ^c	-288.3166883 103.37
6-aminocyclohex-1-enyl+, eq	-288.2842877 100.86
6-aminocyclohex-1-ene, ax	-289.177758 109.18
6-aminocyclohex-1-ene, eq	-289.1774766 109.12
	* * *
6-hydroxycyclohexadienyl+, eq	-306.933576 76.87 -307.230640 -307.267857
6-hydroxycyclohexadienyl+, ax ^d	-306.9197565 77.04 -307.218765 -307.256339
6-hydroxycyclohexadienyl+, bridged (C _s) ^e	-306.9124063 78.30 -307.209180 -307.244736
6-hydroxy-1,3-cyclohexadiene, eq	-307.8169109 85.10 -308.120293 -308.157424
6-hydroxy-1,4-cyclohexadiene (C _s)	-307.8154924 85.24 -308.120577 -
308.157852	
6-hydroxycyclohex-1-enyl+, ax	-308.1317126 92.53
6-hydroxycyclohex-1-enyl+, eq	-308.1321688 92.47
6-hydroxycyclohex-1-ene, eq	-309.0323802 100.90 -309.327634 -309.36544
	* * *

Table S7. Electronic Energies (hartrees), Zero-point Energies, Enthalpies and Free Energies (kcal/mol) for Carbocations and Related Compounds Used in this Work.^a

Compound ^b	Energy (MP2/6-311+G**) ZPVE (HF/6-311+G**) Enthalpy (G3MP2) Free Energy (G3MP2)
6,6-dihydroxycyclohexadienyl+ (C ₂)	-382.0071162 80.26 -382.373007 -382.412212
dihydroxy-1,3-cyclohexadiene	-382.9118155 88.19 -383.280570 -383.319790
6,6-dihydroxycyclohex-1-enyl+	-383.2237015 95.70
6,6-dihydroxycyclohex-1-ene	-384.1273924 104.00
	* * *
6-fluorocyclohexadienyl+, eq (C _s)	-330.9222742 68.86 -331.236890 -331.272932
6-fluoro-1,3-cyclohexadiene, ax	-331.8191337 76.92 -332.139428 -332.176103
6-fluoro-1,3-cyclohexadiene, eq	-331.8181551 76.82
6-fluorocyclohex-1-enyl+, ax	-332.1215521 84.45
6-fluorocyclohex-1-ene, ax	-333.0345038 92.66
6-fluorocyclohex-1-ene, eq	-333.0340215 92.62
	* * *

Table S7. Electronic Energies (hartrees), Zero-point Energies, Enthalpies and Free Energies (kcal/mol) for Carbocations and Related Compounds Used in this Work.^a

Compound ^b	Energy (MP2/6-311+G**)	ZPVE (HF/6-311+G**)	Enthalpy (G3MP2)	Free Energy (G3MP2)
6,6-difluorocyclohexadienyl+ (C _{2v})	-429.9826961	63.60	-430.384231	-430.422504
6,6-difluorocyclohexa-1,3-diene	-430.9115174	71.51	-431.315879	-431.354249
6,6-difluorocyclohex-1-enyl+	-431.2034633	79.02		
6,6-difluorocyclohex-1-ene	-432.1281266	87.32		
	*	*	*	
6-silylcyclohexadienyl+ (C _s)	-522.111922	84.63	-522.390550	-522.430062
6-silylcyclohexa-1,3-diene, ax	-522.9447038	91.60	-523.234603	-523.274850
6-silylcyclohexa-1,3-diene, eq	-622.9420688	91.43		
6-silylcyclohex-1-enyl+	-523.2791741	99.53		
6-silylcyclohex-1-ene, ax	-524.1572948	107.34		
6-silylcyclohex-1-ene, eq	-524.1572711	107.22		
	*	*	*	

Table S7. Electronic Energies (hartrees), Zero-point Energies, Enthalpies and Free Energies (kcal/mol) for Carbocations and Related Compounds Used in this Work.^a

Compound ^b	Energy (MP2/6-311+G**)	ZPVE (HF/6-311+G**)	Enthalpy (G3MP2)	Free Energy (G3MP2)
6,6-disilylcyclohexadienyl+ (C _{2v})	-812.326860	94.76	-812.656084	-812.702461
6,6-disilylcyclohexa-1,3-diene	-813.1524691	101.50	-813.494468	-813.540545
6,6-disilylcyclohex-1-enyl+	-813.4932366	109.69		
6,6-disilylcyclohex-1-ene	-814.3657301	117.31	-814.700440	-814.747109
	*	*	*	
6-phosphinocyclohexa-1,3-dienyl+, ax (C _s)	-573.3277441	79.73	-573.626509	-573.665705
6-phosphinocyclohexa-1,3-diene, ax	-574.1799608	87.24	-574.488341	-574.527732
6-phosphinocyclohexa-1,3-diene, eq	-574.1778829	87.09		
6-phosphinocyclohex-1-enyl+, ax	-574.5143826	94.89		
6-phosphinocyclohex-1-enyl+, eq	-574.5008072	94.58		
6-phosphinocyclohex-1-ene, ax	-575.3937611	103.00		
6-phosphinocyclohex-1-ene, eq	-575.3932918	102.89		
	*	*	*	
6-mercaptocyclohexa-1,3-dienyl+, endo (C _s) ^g	-629.5412988	74.48	-629.856395	-629.893932
6-mercaptocyclohexa-1,3-dienyl+, exo (C _s) ^g	-629.5392679	73.55		

Table S7. Electronic Energies (hartrees), Zero-point Energies, Enthalpies and Free Energies (kcal/mol) for Carbocations and Related Compounds Used in this Work.^a

Compound ^b	Energy (MP2/6-311+G**) ZPVE (HF/6-311+G**) Enthalpy (G3MP2) Free Energy (G3MP2)			
6-mercaptocyclohexa-1,3-dienyl+, ax ^g			-629.852103	-629.891414
6-mercpatocyclohexa-1,3-diene, ax	-630.4113884	81.62	-630.736356	-630.775044
6-mercpatocyclohexa-1,3-diene, eq	-630.4083445	81.46		
6-mercpatocyclohex-1-enyl+ ^h	-630.746226	89.19		
6-mercpatocyclohex-1-ene, ax	-631.6228098	97.26		
6-mercaptocyclohex-1-ene, eq	-631.6228176	97.21		
	*	*	*	
6-chlorocyclohexa-1,3-dienyl+ (C _s)	-690.9108114	68.86	-691.242364	-691.280094
6-chlorocyclohexa-1,3-diene, ax	-691.8028923	75.95	-692.141198	-692.178994
6-chlorocyclohexa-1,3-diene, eq	-691.8006332	75.86		
6-chlorocyclohex-1-enyl+, ax	-692.1123301	83.56		
6-chlorocyclohex-1-enyl+, eq	-692.1087774	83.34		
6-chlorocyclohex-1-ene, ax	-693.0178076	91.73		
6-chlorocyclohex-1-ene, eq	-693.0169046	91.57		
	*	*	*	

Table S7. Electronic Energies (hartrees), Zero-point Energies, Enthalpies and Free Energies (kcal/mol) for Carbocations and Related Compounds Used in this Work.^a

Compound ^b	Energy (MP2/6-311+G**) ZPVE (HF/6-311+G**) Enthalpy (G3MP2) Free Energy (G3MP2)				
6-carbomethoxycyclohexa-1,3-dienyl+, eq	-459.2377278	102.85	-459.679127	-459.725064	
6-carbomethoxycyclohexa-1,3-diene, eq	-460.1102263	110.82	-460.558245	-460.604504	
	*	*	*		
6-nitrocyclohexa-1,3-dienyl+, eq (C _s)	-435.9448883	76.31	-436.360280	-436.402185	
6-nitrocyclohexa-1,3-diene, ax	-436.8497621	84.55	-437.270083	-437.311611	
6-nitrocyclohexa-1,3-diene, eq	-436.8481912	84.45	-437.269337	-437.310968	
<u>Ion-Molecule Complexes</u>					
6-acetylcyclohexa-1,3-dienyl+, exo ⁱ (C _s)	-384.1772196	98.67	-384.541505	-384.585079	
6-acetylcyclohexa-1,3-dienyl+, ax (C _s)	-384.1765196	98.64	-384.540145	-384.584526	
6-acetylcyclohexa-1,3-diene, eq	-385.0211883	106.64	-385.402497	-385.446338	
	*	*	*		

Table S7. Electronic Energies (hartrees), Zero-point Energies, Enthalpies and Free Energies (kcal/mol) for Carbocations and Related Compounds Used in this Work.^a

Compound ^b	Energy (MP2/6-311+G**) ZPVE (HF/6-311+G**) Enthalpy (G3MP2) Free Energy (G3MP2)			
6-methanesulfonylcyclohexa-1,3-dienyl+, ax	-818.8414579	99.69	-819.364195	-819.410617
6-methanesulfonylcyclohexa-1,3-diene, eq	-819.7064944	107.74	-820.247342	-820.293532
	*	*	*	
6-methanesulfinylcyclohexa-1,3-dienyl+, ax	-743.7886124	95.75	-744.220368	-744.265171
6-methanesulfinylcyclohexa-1,3-diene, eq	-744.6328784	103.80	-745.085346	-745.130217
<u>Related Carbocations and their precursors</u>				
cyclohepta-2,4-dien-1-yl+	-271.0504483	93.23	-271.319029	-271.356260
cyclohepta-1,3-diene	-271.9306335	101.03	-272.205743	-272.244043
cyclohepta-2,4-dienol, ax	-347.0100926	104.59	-347.349430	-347.389437
cyclohepta-2,4-dienol, eq	-347.0085544	104.46	-347.349244	-347.389617
cyclohepta-2,6-dienol, eq			-347.341308	-347.382245
cyclohepta-2-ene-1-yl+			-272.517271	-272.555401
cycloheptene			-273.409508	-273.447725
	*	*	*	

Table S7. Electronic Energies (hartrees), Zero-point Energies, Enthalpies and Free Energies (kcal/mol) for Carbocations and Related Compounds Used in this Work.^a

Compound ^b	Energy (MP2/6-311+G**) ZPVE (HF/6-311+G**)	Enthalpy (G3MP2)	Free Energy (G3MP2)
cyclohexa-2,5-dienone (C _{2v})	-306.6336688 69.42	-306.943493	-306.978954
cyclohexa-2,4-dienone (C _s)	-306.6314649 69.21	-306.940947	-306.977641

polycyclic systems

Compound	Energy (MP2/6-31G*)	ZPVE (HF/6-31G*)
1,2-dihydronaphthalene-1-ol-2-+, eq	-459.9456491	109.88
1,2-dihydronaphthalene-1-ol-2-+, ax ^{d, j}	-459.9364221	110.10
	*	*
9,10-dihydrophenanthrene-9-ol-10+, eq	-613.1136437	141.77
9,10-dihydrophenanthrene-9-ol-10+, ax ^{d, k}	-613.1065781	141.78
	*	*

Table S7. Electronic Energies (hartrees), Zero-point Energies, Enthalpies and Free Energies (kcal/mol) for Carbocations and Related Compounds Used in this Work.^a

Compound	Energy (MP2/6-31G*)	ZPVE (HF/6-31G*)
acenaphthene-1-ol-2+, eq ^l	-535.9419162	118.31
acenaphthene-1-ol-2+, ax ^l	-535.9406570	118.35

^aElectronic energies are in hartrees. ZPVE, enthalpy, and free energy values are in kcal/mol. All structures have C1 symmetry unless otherwise specified. ^bFor overall consistency we arbitrarily number all rings placing the substituent(s) at C6. Abbreviations ax and eq refer to the pseudoaxial or pseudoequatorial position of the substituent. Absence of an ax or eq designation means that the one not listed converged to the one listed. ^cIn this conformer the axial amino group is bridged, unsymmetrically, to C1. ^dIn this conformer the axial hydroxyl group was constrained, otherwise the computation converged to the equatorial form. ^eThis symmetrically bridged conformer has the O-H bond endo to the ring. It is identical to *O*-protonated 1,2-benzene oxide. ^fThe phenonium ion. ^gThe exo and endo cations have symmetrical, sulfur-bridged structures, the endo and exo descriptors referring to the orientation of the S-H bond relative to the ring. Input geometries with a pseudoequatorial SH group converged to the bridged structure at MP2/6-311+G**, but an unbridged, pseudoaxial structure, less stable than the endo bridged structure by 2.7 kcal/mol, was found at G3MP2. ^hIn this ion the axial SH group is bridged, unsymmetrically, from C6 to C1. ⁱIn this ion the carbon of the acetyl group is symmetrically bridged to C6 and C1. The carbonyl oxygen is exo to the ring. ^jThe dihedral angle formed by the O-Cβ-Cα-H bonds was constrained to 80°. ^kThe dihedral angle formed by the O-Cβ-Cα-H bonds was constrained to 80°.

^lThese two conformers are very similar; the extent of pseudoaxial and pseudoequatorial character is not large. The five-membered ring is slightly twisted in the pseudoequatorial form, but planar in the pseudoaxial form. The dihedral formed by the H-Cβ-Cα-H bonds was constrained to 55° in the pseudo-axial conformer.

Table S8. Electronic energies, zero-point vibrational energies, selected geometric features for some β -hydroxycarbocations.^a

Carbocation	electronic energy	zpve	d(β C-H) ^b	d(β H-C α) ^c	ϕ (β H- β C-C α) ^d	ω (H-C β -C α -H) ^e
6-hydroxycyclohex-2-enyl+						
pseudo-equatorial	-308.1321688	92.47	1.112	2.054	103.6	91.6
pseudo-axial	-308.1317126	92.53	1.093	2.146	110.2	36.1
6-hydroxycyclohexa-2,4-dienyl+						
pseudo-equatorial	-306.9335760	76.87	1.170	1.793	85.3	91.7
pseudo-axial ^f	-306.9197565	77.04	1.109	2.091, 2.098	106.1, 106.0	69.3, 45.4
1,2-dihydronaphthalene-1-ol-2+						
pseudo-equatorial	-459.9456491	109.88	1.118	2.035	101.7	82.8
pseudo-axial ^g	-459.9364221	110.10	1.094	2.141	110.3	34.1
9,10-dihydrophenanthrene-9-ol-10+						
pseudo-equatorial	-613.1136437	141.77	1.115	2.011	100.9	81.8
pseudo-axial ^h	-613.1065781	141.78	1.093	2.151	112.0	90.0

^aElectronic energies in hartrees; zpve values in kcal/mol, unscaled; distances (d) in Angstroms; angles (ϕ) and dihedrals (ω) in degrees. The six-membered ring compounds were computed at MP2/6-311+G**, and the others at MP2/6-31G*. The descriptors pseudo-axial and pseudo-equatorial refer to the conformational position of the β -hydroxyl group. All tabulated structures have C₁ symmetry. ^bBond distance, C β -H. ^cNonbonding distance between C α and H β . ^dBond angle, C α -C β -H β . ^eDihedral angle formed by the H-C β and H-C α bonds. ^fDihedral formed by the O-C β -C α -H bonds was constrained to 80°. ^gDihedral formed by the O-C β -C α -H bonds was constrained to 80°. ^hDihedral formed by the O-C β -C α -H bonds was constrained to 80° in the pseudo-equatorial form, but planar in the pseudo-axial form. The dihedral formed by the H-C β -C α -H bonds was constrained to 55° in the pseudo-axial conformer.

NMR SPECTRA

Spectra were recorded on a varian 300 MHz spectrometer

1)	2,4-Cycloheptadienol (6)	25
2)	1-Dichloroacetoxycyclohepta-2,4-diene (8) – proton NMR	26
3)	1-Dichloroacetoxycyclohepta-2,4-diene (8) – carbon NMR	27
4)	1-Dichloroacetoxycyclohepta-2,4-diene (8) – carbon NMR DEPT spectrum	28



SAMPLE: rao-4

rao-4

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #74, Operator: SN_Rao
File: Proton01
INNOVA-300 "ucd300"

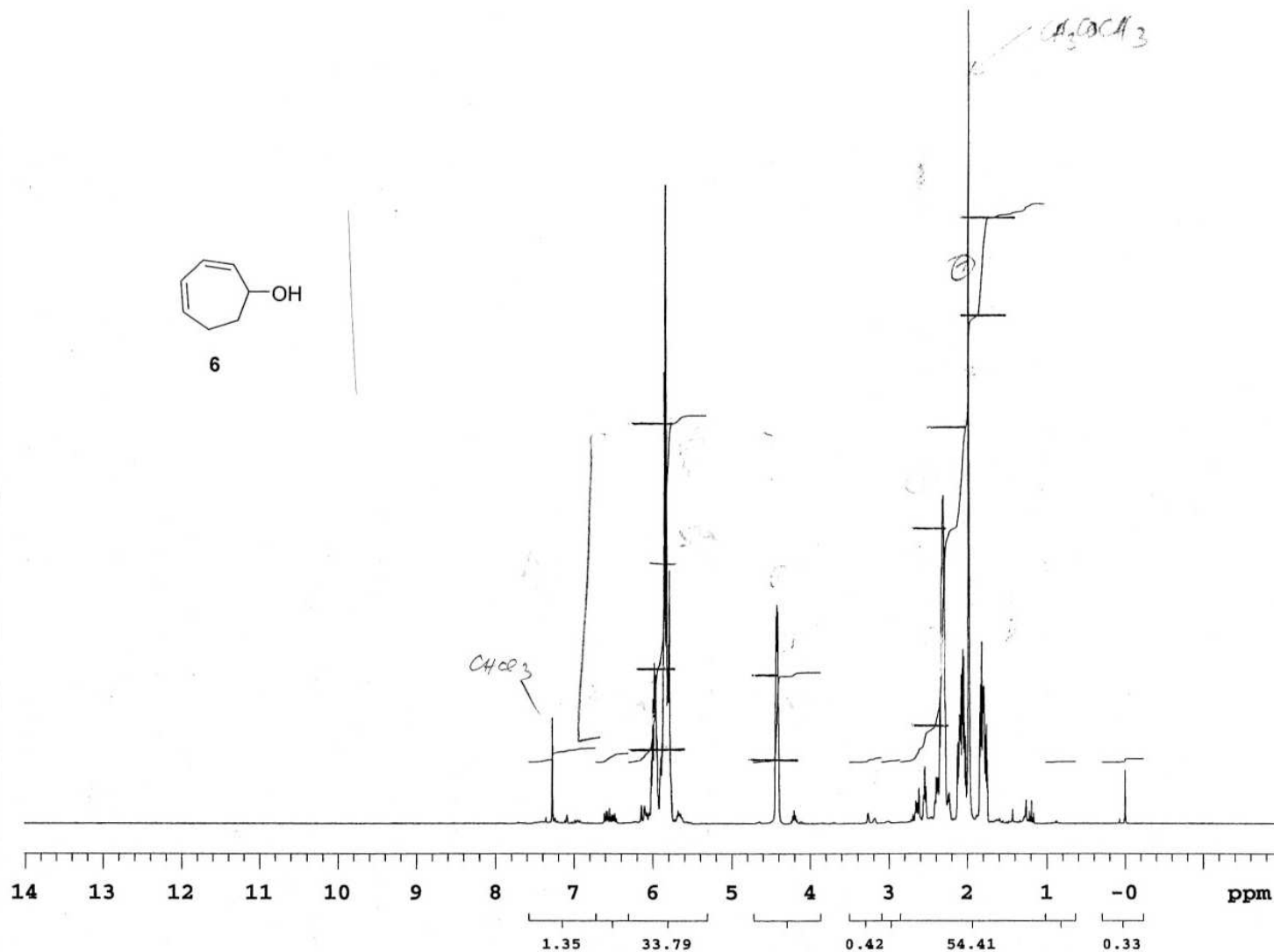
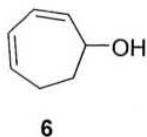
PULSE SEQUENCE

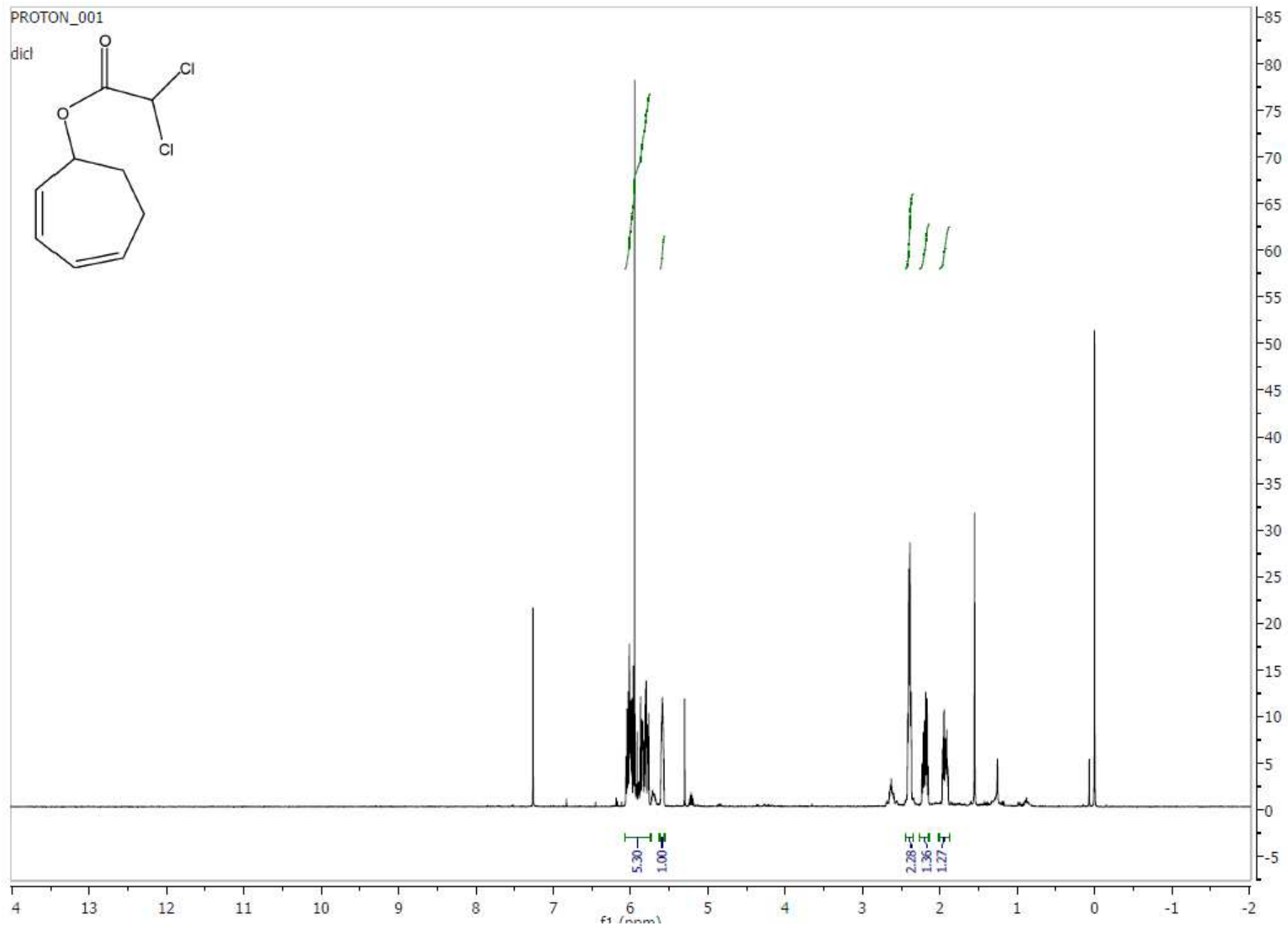
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 4798.2 Hz
8 repetitions

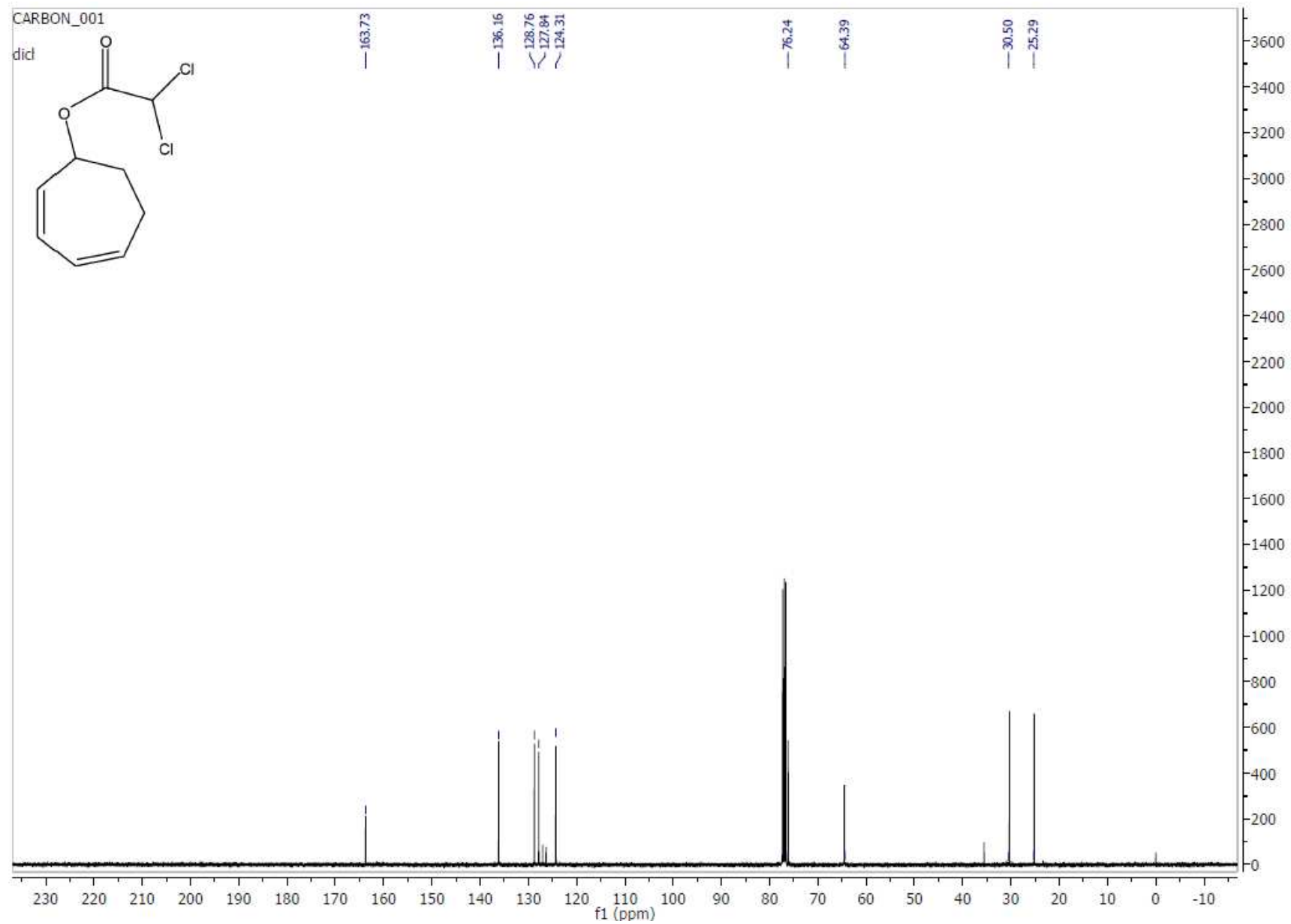
OBSERVE H1, 299.8830064

DATA PROCESSING

Line broadening 0.2 Hz
FT size 65536
Total time 1 minute

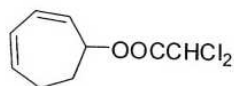






dichloro_acetate

Sample Name:
dichloro_acetate
Data Collected on:
ucd400-vnmrs400
Archive directory:
/home/walkup/vnmrsys/data/KJ
Sample directory:
dichloro_acetate_20110504_01
FidFile: DEPT_001



Pulse Sequence: DEPT
Solvent: cdcl3
Data collected on: May 4 2011

Temp. 25.0 C / 298.1 K
Sample #3, Operator: KJ

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
1024 repetitions
OBSERVE C13, 100.5155771 MHz
DECOUPLE H1, 399.7454753 MHz
Power 40 dB
on during acquisition
off during delay
WALTZ-16 modulated

Line broadening 0.5 Hz

FT size 65536

Total time 39 min

220 200 180 160 140 120 100 80 60 40 20 0 ppm



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