

# THE EFFECT OF CONJUGATION AND HOME CONJUGATION ON STRUCTURE AND REACTIVITY OF VINYL CYCLO PROPANE RADICAL CATION ( $VCP^{\bullet+}$ ) AND A VARIETY OF HIGHLY SUBSTITUTED DERIVATIVES

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**ABSTRACT:** *The phenomenon of conjugation has attracted attention for more than six decades. Particularly, the extent to which it affects the structure and properties of molecules has been the subject of much debate, even if it is generally accepted that electrons in conjugated systems are delocalized to a significant degree. The empty  $\pi^*$ -MO does not contribute to delocalizing electrons in the ground state. In cyclic systems, in which the conjugation of P-orbital's is interrupted by a spacer, such as  $-CH_2-$ , electrons can delocalize in a comparable way, termed as homoconjugation. Significant overlap is indicated between the terminal olefin ethylene group and the secondary cyclopropane hydrogen on the syn-face of syn-  $VCP^{\bullet+}$ , raising the free energy of the syn-conformer  $\sim 2.8$  Kcal/mole above that of anti-  $VCP^{\bullet+}$ . Ab initio calculations suggested that the potential surface of  $VCP^{\bullet+}$  has two minima, anti and syn-  $VCP^{\bullet+}$ , both having two lengthened CP bonds*

**KEYWORDS:** *Conjugation, Homoconjugation, Reactivity, Structure, Hyper conjugation*

## INTRODUCTION

It is widely recognized that open-shell species, such as carbonation and free radicals, gain significant stabilization from conjugation by avoiding localization of charge or spin density. The delocalized structure can be represented by pairs of canonical forms. The  $\pi$ -O is bonding between both pairs of carbon atoms, whereas the n-MO is non bonding, the node on the central carbon atom is flanked by two equally large orbitals. In cyclic systems, in which the conjugation of P-orbitals is interrupted by a spacer, such as  $-CH_2-$ , electrons can delocalize in a comparable way, termed homoconjugation. Evidence for this comes mostly from ions like cyclooctatrienyl cation, 1(1 interruption), and homonorbomadienyl anion, 2(2 interruptions, it is conjugate with the cyclopentadienyl anion).<sup>1,2,3,4</sup> Hyper conjugation is a related form of interaction, in which  $\sigma$ - orbitals are involved, the empty or half filled P-orbital and  $\sigma$ -bond interact most efficiently when they are Co-planar.<sup>35</sup>

Cyclo propane (CP) occupies an important position in organic chemistry; the nature of bonding in CP has been the target of much experimental and theoretical work for five decades.<sup>5</sup> Some models suggest that the bonding in CP is intermediate between  $\pi$  and  $\sigma$  systems to explain the unusual conjugating properties of cyclopropane. Therefore CP shows unusual reactivity for a cycloalkane, similar to olefins, it adds bromine, and, unlike typical cycloalkanes, it fails to undergo free radical halogenations.<sup>6</sup> Similarly, the unique structure and unusual reactivity of  $VCP^{\bullet+}$ , has its origin in the conjugative interaction between CP and ethane (E). Conjugation between these two moieties requires overlap of  $\pi$  and Walsh orbitals. Accepts to understand  $VCP^{\bullet+}$  chemistry benefit from a short review of important features of  $CP^{\bullet+}$

The extent of conjugative interaction in  $VCP^{\bullet+}$  was characterized for derivatives, in which the CP and E functions are locked in either a syn- or anti-conformation. The use of optically active substrates such as Sabinene (Sab)  $\alpha$ - and  $\beta$ -thujene ( $\alpha$ -Thuj and  $\beta$ -Thuj), and Car, helped to elucidate important stereo

chemical features, related to the rearrangement and nucleophilic capture of substituted vinyl cyclo propane radical cation.<sup>7, 8, 9</sup> CIDNP effects observed for these terpenes and some truncated analogs, BC310 and BC410, revealed the extent of delocalization and the position of spin and charge density in the respective radical cation.<sup>10,11</sup>

Ab initio calculation for BC310,1-Methyl bicyclo[3.1.0] hex-2-ene(1 MBC310),5-Methyl bicycle[3.1.0] hex-2-ene(5 MBC310)BC410,2-Methylenebicyclo[3.1.0] hexane(2 MBC310) and 2-Methylene-5-methyl bicycle[3.1.0] hexane(2 M5MBC310) and for the radical cations of these substrates complemented the CIDNP results<sup>11,12</sup>

### EXPERIMENTAL / PROCEDURE

A Solution containing 2.56g (0.25M) DCB and 0.89g (0.063M) Ph in 80 ml acetonitrile /methanol (3/1 by volume) was placed in a 30-mm ID tube and purged with nitrogen for 15 minutes. The tube was sealed with a rubber septum,1.7ml( ~ 0.25M)VCP was injected and the mixture cooled to -10°C.This solution was then irradiated for ~ 67 hours at 350nm.The products were isolated by liquid column chromatography, three passes were required to isolate the products.

CIDNP is a nuclear magnetic resonance technique that is based on enhanced absorption or emission signals for products formed from radical or radical ion pairs in the magnetic field of a NMR spectrometer. The CIDNP signal directions and intensities are determined by four parameters designating the nature of the individual radicals or the radical pair.

The structure and reactivity of VCP<sup>+</sup> was probed by experimental and theoretical means. The results of the electron transfer photochemistry in the presence of methanol were evaluated in light of data derived from ab initio calculations.

Irradiation of an acetonitrile/methanol (3/1 by volume) solution of DCB,Ph and VCP at 350nm for ~ 65 hours led to complete consumption of VCP. The reaction formed three ring-opened adducts bearing methoxy as well as P-Cyan phenyl group,viz, 3 - (P-Cyanophenyl)-5-methoxy-1-pentene,4(38%),(E)-1-(P-Cyanophenyl)5-methoxy-2-pentene,5(34%),and (E)-5-(P-Cyan phenyl)-1-methoxy-2-pentene,6(12%).A fourth product, formed in 2% yield, was not isolated.

The structure of 4 rests on the presence of 3 olefinic protons, H<sub>1trans</sub>( $\delta$  5.08ppm, dd,16.9, ~5HZ), H<sub>1cis</sub>( $\delta$  5.11ppm,dd,10.3,~5HZ) and H<sub>2</sub>( $\delta$  5.905ppm,ddd,16.9,10.3,7.4HZ) indicative of a terminal vinyl group.

Products 4, 5, and 6 are rationalized via nucleophilic capture of VCP<sup>+</sup> by methanol. Energetic considerations suggest that the excited state energy of DCB( $E_{(0,0)}=4.29$  eV)<sup>36</sup> renders electron transfer from VCP( $E_{(D/D^+)} \sim 2.6V$ )<sup>13,14,15</sup> to <sup>1</sup>DCB\* ( $E_{(A-/A)} = \sim 1.6V, *E_{(A-/A)} = 2.7V$ )<sup>16</sup> moderately exergonic( $\Delta G = \sim 0.1eV$ ).Subsequent nucleophilic capture VCP<sup>+</sup> (D<sup>+</sup>) by methanol followed by reaction of the resulting methoxy-substituted free radical(CH<sub>3</sub>O-D<sup>•</sup>) with the radical anion(DCB<sup>•-</sup>) by aromatic substitution can account for all isolated products. The nucleophilic capture of a vinyl cyclopropane system probes the radiochemistry of attack and how the delocalization of spin and charge is reflected in the reactivity pattern of the radical cation.

### RESULT AND DISCUSSION

The results support the preferential( or exclusive) capture of anti VCP<sup>+</sup>.The ratio of trans-5 to cis-5 is ~ 20:1,if the minor, unidentified products(vide supra) is cis-5,other wise, it is even higher. The high ratio suggests that syn-VCP<sup>+</sup> is more severely congested than the parent conformer. Significant overlap is indicated between the terminal olefinic methylene group and the secondary cyclopropane hydrogen on the syn-face of syn-VCP<sup>+</sup>, raising the free energy of the syn-conformer ~2.8Kcal/mole above that of anti-VCP<sup>+</sup> (vide infra).The calculated free energy difference corresponds to an almost seven-fold preference for the anti-conformer. The fact that the ratio of trans-5 to cis-5 is even higher may indicate that the nucleophilic capture of syn-VCP<sup>+</sup> is retarded.

The conformational aspects of VCP have been studied in significant detail by an extensive range of experimental techniques as well as calculations. The neutral parent has several rotational conformers relative to the bond connecting the vinyl and CP functions'-ray diffraction shows that VCP crystallizes as the anti

conformer.<sup>17,18,19</sup> Electron diffraction,<sup>20,21</sup> as well as vibrational,<sup>22</sup> Raman,<sup>23</sup> and NMR spectroscopy<sup>24,25,26</sup> support a rapid equilibrium between the anti- and a lesser conformer.

NMR studies of VCP and derivatives have been interpreted in terms of a two well potential surface with minima at the syn and anti geometries,<sup>24</sup> or a three well potential surface, with minima at the anti and two gauche geometries.<sup>25</sup> The potential energy surface of VCP has been examined also by computational means.<sup>27-30</sup>

The calculations on the potential energy surface of VCP at the RMP 2/6 - 31G\* level are in good agreement with the majority of previous studies.<sup>27-30</sup>

The result of VCP and VCP<sup>+</sup> show similar trends as those for 1:3-Butadiene, BD<sup>31,32</sup> and its radical cation.<sup>33,34</sup> BD also has an s-trans and two equivalent gauche conformers. The rotational barriers of BD<sup>+</sup> and VCP<sup>+</sup> are significantly increased compared to those of BD and VCP respectively.

The calculated (UMP 2/6- 31G\*) bond length for the VCP<sup>+</sup> conformers show similar trends, the allylic cyclopropane bonds C<sub>1</sub>-C<sub>2</sub> (C<sub>1</sub>-C<sub>3</sub>) are lengthened (+6%) whereas the bond connecting the secondary cyclopropane carbons C<sub>2</sub>-C<sub>3</sub> is shortened (-4%) relative to the parent. Overall, both a-anti- VCP<sup>+</sup> and syn- VCP<sup>+</sup> have structure of type B, they resemble an allyl function interacting with an ethane molecule.

In view of the changes in bond length and bond angles in syn- VCP<sup>+</sup> with a specific dihedral angle imposed, we probed the dependence of these parameters on the dihedral angle [C<sub>β</sub>-C<sub>α</sub>-C<sub>1</sub>-midpoint(C<sub>2</sub>,C<sub>3</sub>)] over the full range of rotation. The resulting changes in bond distances and cyclopropane bond angles as a function of imposed dihedral angle demonstrates the significance of stereo-electronic effects for the structure of VCP<sup>+</sup>. Even small deviation from 0° and 180° cause significant changes in the bond lengths and angles of the CP function.

Products 4-6, generated by electron transfer photochemistry of VCP are rationalized by attack of methanol on the radical cation, VCP<sup>+</sup>. The attack occurs at a secondary or the terminal vinylic carbon, centers with substantial orbital coefficients for both SOMO and LUMO.

Ab initio calculations suggested that the potential surface of VCP<sup>+</sup> has two minima, anti- and syn- VCP<sup>+</sup>, both having two lengthened CP bond. The overlap between frontier molecular orbitals of the CP and E constituents is maximizing for dihedral angles of 0° and 180°.

## TABLES

### Tables Relevant to VCP, its radical cation, TS and Intermediate

#### Comparison of Energy differences (kcal/mol) between conformers of VCP

ΔE gauche	anti-	ΔE syn	anti-	ΔE syn	gauche-	Method
1.2						Electron Diff.
1.4		2.8		1.4		Raman
		1.1				NMR
1.4		2.6		1.2		Calculation
1.9		2.7		0.8		Calculation
1.6		2.6		1		Calculation
1.2		2.7		1.5		Calculation
0.98		1.76		0.78		Calculation

**Computed Energy differences (kcal/mol) between conformers of VCP<sup>++</sup>**

Level of Theory	$\Delta E$ anti-syn
UHF	3.15
UB3LYP	3
UMP2	2.81
UMP3	2.76
UMP4(SDQ)	2.81

**Computed Energy Differences (UMP2/6-31G\*) and Estimated Barrier Heights to Rotation between Parent and Radical Cation Conformers of VCP and BD**

System	$\Delta E$ anti-syn (kcal/mol)	$\Delta H$
VCP	1.76	3-4
VCP <sup>++</sup>	2.76	15-20
BD	3.57	3-4
BD <sup>++</sup>	4.19	20-25

**Computed Bond Lengths (pm) for the syn & anti- Conformers of VCP and its Radical Cation**

anti-VCP <sup>++</sup>						anti-VCP
Bond	UHF	UB3LYP	UMP2	UMP3	UMP4	RMP2
C <sub>1</sub> -C <sub>2</sub>	162.1	162.5	160.3	161	161.2	151.3
C <sub>2</sub> -C <sub>3</sub>	141.9	143.5	143.6	143.5	143.5	149.3
C <sub>1</sub> -C <sub><math>\alpha</math></sub>	138.7	140.6	140.1	139.9	140.1	147.5
C <sub><math>\alpha</math></sub> -C <sub><math>\beta</math></sub>	140	139.3	139.6	139.7	139.8	134
syn-VCP <sup>++</sup>						syn-VCP
Bond	UHF	UB3LYP	UMP2	UMP3	UMP4	RMP2
C <sub>1</sub> -C <sub>2</sub>	162.5	162.6	160.1	160.8	161.1	151.3
C <sub>2</sub> -C <sub>3</sub>	141.7	143.3	143.6	143.6	143.5	149.6
C <sub>1</sub> -C <sub><math>\alpha</math></sub>	139.1	141.2	140.6	140.5	140.6	148.5
C <sub><math>\alpha</math></sub> -C <sub><math>\beta</math></sub>	140.2	139.3	139.7	139.8	139.9	134.1

**Computed Spin Densities ( $\rho$ ) for the syn and anti- Conformers of VCP<sup>•+</sup>**

<b>anti-VCP<sup>•+</sup></b>	<b>UHF</b>	<b>UB3LYP // UB3LYP</b>	<b>UB3LYP // UMP2</b>	<b>UMP2 //UMP2</b>	<b>UMP3</b>	<b>UMP4</b>
C <sub>1</sub>	0.264	0.231	0.215	0.216	0.221	0.224
C <sub>2</sub>	0.134	0.13	0.127	0.133	0.134	0.134
C <sub>α</sub>	-0.187	0.013	0.018	-0.132	-0.139	-0.144
C <sub>β</sub>	0.87	0.577	0.592	0.848	0.851	0.853
<b>syn-VCP<sup>•+</sup></b>	<b>UHF</b>	<b>UB3LYP // UB3LYP</b>	<b>UB3LYP // UMP2</b>	<b>UMP2 //UMP2</b>	<b>UMP3</b>	<b>UMP4</b>
C <sub>1</sub>	0.311	0.257	0.238	0.247	0.266	0.258
C <sub>2</sub>	0.113	0.11	0.106	0.112	0.113	0.113
C <sub>α</sub>	-0.219	0.005	0.011	-0.142	-0.167	-0.158
C <sub>β</sub>	0.903	0.59	0.608	0.875	0.881	0.881

**Computed Hyperfine Coupling Constants (G) for the syn and anti- Conformers of VCP<sup>•+</sup>**

<b>anti-VCP<sup>•+</sup></b>	<b>UHF</b>	<b>UB3LYP // UB3LYP</b>	<b>UB3LYP //UMP2</b>	<b>UMP2//UMP2</b>	<b>UMP3</b>	<b>UMP4</b>
H <sub>1</sub>	-10.67	-6.2	-5.83	-9.23	-9.39	-9.54
H <sub>2S</sub>	1.3	0.5	0.32	-1.54	-1.61	-1.59
H <sub>2α</sub>	5.18	7.1	7.63	5.45	5.64	5.63
H <sub>α</sub>	5.61	-1	0.63	3.67	3.94	4.14
H <sub>βS</sub>	-33.12	-14.6	-15.51	-32.88	-32.98	-33.08
H <sub>βα</sub>	-34.12	-15	-15.94	-33.7	-33.86	-33.93
<b>syn-VCP<sup>•+</sup></b>	<b>UHF</b>	<b>UB3LYP // UB3LYP</b>	<b>UB3LYP //UMP2</b>	<b>UMP2 //UMP2</b>	<b>UMP3</b>	<b>UMP4</b>
H <sub>1</sub>	-12.45	-6.95	-6.48	-10.39	-11.06	-10.8
H <sub>2S</sub>	-1.91	-1.06	-1.27	-2.29	-2.08	-2.31
H <sub>2α</sub>	7.23	10.19	11.18	7.91	7.57	8

	7.56	-1.03	-0.65	3.87	4.77	4.43
<b>H<sub>βs</sub></b>	-33.76	-14.68	-15.77	-33.44	-33.61	-33.65
<b>H<sub>βα</sub></b>	-35.25	-15.28	-16.34	-34.76	-34.93	-35

**Computed Bond Lengths and Encounter Distances (pm) for Encounter Complexes (Ecs). Transition States (TSs) and Oxonium Ions (OPs)**

<b>Bond</b>	<b>EC-A</b>	<b>TS-A</b>	<b>OP-A</b>
C <sub>3</sub> -O	295.9	209.3	151.8
C <sub>1</sub> -C <sub>3</sub>	179.9 (11%)	208.2 (28.4%)	245.5 (51.4%)
C <sub>1</sub> -C <sub>2</sub>	152.2 (-6.1%)	151.8 (-6.4%)	150.8 (-7%)
C <sub>2</sub> -C <sub>3</sub>	144.3(1.7%)	145.5 (2.5%)	151.7 (6.9%)
<b>Bond</b>	<b>EC-B</b>	<b>TS-B</b>	<b>OP-B</b>
C <sub>3</sub> -O	279	183.1	156.7
C <sub>1</sub> -C <sub>3</sub>	161.2 (-0.6%)	153.2 (5.5%)	152.5(-5.9%)
C <sub>1</sub> -C <sub>2</sub>	157.6(2.8%)	152.6 (-5.9%)	151.5(-6.5%)
C <sub>2</sub> -C <sub>3</sub>	143.1(0.8%)	147.1(3.7%)	148(4.3%)

**Computed Energies (Hartree) of Encounter Complexes (ECs), Transition States (TSs) and Oxonium Ions (OPs)**

	<b>EC-A</b>	<b>TS-A</b>	<b>OP-A</b>
<b>UHF UB3LXP</b>	-308.7238325	-308.7214746	-308.741213
<b>//UHF</b>	-310.7174247	-310.7188599	-310.7270924
	<b>EC-B</b>	<b>TS-B</b>	<b>OP-B</b>
<b>UHF UB3LYP</b>	-308.7205785	-308.7079458	-308.7104355
<b>//UHF</b>	-310.718004	-310.7164578	-310.7103384

**Computed Energy Differences (kcal/mol) between Encounter Complexes (ECs), Transition States (TSs) and Oxonium Ions (OPs)**

$\Delta E$	EC-A-EC-B	TS-A-EC-A	TS-B-EC-B
UHF UB3LXP //UHF	2.04	1.48	7.92
	-0.36	-0.9	0.97
	TS-A-TS-B	OP-A-TS-A	OP-B-TS-B
UHF UB3LYP //UHF	8.48	-12.38	-1.56
	1.51	-5.16	3.84

Method	$\Delta E$ 9•-8•	$\Delta E$ 8• -TS-C	$\Delta E$ 9• -TS-C
UHF/UHF	-5.17	11.61	16.78
UB3LYB//UHF	-2.34	7.52	9.87
UMP2//UMP2	-0.49	16.95	17.45
UB3LYB//UMP2	-1.86	8.38	10.24

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