

Conformations of Some Bicyclic Monoterpenes Based on Bicyclo[3.1.0]hexane from Their Low-Resolution Microwave Spectra

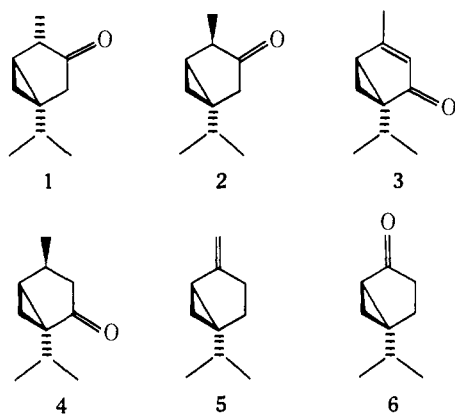
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Abstract: The low-resolution microwave (rotational) spectra of six bicyclic terpenes (thujone, isothujone, umbellulone, dihydroumbellulone, sabinene, and sabina ketone) structurally based on the bicyclo[3.1.0]hexane skeleton have been observed and a value of the rotational constant ($B + C$) has been obtained in each case. By making geometrical assumptions, based on recent microwave studies of bicyclo[3.1.0]hexanone and other model systems, the observed values of ($B + C$) have been used to establish a boat-like conformation for the bicyclic system in all molecules except umbellulone (where the five-membered ring is assumed planar) and to derive the angles ϕ of puckering of the five-membered rings (Table I).

Introduction

The bicyclic monoterpenes thujone (**1**), isothujone (**2**), umbellulone (**3**), dihydroumbellulone (**4**), sabinene (**5**), and sabina ketone (**6**) are all based structurally on the bicyclo[3.1.0]hexane skeleton. A recent review,¹ in discussion of the applications of spectroscopic techniques to the determination of the conformations of such molecules, has alluded to the difficulties of using the usual methods of interpretation of ¹H NMR spectra to establish the dihedral angle τ between the three-membered and five-membered rings (see Figure 1) and the equilibrium conformation of the bicyclic systems (boat-like if ϕ is positive, chair-like if ϕ is negative; see Figure 1). More recently,² ¹³C NMR spectroscopy has been used to indicate boat-like conformations in the cases **1**, **2**, and **4**. Microwave spectroscopic studies of the parent system bicyclo[3.1.0]hexane³ and 3-bicyclo[3.1.0]hexanone⁴ (the skeleton of **1** and **2**)



have established conclusively the predominance of the boat-like conformation in each case and values of $\tau = 64$ and 66.9° , respectively, without assumption in the latter molecule. In addition, similar investigations of 3-oxa-,^{3,5} 6-oxa-,^{3,6} and 3,6-dioxabicyclo[3.1.0]hexane^{3,7} show that $\tau \approx 64^\circ$ is consistent with the experimental data. Clearly, $\tau \approx 64^\circ$ is a geometrical parameter that may in the monoterpenes **1-6** be assumed with some confidence. There remains, however, the need to establish quantitatively the detailed conformations in these molecules.

Unfortunately, the microwave (rotational) spectra of **1-6** under usual high-resolution conditions would be prohibitively complex and in addition to determine uniquely the molecular geometry of such compounds would require extensive isotopic substitution. Encouraged by the existence of a detailed geometrical description of 3-bicyclo[3.1.0]hexanone,⁴ we have

been able nevertheless to make some progress through rotational spectroscopy to determine the conformations of **1-6** for the following reasons. These molecules are expected to approximate (by virtue of the relationship among their three principal moments of inertia but not their symmetry) to symmetric top systems having a major component of the electric dipole moment along the axis of least moment of inertia. Correspondingly, under low resolution the predominant feature in the pure rotational spectrum of such a compound is a set of equally spaced transitions of the R-branch type $J + 1 \leftarrow J$, the frequency of each of which is given approximately by the expression $\nu = (B + C)(J + 1)$. This simple pattern arises because fairly high J transitions are usually investigated in the microwave spectra of such molecules and for these the asymmetry splitting is small and therefore unresolved at low resolution. Clearly the rotational constant $B + C$ is readily obtained and hence the low-resolution spectrum leads to *one* quantity directly related to molecular geometry. If all but one (presumably that of most interest) of the geometrical parameters of the molecule can be safely assumed then the remaining quantity of interest can be obtained from the experimental ($B + C$) value.

We now report low-resolution microwave spectra of the bicyclic monoterpenes **1-6** and, by the use of soundly based geometrical assumptions, the determination in each case of the angle ϕ (see Figure 1), thereby establishing that the bicyclic systems are boat-like.

Experimental Section

Isothujone was obtained by preparative GLC from Oil of Tanacetum Vulgare and its identity confirmed through the ¹H NMR spectrum.

Thujone was prepared as a mixture with isothujone by means of the epimerization of isothujone through refluxing with sodium ethoxide.⁸ The resulting mixture contained ~30% by weight of thujone.

Umbellulone, dihydroumbellulone, sabinene, and sabina ketone were kindly supplied as samples of high purity by Dr. D. V. Banthorpe of the Chemistry Department, University College London.

Low-resolution microwave spectra were recorded in the frequency range 26.5-40.0 GHz using a Hewlett-Packard 8460A spectrometer. Gas pressures were ~0.1 mmHg and all spectra were run with the sample at room temperature (~293 K).

Results

Each of the molecules **1-6** exhibits, as expected, at low resolution a set of equally spaced rotational transitions allowed by the component μ_a of the electric dipole moment along the axis a of least moment of inertia. As an example, we show in Figure 2 the spectra due to a mixture of the epimers thujone and isothujone. It should be noted that, although the major

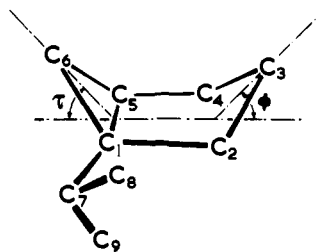


Figure 1. The carbon atom skeleton common to the bicyclic monoterpenes 1-6 showing the angles τ and ϕ which define the conformation of the bicyclic system.

Table I. Observed and Calculated $B + C$ Values (MHz) and the Angle ϕ (deg) for the Bicyclic Monoterpenes 1-6

	$(B + C)_{\text{obsd}}$	$(B + C)_{\text{calcd}}$	ϕ
thujone	1522.1 ± 0.5	1522	15
isothujone	1416.8 ± 1.8	1432	25
umbellulone	1585 ± 2	1591	0 (assumed)
dihydroumbellulone	1540.2 ± 1.2	1562	45
sabinene	1772.0 ± 0.6	1772	55
sabina ketone	1763.5 ± 0.7	1763	50

geometrical difference between the epimers is merely the juxtaposition of the methyl group and the hydrogen atom on C_4 , their rotational constants ($B + C$) differ significantly. In Table I are recorded ($B + C$) values for the compounds 1-6 obtained through the expression $\nu = (B + C)(J + 1)$. Each recorded value is the average of the several independent values obtained from a given observed rotational spectrum. The experimental error varies from molecule to molecule because the line width does likewise, reflecting the variation of the asymmetry parameters κ and hence the asymmetry splitting among the molecules.

The single quantity ($B + C$) available for each molecule is directly related to the molecular geometry, but the latter is determined by many internuclear distances and angles. Clearly, in order to use a given ($B + C$) value it is necessary to assume (or know) all but one of the independent geometrical parameters of the molecule in question. It is obvious that if such an approach is to be useful the assumptions must be soundly based. Fortunately, the recent detailed investigation of 3-bicyclo[3.1.0]hexanone⁴ provides the major part of such a base. Moreover, as indicated above, 1-6 have several common structural features and we can take these as invariant along the series, thus allowing additional confidence in the comparison within the series of the derived quantity. We shall first discuss the common features and then the special geometrical assumptions necessary in the particular cases.

The angle τ (see Figure 1) is sensibly constant among bicyclo[3.1.0]hexane,³ its 3-oxa,^{3,5} 6-oxa,^{3,6} and 3,6-dioxa^{3,7} analogues, and 3-bicyclo[3.1.0]hexanone.⁴ Since $\tau = 66.9^\circ$ in the last case relies on no assumption, we have taken this value for molecules 1-6 also. For a similar reason, the geometry of the three-membered ring is in each case taken from 3-bicyclo[3.1.0]hexanone. The common value $r(\text{C}=\text{O}) = 1.210 \text{ \AA}$ for systems 1-6 is also that used in this model compound. The contributions of the hydrogen atoms to the molecular moments of inertia are small (and of similar magnitude) in the molecules under discussion and the results are quite insensitive to the assumptions made. For the secondary and tertiary C-H bonds attached to saturated carbon atoms in the rings we have taken the values of $r(\text{C}-\text{H})$ used in the microwave investigation of bicyclo[3.1.0]hexane³ and the angles HCH have been assumed as 109.44° . In the case of the tertiary hydrogen atom at C_5 , we have assumed $\angle C_6C_5H = \angle C_1C_5H = \angle C_4C_5H$, which leads in conjunction with the heavy atom geometry established

Table II. Assumed Bond Lengths (\AA) and Angles (deg) Common to the Bicyclic Monoterpenes 1-6

quantity	value	source
Three-Membered Ring		
$r(\text{C}_1-\text{C}_6) = r(\text{C}_5-\text{C}_6)$	1.510	3-bicyclo[3.1.0]hexanone ^a
$r(\text{C}_1-\text{C}_5)$	1.519	
$\angle C_6C_1C_5 = \angle C_6C_5C_1$	59.81	
$\angle C_1C_6C_5$	60.42	
τ (Figure 1)	66.93	
all $r(\text{C}-\text{H})$	1.082	bicyclo[3.1.0]hexane ^b
Ring Hydrogen Atoms		
secondary $r(\text{C}-\text{H})$	1.092	bicyclo[3.1.0]hexane ^b
$\angle \text{HCH}$	109.44	
$\angle C_6C_5H = \angle C_1C_5H = \angle C_4C_5H$	118.3	3-bicyclo[3.1.0]hexanone ^a
Isopropyl and Methyl Groups		
primary $r(\text{C}-\text{H})$	1.101	standard values ^c
tertiary $r(\text{C}-\text{H})$	1.070	
$\angle \text{HCH} = \angle \text{CCH} = \angle \text{CCC}$	109.44	
all $r(\text{C}-\text{C})$	1.541	standard value ^c
$\angle C_6C_1C_7 = \angle C_5C_1C_7 = \angle C_2C_1C_7$	118.3	3-bicyclo[3.1.0]hexanone ^a
dihedral angle $C_1C_6C_7C_9$	78	calculated from umbellulone (see text)
Carbonyl Group		
$r(\text{C}=\text{O})$	1.210	3-bicyclo[3.1.0]hexanone ^a

^a Reference 4. ^b Reference 3. ^c Reference 9.

in 3-bicyclo[3.1.0]hexanone to the value 118.3° . The remaining feature common to 1-6 is the isopropyl group for which the standard bond lengths of $r(\text{C}_1-\text{C}_7) = 1.541 \text{ \AA}$, $r(\text{C}_7-\text{H}) = 1.070 \text{ \AA}$, $r(\text{C}_9-\text{H}) = r(\text{C}_8-\text{H}) = 1.101 \text{ \AA}$ and the standard angles $\angle \text{HCH} = \angle \text{HCC} = \angle \text{CCC} = 109.44^\circ$ have been assumed. The position of this group in relation to the bicyclic system is chosen such that $\angle C_7C_1C_5 = \angle C_7C_1C_6 = \angle C_7C_1C_2 = 118.3^\circ$ (as for H_5 above) and its rotation angle about C_1-C_7 is chosen such that the dihedral angle between C_1-C_6 and C_7-C_9 , as shown in Newman projection in Figure 3, is 78° . This choice of rotation angle is in fact dictated by the work on umbellulone discussed later. All assumed geometrical parameters common to 1-6 are collected together in Table II.

For discussion of the remaining assumptions necessary to specify completely the geometry in each particular case, it is convenient to divide the molecules into three groups. The first of these is composed of umbellulone alone. Chemical experience suggests that the atoms of the five-membered ring, the carbon atom of the exocyclic methyl group, and the carbonyl oxygen atom are coplanar. The additional bond lengths required are assumed as follows: $r(\text{C}_1-\text{C}_2) = r(\text{C}_4-\text{C}_5) = 1.506 \text{ \AA}$, $r(\text{C}_2-\text{C}_3) = 1.468 \text{ \AA}$, $r(\text{C}_4-\text{C}_{10}) = 1.501 \text{ \AA}$, and $r(\text{C}_3=\text{C}_4) = 1.338 \text{ \AA}$ and are respectively the sp^3-sp^2 type single bond length and the sp^2-sp^2 type single bond length from the microwave study of cyclopentadiene,¹⁰ the sp^3-sp^2 type single bond length in propene,¹¹ and the carbon-carbon double bond length in bicyclo[3.1.0]hex-2-ene.¹² In order to specify the internal angles of the five-membered ring we have taken $\angle C_5C_1C_2 = \angle C_1C_5C_4 = 104.9^\circ$, as implied in the recent study of bicyclo[3.1.0]hex-2-ene.¹² Then, since the five-membered ring is planar and all endocyclic bond lengths have been assumed, the remaining internal angles are fixed as shown in Table III, wherein are collected the additional geometrical assumptions for umbellulone, completed by $r(\text{C}_3-\text{H}) = 1.086 \text{ \AA}$, from ethylene,¹³ and $\angle \text{HC}_3\text{C}_2 = 125^\circ$, which is the value that makes $\angle C_4C_3H = \angle C_2C_3H$.

The second group is composed of thujone and isothujone, both of which have the bicyclic skeleton of 3-bicyclo[3.1.0]hexanone. This skeletal geometry has accordingly been as-

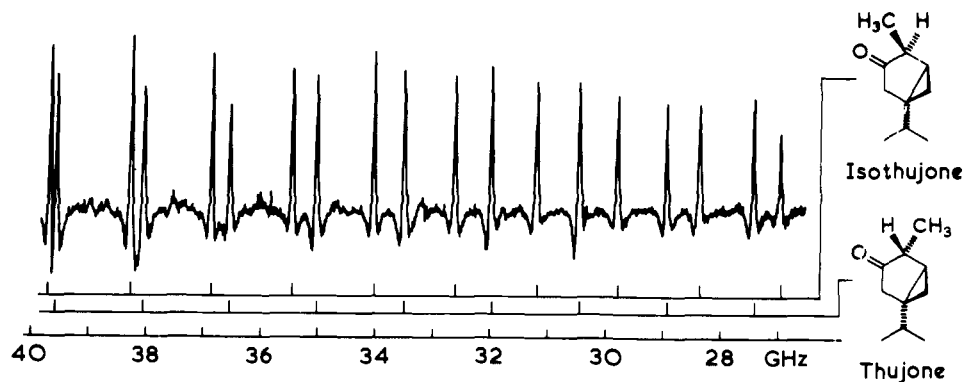


Figure 2. The low-resolution rotational spectra of thujone and isothujone.

Table III. Geometrical Assumptions (Bond Lengths (Å) and Angles (deg) Particular to Umbellulone and Dihydroumbellulone

	value	source and ref	value	source and ref
$r(C_1-C_2)$	1.506	(a)	1.534	(c)
$r(C_2-C_3)$	1.468	(a)	1.541	standard value (d)
$r(C_3-C_4)$	1.338	(b)	1.529	(c)
$r(C_4-C_5)$	1.506	(a)	1.529	
$r(C_4-C_{10})$	1.501	$CH_3-CH=CH_2$ (e)	see Table II	
$\angle C_2C_1C_5 = \angle C_1C_5C_4$	104.9	(b)	108.9	(c)
$\angle C_3C_4C_5$	111.9	fixed by ring C-C distances and $\angle C_2C_1C_5 = \angle C_1C_5C_4^f$	106.5	fixed by assumption of ring C-C distances and $\angle C_2C_1C_5 = \angle C_1C_5C_4^f$
$\angle C_2C_3C_4$	110.0		109.7	
$\angle C_1C_2C_3$	108.2		106.0	

^a Reference 10. ^b Reference 12. ^c Reference 4. ^d Reference 9. ^e Reference 1. ^f Angles assumed independent of value taken for ϕ .

summed from the recent microwave investigation,⁴ with the exception of the angle ϕ (Figure 1), which is the quantity to be determined from the observed ($B + C$) values.

The final group comprises those molecules (dihydroumbellulone, sabinene, and sabina ketone) in which the five-membered ring is saturated and in which the carbonyl group is adjacent to one of the ring junctions. In addition to the geometrical assumptions of Table II, we have taken the various C-C bond lengths of the five-membered ring from 3-bicyclo[3.1.0]hexanone⁴ with the appropriate identification, as indicated in Table IV for sabinene and sabina ketone and Table III for dihydroumbellulone. Then, with the assumption $\angle C_2C_1C_5 = \angle C_1C_5C_4 = 108.9^\circ$, as in 3-bicyclo[3.1.0]hexanone, the remaining internal angles of the five-membered rings are constrained to have the values shown in Tables III and IV if it is assumed that these are independent of the angle ϕ , which is to be varied in order best to reproduce the observed ($B + C$) values. This last assumption negligibly affects our conclusions and has been made in the case of the second group also. In the case of sabinene, it is necessary to assume additionally $r(C_4=C_{10}) = 1.339 \text{ \AA}$,¹³ $r(C_{10}-H) = 1.086 \text{ \AA}$ ¹³ from ethylene, and $\angle HC_{10}H = 120^\circ$.

The molecular geometry of each of 1-6 is thus specified by the assumptions of the preceding paragraphs, except for the one parameter of most interest in each case. In umbellulone, the planarity of the five-membered ring fixes ϕ at 0° and allows

the configuration of the isopropyl group to be determined. Given the isopropyl group geometry (Table II) and the assumption that C_1-C_7 makes equal angles with the other three bonds attached to the C_1 bridgehead, the rotation angle of the isopropyl group (see Figure 3) which best reproduces the observed ($B + C$) value for umbellulone is 78° . This configuration is that expected if the isopropyl group is staggered with respect to C_1-C_6 and C_1-C_2 (see Figure 3) and lends further credibility to our assumptions. The assumed parameters to which this result is most sensitive relate to the isopropyl group. For example, if the angle $C_7C_1C_2$ is increased by 1° either by moving C_7-C_1 while keeping it in the original $C_7C_1C_2$ plane (Figure 1) or by moving C_7-C_1 in the perpendicular plane, the rotation angle increases by 1.5 or 3° , respectively. Also, an increase of $r(C_1-C_7)$ by 0.01 \AA leads the rotation angle to decrease by 4.5° .

For the remaining molecules, 1, 2, 4, 5, and 6, this isopropyl group rotation angle was assumed and the angle ϕ varied until the experimental ($B + C$) value was in each case reproduced. The resulting values of ϕ and the values of ($B + C$) so calculated are included in Table I. The uncertainty in ϕ which results from errors in the assumptions is difficult to assess because of the geometrical complexity of the molecules. The close family relationship means, however, that conclusions for, e.g., thujone should be typical. Therefore, in Table V are shown $\Delta\phi$ values resulting for thujone when various assumed bond lengths

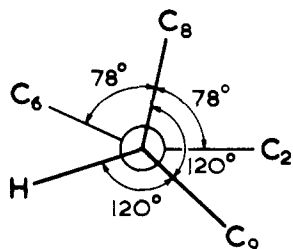


Figure 3. The relative orientation of the isopropyl group and the bicyclic system for 1-6 illustrated as a Newman projection along the C₇-C₁ bond.

and angles to which ϕ is expected to be sensitive are changed by 0.01 Å and 1°, respectively. Although some $\Delta\phi$ values are quite large, there is some evidence that the ϕ , especially when compared within the terpene series, are probably more reliable than these considerations indicate. Little change in ϕ is expected to result merely through the substitution of isopropyl and methyl groups for H at C₁ and C₄, respectively, in 3-bicyclo[3.1.0]hexanone to give thujone and isothujone. The fact that ϕ is $\sim 20^\circ$ for all three presumably means that the assumed alkyl group geometries and orientations used here, to which ϕ is quite sensitive, suffer very small errors.

Discussion

It has been established from the low-resolution rotational spectra of the bicyclic monoterpenes **1**, **2**, **4**, **5**, and **6** that the boat-like conformation ($\phi \sim 15\text{--}55^\circ$, $\tau = 66.9^\circ$, see Figure 1) is the most stable for each in the gas phase. This result is in agreement with recent studies of the rotational spectra of some model systems^{3,5-7} and with the ¹³C NMR study² of **1**, **2**, and **4** and is readily understood when it is noted that the C-H bonds on adjacent carbon atoms are all staggered in the boat-like form. In the chair-like conformation, on the other hand, the exocyclic bonds attached at C₅ and C₁ are eclipsed by those on adjacent carbon atoms in the five-membered ring.

Notwithstanding the many geometrical assumptions, it is instructive to compare the boat-like conformations. Table I makes it clear that the terpenes **1**, **2**, **4**, **5**, and **6** divide broadly into two groups: those in which ϕ is $\sim 20^\circ$ and those in which ϕ is $\sim 50^\circ$. This division is readily rationalized in terms of the competition between angle strain in the five-membered ring, which favors a planar ring, and the preferred staggering of C-H bonds on adjacent carbon atoms, which favors puckering of the ring. In the first group (thujone and isothujone) the carbonyl group is at the 3 position and consequently only the staggering between the exocyclic bonds on C₁ and C₂ and on C₅ and C₄ need be considered. Apparently, the ring must pucker only to the extent of $\phi \sim 20^\circ$ to relieve the eclipsed configuration of these bonds in the planar ring. The value $\phi = 18.8^\circ$ occurs in the precursor of these molecules, 3-bicyclo[3.1.0]hexanone,⁴ for the same reason. In the second group (dihydroumbellone, sabinene, and sabina ketone), on the other hand, the carbonyl group is now at the 2 position or (equivalently) the 4 position. As a result, in the planar five-membered ring, a pair of methylene groups is exactly eclipsed while the bonds C₅-H and C₄-H (umbellone) or C₁-C₇ and C₂-H (sabinene and sabina ketone) are nearly so. The extra eclipsing thereby existing in the planar ring is presumably relieved only at the cost of further puckering of the ring and hence ϕ increases to $\sim 50^\circ$.

Finally, the difference between thujone ($\phi = 15^\circ$) and isothujone ($\phi = 25^\circ$) is worthy of note. The conclusion from the ¹³C NMR investigation² is also that the five-membered ring is slightly more puckered for isothujone.

Table IV. Geometrical Assumptions (Bond Lengths (Å) and Angles (deg)) Particular to Sabinene (R = CH₂) and Sabina Ketone (R = O)

quantity	value	source and ref
$r(\text{C}_1\text{-C}_2)$	1.534	(a)
$r(\text{C}_2\text{-C}_3)$	1.541	standard value (see Table III)
$r(\text{C}_3\text{-C}_4)$	1.529	(a)
$r(\text{C}_4\text{-C}_5)$	1.529	
$\angle \text{C}_2\text{C}_1\text{C}_5 = \angle \text{C}_1\text{C}_5\text{C}_4$	108.9	(a) fixed by assumption of ring C-C distances and $\angle \text{C}_2\text{C}_1\text{C}_5$ $= \angle \text{C}_1\text{C}_5\text{C}_4^c$
$\angle \text{C}_3\text{C}_4\text{C}_5$	106.5	
$\angle \text{C}_2\text{C}_3\text{C}_4$	109.7	
$\angle \text{C}_1\text{C}_2\text{C}_3$	106.0	
R = CH ₂		ethylene (b)
$r(\text{C}=\text{CH}_2)$	1.338	
$r(\text{C}-\text{H})$	1.086	
$\angle \text{HCH}$	120	

^a Reference 4. ^b Reference 13. ^c Angles assumed independent of the value taken for ϕ .

Table V. Changes in the Dihedral Angle ϕ of Thujone Resulting from Changes of 0.01 Å and 1°, Respectively, in Assumed Bond Lengths and Angles

bond length	$ \Delta\phi $, deg	angle	$ \Delta\phi $, deg
$r(\text{C}_1\text{-C}_7)$	3.2	isopropyl rotation ^a	1.1
$r(\text{C}_1\text{-C}_6) = r(\text{C}_1\text{-C}_5)$	0.2	in-plane C ₇ C ₁ C ₂ ^b	2.8
$r(\text{C}_2\text{-C}_3)$	3.2	out of plane C ₇ C ₁ C ₂ ^c	3.0
$r(\text{C}_4\text{-C}_{10})$	0.7	HC ₄ C ₁₀ ^d	2.4
$r(\text{C}=\text{O})$	1.3		

^a See Figure 3. ^b C₁-C₇ moves but remains in original C₇C₁C₂ plane. ^c C₁-C₇ moves perpendicular to original C₇C₁C₂ plane. ^d CH₃ group moves but remains in original HC₄C₁₀ plane.

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