

Conformations of Conjugated Hydrocarbons. Part 2.¹ A Spectroscopic and Thermodynamic Study of *cis*- and *trans*-Penta-1,3-diene

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Vibrational spectra of both *cis*- and *trans*-penta-1,3-diene have been recorded over a range of temperatures for three phases. Complete vibrational assignments for both compounds have been made and new thermodynamic functions calculated over a range of temperatures by statistical methods. No spectroscopic or thermodynamic evidence of a high energy conformer for either compound has been found. Assignment of torsions leads to values (in kJ mol⁻¹) for *cis*- and *trans*-penta-1,3-diene respectively of 12.3 and 10.4 for the three-fold barrier height V_3 and 133 and 120 for the two-fold barrier parameter V^* .

IN Part 1¹ we investigated the conformational equilibrium present in buta-1,3-diene and 2-methylbuta-1,3-diene (isoprene) and concluded from spectroscopic and thermodynamic data that both compounds existed as a mixture of *s-trans* and *s-cis* conformers, to the exclusion of any non-planar *gauche* forms. The energy difference between conformers (ΔH^θ) were found to be 10.4 kJ mol⁻¹ for butadiene and 4.6 for isoprene. Torsional frequencies and barrier heights were calculated for both conformers of isoprene.

Molecular models of *cis*-penta-1,3-diene show that

severe steric hindrance of the *s-cis* conformer occurs by interaction of the methyl hydrogens with a vinyl hydrogen on C-1, and the interaction is severe enough to exclude *gauche* conformers as well, so we would only expect the *s-trans* conformer to exist. *trans*-Penta-1,3-diene shows no such exclusion of high energy form.

Hsu and Flygare² showed by microwave spectroscopy that the predominant conformer of both compounds is

¹ Part 1, D. A. C. Compton, W. O. George, and W. F. Maddams, *J.C.S. Perkin II*, 1976, 1666.

² S. L. Hsu and W. H. Flygare, *J. Chem. Phys.*, 1970, **52**, 1053.

s-trans, and obtained methyl barrier heights of 3.10 and 7.55 kJ mol⁻¹ for *cis*- and *trans*-penta-1,3-diene respectively. They searched for evidence of high energy conformers but reported finding none for either compound.

We present complete vibrational spectra and full assignments for both compounds, which lead to a calculation of gas-phase thermodynamic functions over a range of temperatures by statistical methods.

TABLE I
cis-Pentadiene

Raman (cm ⁻¹)			I.r. (cm ⁻¹)					
Liquid	Solid	Polarisation	Contour	Gas	Liquid	Solid	Matrix isolation	
140vw	158	<i>dp</i>						A''
214vw	230	<i>dp</i>						A''
	310vvw			212vw	228vw			A''
359vw	361m	<i>dp</i>	C	353vw	358vw			A''
390m	394s	<i>sp</i>	B	385m	391m	388m	390w	A'
482vvw	480vvw	<i>sp</i>		484vvw	490vvw			A'
612w	610w	<i>sp</i>		605wsh	610wsh	610msh	610m	A'
622w	630w	<i>dp</i>	C	621s	623s	631s	633s	A''
765w	765vw	<i>sp</i>		772wsh		765wsh		A'
776w	780w	<i>dp</i>	C	777s	774s	775s	782m	A''
					850vw			
886m	885w	<i>sp</i>		884w	886wsh	882wsh	881w	A'
905w	907w	<i>dp</i>	C	905vs	905vs	902vs	905s	A''
				954w}				
955	960w	<i>mp</i>		958w}	955m	953m	951m	A'
	1 000vw		C	997s	996s	997s	1 004s	A''
1 035w	1 032w	<i>dp</i>		1 035w	1 030w	1 030w	1 031w	A''
1 043w	1 043w	<i>p</i>		1 055br	1 045vw	1 045vw	1 043vw	
			B	1 127w	1 129w	1 133vw		A'
1 166m	1 165m	<i>p</i>		1 166w	1 163w	1 163w	1 164w	A'
1 252s	1 251s	<i>p</i>		1 251w	1 250w	1 250w	1 250w	A'
1 297s	1 295m	<i>sp</i>		1 297w	1 295w	1 294w	1 294w	A'
1 361w	1 359w	<i>p</i>		1 358w	1 358w	1 357m	1 356m	A'
1 385m	1 384m	<i>sp</i>		1 390m	1 384m	1 381m	1 380m	A'
1 439w	1 440w	<i>mp</i>	A	1 437m	1 433s	1 432s	1 433s	A'
1 453m	1 451vw	<i>dp</i>		1 452w	1 449w	1 450w	1 450m	A''
	1 540vw			1 530w	1 530w	1 530w		
	1 578vw			1 575w	1 577w	1 580w		
1 594m	1 594m	<i>sp</i>	A	1 603	1 595s	1 596s	1 592s	A'
1 645vs	1 643vs	<i>sp</i>	A	1 655	1 645m	1 646m	1 642m	A'
1 745vvw	1 745vvw	<i>p</i>		1 736w	1 730w	1 730w		
1 769w	1 768w	<i>sp</i>		1 775w	1 776w	1 776w		
				1 819m	1 810m	1 812m	1 820w	
1 907w	1 906w	<i>sp</i>	A	1 987w	1 988	1 990w	1 992w	
2 861	2 863	<i>sp</i>		2 874m	2 864m	2 862m	2 858w	
2 893	2 888	<i>p</i>		2 899vw	2 894w	2 892w	2 893w	
2 918m	2 910m	<i>sp</i>		2 928m	2 922m	2 920m	2 918m	A'
2 940vw	2 938vw	<i>dp</i>	C?	2 949w	2 940wsh	2 940w	2 937m	A''
2 969w	2 964w	<i>p</i>		2 970vw	2 970w	2 972w	2 965w	A'
							2 982w	
2 992w	2 998w	<i>sp</i>		2 990wsh	2 994w	2 997w	2 991w	A'
3 010s	3 005s	<i>sp</i>		3 012wsh			3 010w	A'
3 020wsh			B	3 033s	3 024s	3 022s	3 021m	A'
3 052vw	3 050vw	<i>p</i>		3 068w	3 054w	3 058w	3 057w	A'
3 087	3 082m	<i>mp</i>	B	3 097m	3 089m	3 090m	3 082m	A'

Variable temperature n.m.r.³ found no temperature dependence on coupling constants for *cis*-penta-1,3-diene but found a temperature dependence for butadiene, isoprene, and *trans*-penta-1,3-diene in solution which they explained on the basis of an equilibrium involving a 90° out-of-plane form. This however does not agree with our results in Part I on butadiene and isoprene, which we concluded existed as mixtures of planar conformers.

Tarasova and Sverdlov⁴ calculated the vibrational frequencies for both compounds, predicting all frequencies except for the methyl torsion, but they attempted to fit their results to incomplete spectral data.

³ A. L. Segre, L. Zetta, and A. DiCorato, *J. Mol. Spectroscopy*, 1969, **32**, 296.

EXPERIMENTAL

Samples of 99% purity were obtained from Fluka in sealed ampoules. Raman spectra of liquid and solid samples were recorded over a range of temperatures as in Part I. I.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer which covers the range 4 000—180 cm⁻¹. Gas samples were held between KBr or polyethylene windows in a 20 cm cell, liquid samples in CsI or polyethylene cells and solid samples in KRS5 cells of varying thickness. A high temperature gas cell of 10 cm path length was used to record i.r. spectra up to 200 °C. I.r. spectra of samples held in argon matrices at 20 K between 600 and 4 000 cm⁻¹ were run using an Air Products AC2L cryostat.

⁴ N. V. Tarasova and L. M. Sverdlov, *Optika i Spektrosk., Akad. Nauk S.S.S.R., Otdel. Fiz. Mat. Nauk, Sb. Statei*, 1967, **3**, 140.

Tables 1 and 2 give the complete vibrational spectra of both compounds.

Variable Temperature Studies.—The Raman and i.r. spectra of both compounds were recorded over a range of liquid temperatures from the m.p. to above room temperature. The liquids were frozen and solid spectra recorded

window temperature was raised slowly with repeat recording. No spectral changes were observed until new peaks appeared (at *ca.* 35 K) which were assumed to be due to aggregation of the sample molecules as the matrix degraded. No marked differences either in band frequencies or intensities were noticed by altering the matrix : sample ratio,

TABLE 2
trans-Pentadiene

Raman (cm ⁻¹)			I.r. (cm ⁻¹)				
Liquid	Solid	Polarisation	Contour	Gas	Liquid	Solid	Matrix isolation
	112w						
150vw	156vw	<i>dp</i>		196vw			<i>A''</i>
202	203w	<i>dp</i>		205vw	205vw		<i>A''</i>
	210vwsh	<i>dp</i>		250m	262m		<i>A''</i>
265w	268w	<i>dp</i>	C	383vw	390vw		<i>A'</i>
392vw		<i>sp</i>		454w	453w	450w	<i>A'</i>
450vw	449vw	<i>mp</i>	B?	483vw	489vw		<i>A'</i>
479s	483s	<i>sp</i>		530vw			
522w	516w	<i>sp</i>			600wsh		600vw
				630w	631m	632w	630w
			C	698w	700wsh	700w	700w
					739vw	737w	
742vw		<i>sp</i>		818w	817m	817m	818m
818w	820w	<i>dp</i>	C	899.0s	896s	892s	896vs
898w	892w	<i>dp</i>	C	948.5m	948m	948m	948m
944vw		<i>mp</i>	C?	977w	976wsh	973m	974w
978vw	975vw	<i>mp</i>		1 003.3vs	1 000s	1 000s	1 004vs
			C	1 048vw	1 040vwsh	1 035wsh	1 037w
1 037w	1 034w	<i>dp</i>	C		1 070vwsh		
1 082w	1 078vw	<i>sp</i>			1 160wsh	1 175wsh	1 176w
1 170wsh	1 174wsh	<i>mp</i>			1 183w	1 185w	1 188w
1 180m	1 184m	<i>sp</i>			1 269w	1 269w	1 269w
1 262wsh	1 272wsh	<i>p</i>		1 280	1 280wsh	1 292wsh	1 290w
1 279s	1 292s	<i>sp</i>			1 306m	1 306m	1 307m
1 323vwsh		<i>p</i>			1 350vwsh		
					1 376m	1 374m	1 379m
1 378w				1 420	1 413m	1 411m	1 412m
1 415w		<i>p</i>	A/B		1 435wsh	1 433m	1 436m
1 432vwsh		<i>dp</i>			1 499m	1 448m	1 449m
1 452w		<i>p</i>			1 526w	1 528w	
					1 584wsh	1 584w	
1 599w		<i>sp</i>		1 608m	1 602m	1 604s	1 606m
1 663vs		<i>sp</i>	B	1 660m	1 653m	1 657m	1 653m
					1 700w		
					1 723w		
				1 770w	1 762w	1 768w	
			B	1 802m	1 796m	1 800m	1 793m
				1 850w	1 850w	1 856w	1 854w
2 734w	2 730w	<i>sp</i>	B	2 742w	2 735w	2 733w	2 735w
2 855w	2 855w	<i>sp</i>	B	2 867w	2 855m	2 852m	2 856m
2 887w	2 887w	<i>sp</i>	B	2 899w	2 885m	2 885m	2 888m
2 918s	2 916s	<i>sp</i>	B?	2 931m	2 917m	2 918m	2 922m
2 937wsh	2 935w	<i>dp</i>	C?	2 946w	2 935m	2 937m	2 942m
2 967vw	2 970w		B	2 937m	2 964m	2 963m	2 973m
					2 980wsh	2 980wsh	2 980wsh
2 997s	3 000s	<i>sp</i>					
3 012vwsh	3 015vwsh	<i>p</i>	B	3 018s	3 013s	3 014s	3 016s
	3 035vw			3 050wsh	3 035m	3 039m	3 041m
3 092w	3 088m	<i>sp</i>	A/B	3 098m	3 090m	3 090m	3 092m

at liquid nitrogen temperature after careful annealing. High temperature gas i.r. spectra were recorded up to 200 °C. No peaks present in liquid spectra of either compound were absent in the solid spectra in Raman or i.r., and no weak peaks in the liquid or gas spectra intensified on heating. These results led us to assume that neither compound existed as a measurable mixture of conformers.

Matrix Isolated Spectra.—We recorded i.r. spectra of samples deposited in an inert argon matrix at 20 K over a range of concentrations 100 : 1—1 000 : 1 (matrix : sample). The mixtures were sprayed slowly on to the cold window and spectra run at medium (2 cm⁻¹) resolution. Then the

except that higher ratios enabled sharper peaks and better resolution. The frequencies given in Tables 1 and 2 refer to the highest matrix : sample ratio where the peak was observable.

RESULTS AND DISCUSSION

Assignments.—Assignment of the fundamental vibrations of both compounds is simplified by the planar nature of the molecules which cause the 33 fundamentals to be all i.r. and Raman active and fall into two groups 22 *A'* in-plane polarised vibrations and 11 *A''* out-of-plane depolarised vibrations which give C type gas

bands contours. The assignments follow the assignments of butadiene and isoprene in Part I.

A''. The central C-C torsion was assigned to the weak *dp* Raman band present at 150 and 140 cm^{-1} in the liquid spectrum of *trans*- and *cis*-penta-1,3-diene respectively, which compares with the values obtained for buta-1,3-diene and isoprene of 160 and 165 cm^{-1} in the liquid state. The methyl torsions were assigned to weak i.r. peaks found to be broad in the liquid and absent in the Raman liquid spectrum, although a very weak shoulder present in the solid spectrum of *trans*-penta-1,3-diene at 210 cm^{-1} corresponds to methyl torsion. The out-of-plane wags were assigned on the basis of their intense C contour bands in the gas i.r. spectrum and depolarised nature in the Raman.

A'. We did not attempt to characterise the low frequency skeletal modes. It is difficult to assign the two C-C stretches as these appeared to couple in the isoprene molecule and our assignments of the in plane modes between 950 and 1200 cm^{-1} are ambiguous. Table 3 shows our selected assignments for both compounds.

Methyl rotation barrier. Hsu and Flygare² measured the methyl barrier heights of *cis*- and *trans*-penta-1,3-diene as 3.10 and 7.55 kJ mol^{-1} in the gaseous state.

TABLE 3
Fundamental frequencies (cm^{-1})

<i>trans</i> -Penta-1,3-diene	Vibration	<i>cis</i> -Penta-1,3-diene
	<i>A''</i> out-of-plane vibrations	
150 (L)	=C-C= torsion	140 (L)
196	Skeletal mode	214 (L)
205	Methyl torsion	212
250	Skeletal mode	353
698	<i>cis</i> -CH=CH wag	621
	<i>cis</i> -CH=CH wag	777
899.0	=CH ₂ wag	905
948.5	<i>trans</i> -CH=CH wag	997
1 003.3	<i>trans</i> -CH=CH wag	
1 048	Methyl rock	1 035
1 435 (L)	Methyl deformation	1 452
2 946	Methyl C-H stretch	2 949
	<i>A'</i> in-plane vibrations	
383	Skeletal mode	385
454	Skeletal mode	484
483	Skeletal mode	612 (L)
630	Skeletal mode	772
977	=CH ₂ rock	884
1 082 (L)	C-CH ₃ stretch	954
1 170 (L)	=C-C= stretch	1 166
1 180 (L)	Methyl rock	1 127
1 280	-CH= bend	1 251
1 306 (L)	-CH= bend	1 297
1 376 (L)	Methyl <i>sym</i> -deformation	1 358
1 420	=CH ₂ scissor	1 390
1 449 (L)	Methyl <i>asym</i> -deformation	1 437
1 608	C=C <i>asym</i> -stretch	1 603
1 660	C=C <i>sym</i> -stretch	1 655
2 931	<i>sym</i> methyl C-H stretch	2 928
2 973	<i>asym</i> methyl C-H stretch	2 970
2 980 (L)	<i>sym</i> =C-H stretch	2 990
2 997 (L)	<i>sym</i> =C-H stretch	3 010 (L)
3 018	<i>sym</i> -CH= stretch	3 033
3 050	<i>asym</i> -CH= stretch	3 068
3 098	<i>asym</i> =C-H stretch	3 097

Durig *et al.*⁵ measured barrier heights in solid *cis*- and *trans*-crotonitrile as 12.9 and 7.36 kJ mol^{-1} , and the

methyl groups in the crotonitriles have similar methyl environments to the pentadienes. In Part I we obtained a value of 11.3 kJ mol^{-1} for isoprene which compared well with a microwave value of 11.0, and the methyl group in isoprene is in a similar environment to the methyl group in *cis*-penta-1,3-diene. Our values of 12.25 and 10.38 kJ mol^{-1} for *cis*- and *trans*-pentadiene respectively which were measured from i.r. torsional frequencies are significantly different from those previously measured.² A summary of methyl barrier heights and calculation parameters is given in Table 4.

TABLE 4
Barrier heights

Two-fold barrier		
$10^{40}Im/g \text{ cm}^2$	15.936	12.422
F/cm^{-1}	1.757	2.253
ν/cm^{-1}	140	150
$V^*/\text{kJ mol}^{-1}$	133.4	119.5
Three-fold barrier		
$10^{40}I\alpha/g \text{ cm}^2$	5.087	4.515
F/cm^{-1}	5.502	6.199
ν/cm^{-1}	212	205
$V_s/\text{kJ mol}^{-1}$	12.25	10.38

Rotational fine structure. An asymmetric rotor may show rotational fine structure on out-of-plane (C type contour) vibrational gas bands if it approximates to either an oblate or prolate rotor, in which the ratio $2C : B$ has values of 1.0 and 2.0 respectively where $A-C$ are the conventional rotational constants. *trans*-Penta-1,3-diene approximates to a prolate rotor with a value of $2C : B$ of 1.88 but *cis*-penta-1,3-diene approximates poorly to a prolate rotor with a value of 1.73. For a prolate rotor satellite bands should be observed with a spacing of $2(A - B)$.

The rotational constants from microwave measurements² predict spacings of approximately 1.74 cm^{-1} for *trans*-penta-1,3-diene.

trans-Penta-1,3-diene shows fine structure on all the strong C bands. The *trans* wag at 1 003 cm^{-1} shows a series of satellites at higher frequency. A plot of nine peaks between 1 005 and 1 020 cm^{-1} gave a straight line of slope 1.73 cm^{-1} . Plots of satellites of the *trans* wag at 948.5 and the vinyl =CH₂ wag at 899 cm^{-1} gave slopes of similar values.

The close agreement between the predicted spacing of the satellite bands and that observed confirms the structure of the *trans*-penta-1,3-diene molecule as *s-trans*.

We examined the high resolution gas spectrum of *cis*-penta-1,3-diene for rotational splitting of the out-of-plane vibrations: however no splitting was observable under the resolution of ca. 0.6 cm^{-1} available.

Thermodynamic Calculations.—We calculated the thermodynamic functions for the *s-trans* conformers of both *cis*- and *trans*-pentadiene by normal statistical methods for both compounds. In our calculations we used the structures postulated by Hsu and Flygare,² and we assumed all the fundamentals to be harmonic oscil-

⁵ J. R. Durig, C. K. Tong, C. W. Hawley, and J. Bragin, *J. Phys. Chem.*, 1971, **75**, 44.

lators except for the methyl torsions. Thermodynamic contributions for the methyl torsions were calculated using the Tables of Pitzer and Gwinn in refs. 6 and 7. The results are shown in Tables 5 and 6. The previous values for the thermodynamic functions were calculated from other compounds by Kilpatrick *et al.*⁸ We decided in Part I that the values for isoprene calculated in the

In equations (5)–(8) of Part I we showed that a mixture of conformers gave rise to higher values of thermodynamic functions than a single conformer,¹ and calculated the concentration of the high energy *s-cis* conformer of buta-1,3-diene and the energy difference between conformers ΔH_0^\ominus .

We also calculated the concentration of *s-cis* isoprene

TABLE 5
Thermodynamic functions for *cis*-penta-1,3-diene

T/K	$-(G^\ominus - H_0^\ominus)T^{-1}/J\ K^{-1}\ mol^{-1}$		$(H^\ominus - H_0^\ominus)T^{-1}/J\ K^{-1}\ mol^{-1}$		$S^\ominus/J\ K^{-1}\ mol^{-1}$		$C_P^\ominus/J\ K^{-1}\ mol^{-1}$	
	Previous work ⁶	This work	Previous work ⁶	This work	Previous work ⁶	This work	Previous work ⁶	This work
273.15		245.65		55.91		301.56		88.93
298.15	263.6	250.68	60.7	58.97	324.1 *	309.64	94.6	95.86
300.0	263.6	251.04	61.1	59.19	324.7	310.24	95.0	96.37
400.0	282.9	269.80	73.2	71.87	356.1	341.66	123.4	123.02
500.0	300.4	287.20	85.8	84.48	386.2	371.69	147.7	146.14
600.0	317.2	303.67	97.9	96.42	415.1	400.09	166.9	165.47
700.0	333.4	319.38	108.8	107.47	442.2	426.85	183.3	181.70
800.0	348.2	334.40	119.2	117.64	467.4	452.04	196.6	195.53
900.0	362.8	348.80	128.4	126.97	491.2	475.78	208.4	207.43
1 000.0	377.8	362.63	136.8	135.54	514.6	498.18	218.4	217.71

* 322.8.⁷

TABLE 6
Thermodynamic functions for *trans*-penta-1,3-diene

T/K	$-(G^\ominus - H_0^\ominus)T^{-1}/J\ K^{-1}\ mol^{-1}$		$(H^\ominus - H_0^\ominus)T^{-1}/J\ K^{-1}\ mol^{-1}$		$S^\ominus/J\ K^{-1}\ mol^{-1}$		$C_P^\ominus/J\ K^{-1}\ mol^{-1}$	
	Previous work ⁶	This work	Previous work ⁷	This work	Previous work ⁷	This work	Previous work ⁷	This work
273.15		249.84		62.98		312.82		98.66
298.15	255.7	255.52	64.0	66.23	319.7 *	321.75	103.3	105.06
300.0	255.9	255.93	64.4	66.47	320.3	322.40	104.2	105.53
400.0	276.2	276.89	77.8	79.34	354.0	356.24	130.5	130.41
500.0	295.0	295.99	90.8	91.79	385.8	387.78	161.5	162.44
600.0	312.6	313.78	102.5	103.48	415.1	417.26	171.1	171.15
700.0	329.3	330.54	113.4	114.31	442.7	444.86	186.6	187.02
800.0	345.2	346.44	123.4	124.28	468.6	470.72	199.6	200.64
900.0	360.3	361.59	132.6	133.44	492.9	495.03	210.5	212.38
1 000.0	374.5	376.06	141.0	141.87	515.5	517.93	220.1	222.56

* 315.6.⁷

same manner⁸ were not adequate, and as our values for entropy and heat capacity are significantly higher for *trans*-penta-1,3-diene and our value for the heat capacity of *cis*-penta-1,3-diene is also higher we must assume that their values are too low. Messerley *et al.*⁹ estimated the gas-phase entropy for both compounds from liquid phase measurements, and these values are also given in Tables 5 and 6.

⁶ D. R. Stull, E. F. Westram, and G. C. Sinke, 'Chemical Thermodynamics of Organic Compounds,' Wiley, New York, 1969.

⁷ G. N. Lewis and M. Randall, 'Thermodynamics,' McGraw-Hill, New York, 1961.

and the thermodynamic functions for isoprene gas using an experimental value of ΔH_0^\ominus . As we obtained no spectroscopic evidence for either *cis*- or *trans*-penta-1,3-diene existing in the *s-cis* conformer we present the thermodynamic functions of the *s-trans* conformers only of both compounds, with no increase in thermodynamic functions due to a mixture of conformers.

[6/1949 Received, 18th October, 1976]

⁸ J. E. Kilpatrick, C. W. Beckett, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, 1949, **42**, 225.

⁹ J. F. Messerley, S. T. Todd, and G. B. Guthrie, *J. Chem. and Eng. Data*, 1970, **15**, 227.