

Structure of Cyclohepta-1,3-diene from Nuclear Magnetic Resonance Analysis

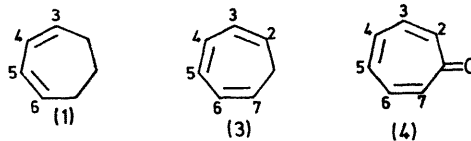
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Summary ^1H N.m.r. coupling constants obtained from spectral analysis of cyclohepta-1,3-diene (**1**) at 300 MHz are not in accord with an earlier proposed C_s structure in which all but one of the carbon atoms are coplanar; instead these data indicate a distorted tub conformation of C_2 symmetry.

CYCLOHEPTA-1,3-DIENE (**1**) has been assumed on the basis of electron diffraction data to have a C_s structure in which the allylic and olefinic carbon atoms are entirely coplanar.¹ This contrasts with the observed structures for cyclohexa-1,3-diene (**2**)^{2(a)} and cyclohepta-1,3,5-triene (**3**)^{2(b)} both of which have a skewed orientation across the trigonal single bonds.† Since the increment of π -conjugation energy gained by planar alignment of the olefinic carbons for

either (**2**) or (**3**) is not large enough to offset the corresponding increase in strain and repulsion energies, the balance between these sets of terms should not be drastically different for the intermediate member of this series, (**1**).



^1H N.m.r. coupling constant data can be a sensitive probe for changes in molecular structure and conformation.³ An analysis of the 300 MHz spectrum of yields data which suggests that the angle of twist between the two olefinic

† Reported angles of twist are: 18° for (**2**) and 36° for (**3**).

bonds in (1) is not zero but roughly in between that reported for (2) and (3). (1) (J_{34} 11.6) although slightly larger than the similar coupling in (3) (J_{45} 11.2) or (4) (J_{45} 11.0) is in the expected

TABLE

Compound	Chemical shift ^a		Coupling constant		Ref.
	Proton	δ (Hz)	Proton	J (Hz)	
(1)	4 \equiv 5	37.9	3,4 \equiv 5,6	11.55	This work ^b
	3 \equiv 6	23.4	3,5 \equiv 4,6	0.67	
			36	0.72	
			45	6.89	
(3)			2,3 \equiv 6,7	8.9(8.6)	9 and 10
			2,4 + 2,5	1.5 (—)	
			2,6 \equiv 3,7	0.0(0.0)	
			27	—	
			3,4 \equiv 5,6	5.5(5.3)	
			3,5 \equiv 4,6	0.7(0.8)	
			36	0.7(0.0)	
			45	11.2(10.7)	
(4)			2,3 \equiv 6,7	12.0	5
			2,4 \equiv 5,7	1.1	
			2,5 \equiv 4,7	0.7	
			2,6 \equiv 3,7	-0.3	
			27	3.2	
			3,4 \equiv 5,6	8.2	
			3,5 \equiv 4,6	1.1	
			36	0.1	
			45	11.0	

^a Relative to an arbitrary zero point at low field; ^b Although the largest probable error in J from the final iterative calculation was <0.05 Hz a more reasonable error estimate is ± 0.1 Hz. CDCl_3 was used as solvent.

The ^1H nmr spectrum of cyclohepta-1,3-diene at 60 MHz shows a narrow vinyl resonance (δ 5.6–5.75) with only a small amount of fine structure. At 300 MHz with spin decoupling at the allylic absorptions a symmetrical pattern, 40 Hz in width, characteristic of an AA'BB' spin system is observed. Analysis of this spectrum by the iterative least squares program LAOCN3⁴ gave a theoretical spectrum providing a good fit of the experimental one. The parameters from this analysis are recorded in the Table along with some literature data relevant to the discussion below.

Complete sets of nmr coupling constants are available for unsaturated 7-membered rings of known geometries.⁵ For such systems the large variation observed in the coupling across the C (sp^2)—C (sp^2) single bond is an indication of the conformation,⁵ a twisted diene chromophore is characterized by J_{34} 5.5 (3) and a completely planar diene moiety displays J_{34} 8.2 (4).

The coupling constant computed for the double bond in

range for a coupling across an unstrained olefinic bond (e.g. J_{cis} for ethylene is 11.5 ± 0.1 Hz)⁶. The vicinal coupling found between C₄ and C₅ (6.89 Hz) in (1) is almost midway between the value for a largely skewed and an entirely planar 7-membered ring diene chromophore. This coupling constant is identical (within experimental error) to the coupling across the formal single bond (J_{34} 6.96) in thiopin 1,1-dioxide,⁷ which has a flattened tub structure according to X-ray analysis (C₄—C₅ is at an angle of 22.8° from the plane defined by the remaining carbons)⁸. It is tempting to conclude that a similar angle describes HC₄C₅H for cyclohepta-1,3-diene, but in any case the above comparisons point to a distorted tub conformation for (1) of C₂ symmetry.

We thank the Faculty Research Committee at UCSC for support of this work, and Mr. Le Roy F. Johnson of Varian Associates for the 300 MHz nmr spectrum.

(Received, March 24th, 1971, Com 382)

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