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THE PROTON MAGNETIC RESONANCE SPECTRA OF CYCLOPENTADIENE TRIMERS AT 220 MHz

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Abstract—Detailed interpretations of the spectra of four of the possible isomeric cyclopentadiene trimers are given. It is shown that the geometry of the ring fusion can be determined by measuring the chemical shifts of the bridge protons and of the allylic proton on the cyclopentene ring 3a-H.

WE HAVE recently offered a detailed interpretation of selected oligomers of cyclopentadiene.¹ Of particular interest in the spectra of cyclopentadiene trimer and tetramer was the large deshielding effect experienced by bridge protons compressed against C—C single or double bonds. The magnitude of this effect is of the order of 1 to 1.5 ppm. In this paper the PMR spectra of three of the possible trimers of cyclopentadiene are described and compared with that of the normal trimer already reported.

The structure of the normal trimer, which is obtained by heating cyclopentadiene at 180° C, is 1.¹ This is described as the *endo*, *exo*, *endo* isomer. Upon heating *exo*-



cyclopentadiene dimer with cyclopentadiene the *endo*, *exo*, *exo*-cyclopentadiene trimer (2) was obtained. The procedure employed for conversion of *endo*-cyclopenta-



diene dimer to the *exo* isomer, i.e. addition of HCl followed by dehydrochlorination,² is outlined in Scheme 1. Subjecting trimers 1 and 2 to this series of reactions produced





two isomers, which are formulated as exo, exo, endo- and exo, exo-cyclopentadiene trimers, (3) and (4) respectively. Compounds 2, 3 and 4 as obtained from the reaction products by distillation were slightly viscous liquids. 4 could be obtained



pure as colourless, glistening plates, m.p. 69 to 70° C, by recrystallization of the crude product from methanol. 2 and 3 could not be purified in this way and it was necessary to use preparative GLC to obtain pure samples of these trimers.

The PMR spectra of trimers 1 to 4 are given in Spec. No. 0064 to 0067. The numbering system which will be used for referring to the various protons in the molecules is given in formula 5.



A difference which is immediately apparent on comparing the spectra of 1 to 4 is that the high field doublet present in Spec No. 0064 and 0065 is absent in 0066 and 0067. We have already assigned this high field doublet to $10-H_y$ in the spectrum of 1 and we submit that this assignment is also correct for 2. Decoupling establishes that

the doublet coupling of the $\delta 0.67$ band in Spec. No. 0065 is due to a proton situated at $\delta 1.90$ and hence 10-H_x is strongly deshielded due to compression against the C(6)—C(7) double bond as is the case in 1.¹ The chemical shifts of 10-H_x and 10-H_y thus confirm the *endo*, *exo* nature of the C(4a)—C(8a) ring fusion.

It was previously established that the chemical shift of the allylic proton 3a-H indicated the geometry of the fusion between the bicycloheptane and the cyclopentene nuclei.¹ When the cyclopentene ring is *endo* fused 3a-H has a shift of *ca*. $\delta 3.0$ whereas when it is *exo* fused 3a-H lies at *ca*. $\delta 2.5$. By comparison of Spec. No. 0064 and 0065 it was deduced that 1 has an *endo* fused cyclopentene ring, while 2 has an *exo* fused one.

The assignments of the bands of 1 and 2 are collected in Table 1 and follow from our previous interpretation of the spectra of the cyclopentadiene oligomers.

The spectra of trimers 3 and 4 reveal a further example of the considerable deshielding of protons due to compression arising from crowding inside polycyclic structures of this type.

From the structures of 3 and 4, shown in Spec. No. 0066 and 0067, it is clear that $10-H_x$ and $11-H_y$ would be expected to interact with one another and thus, from our previous experience, should be strongly deshielded. The proton $10-H_y$ does not now lie in the positive shielding zone of the C(6)—C(7) double bond, as in the case of 1 and 2 and is therefore expected, as for $11-H_x$, to have a chemical shift similar to that of a normal bicycloheptane or bicycloheptane bridge proton, i.e. $\delta 1\cdot 2.^3$ Inspection of Spec. No. 0066 and 0067 shows that these expectations are fulfilled. The high field portions of two separate AB splitting patterns are seen at $\delta 1\cdot 0$ to $1\cdot 3$. Decoupling experiments showed that the low field portions of both of these spectra lie at $\delta 1\cdot 7$ to $2\cdot 1$. Following the arguments above, the bands at $\delta 1\cdot 0$ to $1\cdot 3$ are assigned to $10-H_y$ and $11-H_x$ and those at $\delta 1\cdot 7$ to $2\cdot 1$ to $11-H_y$ and $10-H_x$.

As in the case of 1 and 2, measurement of the shift of 3a-H confirms that 3 has an *endo* fused cyclopentene ring and that 4 has an *exo* fused C_5 ring. The full interpretations of the spectra of 3 and 4 are given in Table 1.

Apart from the change in the shift of the bridge protons on altering the fusion of the rings at C(8a)—C(4a) from *endo*, *exo* to *exo*, *exo* it may also be noted that this alteration also results in 4a-H and 8a-H moving upfield by *ca*. 0.5 ppm.

From the interpretation of these spectra it is thus shown that, by the measurement of the chemical shifts of the bridge protons and 3a-H, it is possible to establish very simply the structures of fused polycyclic systems of this type.

Coupling constants

As would be expected the observed coupling constant between protons such as $10-H_x$ and $10-H_y$, where one of the protons is compressed, is greater than that normally observed for bicycloheptene or bicycloheptane bridge protons. The difference between J_{xy} for the normal (i.e. according to shift) and compressed systems is clear from Table 2. If it is assumed that in 3 and 4 the angle between $C(10)-10H_y$ and $C(10)-10H_x$ is less than $C(11)-11H_y$ and $C(11)-11H_x$, due to the reduced ability of the compressional strain on $10H_x$ and $10H_y$ to be released by deformation in other parts of the molecule, then it is possible to assign the two AB systems in Spec. No. 0066 and 0067 specifically because of the two quite different coupling constants observed (see Table 2).

It is well known that the exo protons of bicycloheptene and bicycloheptane

	11y	1.10	1.20			1.95		1-94	
	11x	1.22	1-33			1.00		1-03	
	10y	0.75	0.67			1.17		1.10	
	10x	2-24	06-1			2.10		1.70	
	9 a		2.00			2.48			
ul shift (8	6	1-98	1.77	or	1.86	2·01		06-1	or 1·83
1 chemica	6,7	5.92	5.95			90.9		6.11	
el: protor	5,8	2-72	2.83			2.58		2.67	
roton lab	4a, 8a	1-90	2.05		1.97	1-39	1.32	1-46	1-39
	4	1.98	1.77	or	1.86	2.22		06·1	or 1-83
	3a	2.95	2.44			3-02		2.46	
-	2,3	5-60 5-46	5.63		5-40	5.58	5.44	5.65	5-41
	1y					2.15	or 2·12	t l	
	1x		2.48			2.15	or 2·12	2.50	
Commonied	Compound -	(1)	(2)			(3)		(4)	
Spec.	No.	0064	0065			0066		0067	

TABLE 1. ASSIGNMENT OF RESONANCES IN THE SPECTRA OF CYCLOPENTADIENE TRIMERS

R. G. FOSTER and M. C. McIvor

Common d	Proton label:coupling constant (Hz)						
Compound	11 _x , 11 _y	$11_x, 11_y$ $10_x, 10_y$ 4, 3a	4a, 8a				
(1)	7.5	10					
(2)	8.0	10.5		7.8			
(3)	9.5	11.0	5.0	7.5			
(4)	9.5	11.5		7.0			

TABLE 2. COUPLING CONSTANTS

TABLE 3. STRONG BANDS IN THE 700 TO 800 cm^{-1} region of the infra-red spectra of 1 to 4

	Strong bands			
Trimer	(cn	1 ^{−1})		
(1)	752	690		
(2)	753	691		
(3)		698		
(4)		704		

systems show a greater coupling to the neighbouring bridgehead protons than the corresponding *endo* protons.⁴ Therefore it should be possible to observe coupling between 4-H and 3a-H, or between 9-H and 9a-H, in 1 and 3 since it was established that in both these compounds the C_5 ring is *endo* fused. In the case of 3 we were successful in observing a coupling of 4-H to 3a-H of 5.0 Hz, this was established by decoupling and enabled 4-H and 9-H to be assigned precisely.

Infra-red spectra

Since the structures of trimers 1 to 4 were established by PMR a feature in the infra-red spectra of these compounds has been identified, which can also be used for the identification of the part structures 6 and 7. Bicycloheptene derivatives have



characteristic bands at 700 to 800 (s), 1580 to 1590 (w) and 3010 to 3020 (m) cm⁻¹. It was noticed that in the cyclopentadiene trimers containing the unit **6** *two* strong bands are seen in the 700 to 800 cm⁻¹ region of the spectrum whereas those containing unit 7 exhibit only *one*, relatively broad band (see Table 3).

EXPERIMENTAL

Endo, exo, exo-cyclopentadiene trimer (2) was prepared by heating endo-cyclopentadiene dimer (10 cc) with exo-cyclopentadiene dimer (2 cc) in a Carius tube for 10 hrs. at 180° C. Distillation of the reaction product gave a main fraction, b.p. 124 to 130° C/2 mm, which consisted of 90% of the desired product.

Exo, exo, endo (3) and exo, exo, exo (4) cyclopentadiene trimers were prepared by addition of hydrochloric acid to trimers 1 and 2, respectively, followed by dehydrochlorination with potassium *tert*. butoxide in dimethyl sulphoxide in the manner described in the literature² for the preparation of *exo*-cyclopentadiene dimer from the *endo* dimer. The main fraction from the preparation of (3) had a b.p. of 100 to 110° at 1 mm and contained approximately 85% of the desired product. The main fraction from the preparation of 4 had a b.p. of 120 to $125^{\circ}/2$ mm and crystallized in the receiver. Recrystallization of this fraction from methanol gave glistening plates, m.p. 69 to 70° .

The molecular weights of 2, 3 and 4 were confirmed by mass spectrometry.

The ¹H NMR spectra were measured, using deuteriochloroform solutions, at 13° with a Varian Associates 220 MHz spectrometer, model HRSC-1.

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