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CARBON–HYDROGEN STRETCHING VIBRATIONS IN FLUORO*CYCLO*HEXANES

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Abstract—For perfluoro*cyclo*hexane derivatives in which not more than one fluorine at each carbon atom is replaced by a hydrogen atom, it is established that C–H groups with an axial hydrogen show infra-red absorption at 2980 cm^{-1} and with equatorial hydrogen at 2974 cm^{-1}. With 1H/2H-, 1H:2H/- and 1H:3H/-decafluoro*cyclo*hexane the frequencies are reduced somewhat. When the C–H groups are adjacent to a double bond the absorption is at 2961 cm^{-1}, while olefinic C–H groups absorb near 3095 cm^{-1} in the fluorocarbon series. The C–H absorption is at 3102 cm^{-1} in pentafluorobenzene.

MANY perfluoro*cyclo*hexane derivatives have recently become available[1–5] for infra-red spectral investigation* and when provided several of their structures were uncertain. In order to establish spectral correlations which might be useful in structure determination, it was decided to measure the carbon–hydrogen stretching frequencies near 3000 cm^{-1} under high resolution to see if hydrogen atoms in the axial and equatorial positions could be differentiated.

RESULTS

Table 1 shows the frequencies and approximate extinction coefficients in the gas phase. The boiling points are given to aid identification with the literature[1–5] where the preparation and the structure determinations are discussed. The second column of the table indicates the axial, *a*, equatorial, *e*, or olefinic, *o*, nature of the hydrogen atoms in the order quoted in the name. For the polyhydro compounds the numbering of the hydrogen atoms on one side of the *cyclo*hexane ring are given in front of the solidus and the substituents *trans* to these, thereafter.

DISCUSSION

For the saturated compounds at the head of Table 1 the carbon–hydrogen stretching frequency lies in the narrow range 2968 to 2984 cm^{-1}, and it would seem that the variation between axial and equatorial substituents is much less than in the deuterated steroids[7] where the axial C–D links are found to absorb about 40 cm^{-1} below the equatorial. Nevertheless a closer inspection shows that an isolated axial hydrogen,

* The full spectra will be submitted to the Documentation of Molecular Spectroscopy punched card collection. Comparison of the spectra of dodecafluoro*cyclo*hexane and undecafluoro*cyclo*hexane confirm that the sample of the former used by Rowlinson and Thacker[6] contained some of the undecafluoro-body indicated by absorption at 730, 830 and 943 cm^{-1} as these authors themselves suggest.

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TABLE 1

Name		cm^{-1}	ε	Boiling point
Saturated				
Undecafluoro*cyclo*hexane	*a*	2979	8	63°C
1H/2H-decafluoro*cyclo*hexane	*a/a*	2977	12	70
1H:2H/- „ „ „	*a:e/*	2974, 2969	10, 6	91
1H/3H- „ „ „	*a/e*	2979, 2973	15, 3	78
1H:3H/- „ „ „	*a:a/*	2974	20	89
1H/4H- „ „ „	*a/a*	2980	15	78
1H:4H/- „ „ „	*a:e/*	2979, 2973	11, 11	86
1H/2H:4H-nonafluoro*cyclo*hexane	*a/a:a*	2983, 2974	5, 20	101
1H:4H/2H- „ „	*a:e/a*	2984, 2979, 2973	9, 10, 9	93
1H:2H/4H- „ „	*a:e/a*	2979, 2974	12, 10	107
1H:2H:4H/- „ „	*e:a:a/*	2973, 2968	10, 8	136
1H:4H/2H:5H-octafluoro*cyclo*hexane	*a:e/a:e*	2979, 2974, 2970	10, 15, 8	118
*1CF_3/4H-tridecafluoromethyl-*cyclo*hexane	*/e*	2974	9	88 II[8]
*1CF_3:4H/- „ „ „	*e/*	2981	11	88 I[8]
Mono-olefines				
1H-nonafluoro*cyclo*hexene	*o*	3104, 3073	7, 4	63
3H- „ „	*x*	2961	8	69
4H- „ „	*(a)*	2983	8	71
1H:2H-octafluoro*cyclo*hexene	*o:o*	3085	liq.	87
3H/4H- „ „	*x/(a)*	2980, 2962	9, 7	86
3H:4H/- „ „	*x:(a)/*	2979, 2960	7, 7	116
4H/5H- „ „	*(a)/(a)*	2977, 2970	10, 8	90
4H:5H/- „ „	*(a):(e)/*	2979, 2975	8, 8	99
1H:5H- „ „	*o:(a)*	3102, 3067, 2980	3, 6, 8	85
Polyenes				
1H-heptafluoro*cyclo*hexa-1:3-diene	*o*	3113, 3084	15, 4	72
2H- „ „	*o*	3098	6	76
1H-heptafluoro*cyclo*hexa-1:4-diene	*o*	3097	8	67
*1H:4H-hexafluoro*cyclo*hexa-1:4-diene	*o:o*	3087	19	—
*1H:5H- „ „ „	*o:o*	3082	19	71
Pentafluorobenzene	*ar*	3102	4	89

a = axial, *(a)* = pseudoaxial, *e* = equatorial, *(e)* = pseudoequatorial, *o* = olefinic, *x* = adjacent to double bond, *ar* = aromatic.
* These structures are not yet proved by chemical means, but are based on the methods of preparation and the infra-red spectra.

as in undecafluoro-, 1H/3H-, 1H:4H/- or 1H/4H-decafluoro*cyclo*hexane, absorbs at 2980 ± 2 cm^{-1} and that an isolated equatorial hydrogen absorbs at 2974 ± 2 cm^{-1}, as in the 1H/3H- and 1H:4H/-decafluoro*cyclo*hexanes. Indeed the identification between the *cis/trans* 1H:4H-isomers was originally made on the grounds that the first isomer obtained showed two overlapping bands and was therefore unlikely to be the *trans*-isomer which would be centrosymmetric and have only one infra-red active C–H stretch. This expectation was confirmed when the *trans*-isomer became available

and shown to have only one band: the identification has subsequently[3] been confirmed by dipole moment measurements. Based on the infra-red differentiation between axial and equatorial hydrogen atoms, it is possible to identify the isomers of 4H-tridecafluoromethyl*cyclo*hexane.[4,8] The bulky trifluoromethyl group in these compounds will ensure that the molecules adopt that conformation of the *cyclo*hexane ring in which the $—CF_3$ group is lying equatorially. A *trans*-hydrogen atom at position 4 must also be equatorial and would absorb at 2974 cm^{-1} as observed for the isomer designated[8] II, whereas a *cis*-hydrogen at position 4 would be axial and the observed absorption at 2981 cm^{-1} for isomer I is in accord with the predicted 2980 cm^{-1} for this arrangement.

The frequencies given above for axial and equatorial hydrogens are shifted slightly when two hydrogens are on adjacent atoms in the ring or are both in axial positions on the same side of the plane of the ring. In the 1H/2H-compound one band is observed at 2977 cm^{-1} which is only 3 cm^{-1} from the expected position since both hydrogens are axial. This will be the out-of-phase C–H stretch, as the in-phase vibration will be almost inactive in the infra-red since the dipole moment change would, from symmetry considerations, be parallel to the twofold symmetry axis and consequently approximately perpendicular to the C–H bonds which are stretching. With 1H:2H/-decafluoro*cyclo*hexane the decrease in frequency is slightly greater and the bands are at 2974 and 2969 cm^{-1}; in this compound the hydrogens are closer together in space and it is perhaps a consequence of this that the frequencies move towards the hydrocarbon values. The hydrogens are also close in space in the 1H:3H/-compound in which they occupy axial positions on the same side of the ring plane and the frequency is again reduced about 6 cm^{-1} to 2974 cm^{-1}. In this case the single band observed will be the in-phase motion, since the out-of-phase motion must produce a dipole moment change perpendicular to the plane of symmetry and approximately perpendicular to the C–H bonds and so be very weak.

Experience with the 1H:2H:4H-nonafluoro*cyclo*hexanes suggests that their C–H stretching frequencies are governed by similar rules. Except when involved in 1H:2H/- or 1H:3H/-structures the C–H absorptions remain near 2980 cm^{-1} when axial, and 2974 cm^{-1} when equatorial, with a slight lowering for the 1H/2H-system. Again the characteristic frequency for the 1H:3H/-structures is 2974 cm^{-1} when diaxial and the 1H:2H/-arrangement again gives a pair of bands near 2974 and 2969 cm^{-1}. For example 1H/2H:4H-nonafluoro*cyclo*hexane (*a*/*a*,*a*) has absorption at 2974 cm^{-1} attributable to the 1 : 3 diaxial structure of hydrogens on $C_{(2)}$ and $C_{(4)}$; this band is about double the intensity of that at 2983 cm^{-1} which must be attributed to the isolated axial hydrogen on $C_{(1)}$.

In the fluoro*cyclo*hexene series there is seen from Table 1 to be a possibility of distinguishing hydrogen substitution at positions 4 and 5 from that at 3 and 6. The conformation will be the usual half chair form and the local arrangement at positions 4 and 5 is hardly to be distinguished from that in the *cyclo*hexane series; the substituents are normally designated pseudo-axial and pseudo-equatorial. It is to be expected that the hydrogen atoms will prefer the pseudo-axial position and this is consistent with the frequency of 2983 cm^{-1} in 4H-nonafluoro*cyclo*hexene. The three *cyclo*hexene derivatives with the hydrogen at position 3 absorb at 2960, 2961 and 2962 cm^{-1} respectively, and absorption at 2961 cm^{-1} must be considered characteristic

[8] R. P. Smith, Ph.D. Thesis, University of Birmingham.

for substitution at this position. Indeed when first available the 3H:4H/- and 4H:5H/-octafluoro*cyclo*hexenes were merely known to be products of dehydrofluorination of 1H:2H/4H-nonafluoro*cyclo*hexane and these structures were suggested from the infra-red spectra and their confirmation by chemical methods consequently accelerated. In assigning structures the 3H-absorption in the *cyclo*hexenes at 2961 cm^{-1} was especially valuable.

Olefinic hydrogens appear to absorb in the range 3070 to 3120 cm^{-1} according to the type of unsaturated system and the point of attachment thereto. There are insufficient examples to indicate the exact pattern to be expected except to comment that hydrogen attached to a 1:3-diene system absorbs at the upper end of this range and that in some cases the band was unexpectedly split, possibly by Fermi resonance. In the one case examined with hydrogens attached at both ends of a double bond, 1H:2H-octafluoro*cyclo*hexene, the absorption was too weak to measure accurately in the vapour.

In pentafluorobenzene the C–H stretching frequency at 3102 cm^{-1} is slightly higher than the fundamental frequencies of 1:2:4:5-tetrafluorobenzene[8,9] at 3097 cm^{-1} (A_g) and 3088 cm^{-1} (B_{1u}).

It is clear that in all these compounds the presence of the fluorine raises the C–H stretching frequency by about 70 cm^{-1} compared with the hydrocarbons. Taking average hydrocarbon frequencies[10,11] the comparison shown in Table 2 is obtained. The frequency shifts are probably electronic in origin.

TABLE 2

	Hydrocarbon	Fluorocarbon	Difference
Naphthenic C–H	2890 cm^{-1}	2980 cm^{-1}	+90 cm^{-1}
Olefinic C–H	3020 cm^{-1}	3080 cm^{-1}	+60 cm^{-1}
Aromatic C–H	3040 cm^{-1}	3100 cm^{-1}	+60 cm^{-1}

EXPERIMENTAL

The compounds were measured in the gas phase in a 10 cm absorption cell using a 2500 l.p.i. N.P.L. replica grating of size 6 in. × 6 in. in the third order on the spectrometer previously described.[12] The frequencies are thought to be correct to ±2 cm^{-1} the chief error being that of locating the centre of the wide bands, especially when they overlap. The extinction coefficients[11], ε, are maximum values for non-overlapping bands and are approximate estimates of the separate intensities for overlapping bands; they are quoted to indicate relative intensities in each compound.

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