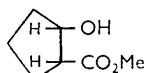


948. An Infrared Study of Methyl *cis*- and *trans*-2-Hydroxycycloalkanecarboxylates.*

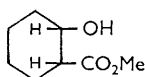
By JOSÉ CASTELLS and JAIME PALAU.

The positions and shapes of the hydroxyl and carbonyl infrared absorption bands of the *cis*- and *trans*-isomers of methyl 2-hydroxycyclopentanecarboxylate, 2-hydroxycyclohexancarboxylate, and 2-hydroxycycloheptancarboxylate have been studied under successive dilutions in carbon tetrachloride. The clear-cut distinction found between the behaviour of the *cis*- and the *trans*-isomer, which can be rationalised on the basis of intra- and/or inter-molecular hydrogen-bonding, may be used for diagnostic purposes. The finer details of the spectra are discussed with relation to the geometry of the rings.

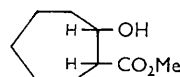
PASCUAL and his co-workers have described the *cis*- and *trans*-isomers of methyl 2-hydroxycyclopentanecarboxylate (*cis*-I and *trans*-I), methyl 2-hydroxycyclohexancarboxylate (*cis*-II and *trans*-II), and methyl 2-hydroxycycloheptancarboxylate (*cis*-III and *trans*-III),¹ assigning configurations on the basis of non-spectral physical and chemical properties. In the present Paper we present the results of a study of the positions and shapes of the hydroxyl and carbonyl stretching bands of the three pairs of stereoisomers, under successive dilutions in carbon tetrachloride.



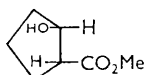
(*cis* - I)



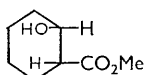
(*cis* - II)



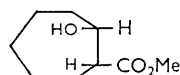
(*cis* - III)



(*trans* - I)



(*trans* - II)



(*trans* - III)

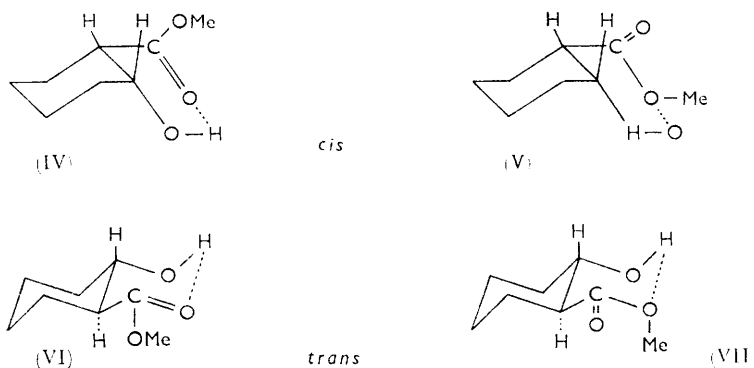
Hydrogen-bonding is the factor that governs infrared (i.r.) behaviour, and (a) a hydrogen-bond between a hydroxyl and a carbonyl group causes a bathochromic shift in those i.r. bands that correspond to the stretching modes of both groups;² and (b) intramolecular hydrogen-bonds are insensitive to dilution, whereas the inter-molecular ones are influenced by concentration, in that the higher the dilution, the smaller

* Presented at the XIXth Internat. Congress Pure Appl. Chem., July 1963, London.

¹ (a) F. Lacasa and J. Pascual, *Anales real Soc. españ. Fis. Quim.*, 1955, **51**, B, 551; (b) J. Pascual, J. Sistaré, and A. Regás, *J.*, 1959, 1943; (c) J. Palau, J. Pascual, and J. M. Ráfols, *Bull. Soc. chim. France*, 1964, 269.

² Cf., G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco and London, 1960.

the intermolecular association. At very high dilutions no intermolecular association should exist and the i.r. bands should be typical of the free groups. However, there seems to be no generally accepted frequency above which a band would represent absorption of a completely free hydroxyl group, but the limit should lie somewhere between 3600 and 3650 cm^{-1} . Depending on the molecular structure, concentrations even



$<0.0003\text{M}$ (in CCl_4) may be necessary to observe absorption assignable to free hydroxyl groups.³

EXPERIMENTAL

The spectrophotometer employed was an Infracord 137 G, and an accuracy of ± 6 units in the region of 3500 and of ± 3 units in the region of 1700 cm^{-1} is accepted.

For each isomer, the hydroxyl and carbonyl bands were registered at eight different dilutions: *cis*-I: 0.197, 0.099, 0.050, 0.025, 0.0015, 0.0008, 0.0004, 0.0002; *trans*-I: 0.211, 0.105, 0.052, 0.026, 0.0015, 0.0008, 0.0004, 0.0002; *cis*-II: 0.214, 0.107, 0.053, 0.026, 0.0014, 0.0007, 0.0004, 0.0002; *trans*-II: 0.206, 0.103, 0.052, 0.026, 0.0016, 0.0008, 0.0004, 0.0002; *cis*-III: 0.209, 0.104, 0.052, 0.026, 0.0014, 0.0007, 0.0004, 0.0002; *trans*-III: 0.213, 0.107, 0.054, 0.027, 0.0014, 0.0007, 0.0004, 0.0002M. In each case, a 1.0-mm. NaCl cell was used for the first four dilutions and a 7.4-cm. cell for the other four.

Materials were the purest samples obtained in previous work;¹ their purity was now further checked by v.p.c. The solvent, CCl_4 , was refluxed and distilled over P_2O_5 ; great care was taken to avoid the presence of humidity, in particular, when using the 7.4-cm. cell.

RESULTS AND DISCUSSION

Some representative curves of hydroxyl and carbonyl absorption bands of the six compounds studied are presented in the Figure (see also the Table); for the sake of clarity, traces corresponding to dilute solutions have been displaced vertically.

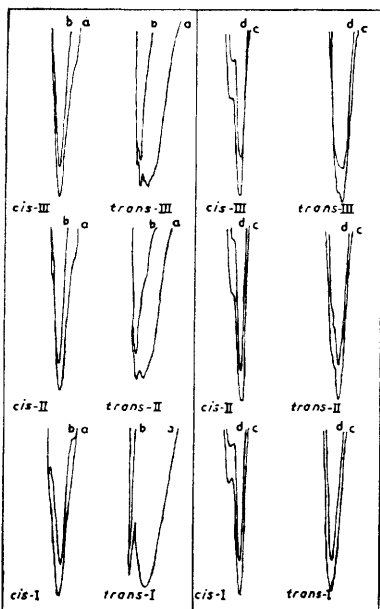
Hydroxyl Bands.—The gross behaviour of the three pairs of stereoisomers is similar: the hydroxyl bands of *cis*-derivatives are highly symmetric, and the absorption curve for each dilution appears as an envelope of the next one, the position of the maxima being almost constant; contrariwise, the absorption of *trans*-derivatives changes dramatically with dilution. However, closer comparison reveals some differences, mainly that, while the high-dilution spectra of *trans*-I show a very accute band at 3610 cm^{-1} , indicative of a free secondary hydroxyl group, the position and shape of the corresponding bands of compounds *trans*-II and *trans*-III show the existence of some residual association. This association is believed to be of an intramolecular type on the grounds of the high dilutions attained and of preliminary apparent-molecular-weight determinations.

The above results confirm the accepted configurations of the three pairs of methyl esters; as models show, in the *cis*-derivatives the substituents are optimally placed for intramolecular hydrogen-bonding. As a representative example, in formulæ (IV) and (V),

³ J. D. Connolly and K. H. Overton, *J.*, 1961, 3366.

4940 Study of Methyl *cis*- and *trans*-2-Hydroxycycloalkanecarboxylates.

methyl *cis*-2-hydroxycyclohexanecarboxylate has been drawn in its most stable conformation, *i.e.*, with the bulkier substituents (methoxycarbonyl) joined by an equatorial bond to the ring in a chair form. The differences between the spectra of *trans*-II and *trans*-III and that of *trans*-I are partly due to the greater flexibility of the cyclohexane and cycloheptane rings than of the cyclopentane ring, so that the *trans*-derivatives of the former are more susceptible to intramolecular hydrogen-bonding: this is illustrated by the chair



Hydroxyl (curves *a* and *b*) and carbonyl (curves *c* and *d*) absorption bands of compounds *cis*-I and *trans*-I, *cis*-II and *trans*-II, and *cis*-III and *trans*-III. See Table.

Compound	Curve	Concn. (mole l. ⁻¹)	Max. (cm. ⁻¹)	Compound	Curve	Concn. (mole l. ⁻¹)	Max. (cm. ⁻¹)
<i>cis</i> -I	a	0.1970	3509	<i>cis</i> -I	c	0.0250	1739, 1715
<i>cis</i> -I	b	0.0015	3509	<i>cis</i> -I	d	0.0002	1739, 1715
<i>trans</i> -I	a	0.2110	3610, 3460	<i>trans</i> -I	c	0.0260	1730
<i>trans</i> -I	b	0.0015	3610	<i>trans</i> -I	d	0.0002	1730
<i>cis</i> -II	a	0.2140	3521	<i>cis</i> -II	c	0.0260	1736, 1715
<i>cis</i> -II	b	0.0007	3521	<i>cis</i> -II	d	0.0002	1736, 1715
<i>trans</i> -II	a	0.2060	3571, 3509	<i>trans</i> -II	c	0.0260	1721
<i>trans</i> -II	b	0.0008	3584	<i>trans</i> -II	d	0.0002	1721
<i>cis</i> -III	a	0.2090	3534	<i>cis</i> -III	c	0.0260	1736, 1718
<i>cis</i> -III	b	0.0007	3534	<i>cis</i> -III	d	0.0002	1736, 1715
<i>trans</i> -III	a	0.2130	3571, 3509	<i>trans</i> -III	c	0.0270	1721
<i>trans</i> -III	b	0.0007	3571	<i>trans</i> -III	d	0.0002	1721

conformation, with two equatorial substituents, of methyl *trans*-2-hydroxycyclohexanecarboxylate (VI, VII). Nevertheless, intramolecular association in *trans*-isomers is less favoured than that in *cis*-isomers, because it implies an extra puckering of the ring⁴ and, when possible (not too high dilutions), the intermolecular association prevails.

Carbonyl Bands.—The shape of the carbonyl band of *trans*-I is quite regular and the position of the maximum, 1730 cm.⁻¹ in dilute solutions, is normal for an ester carbonyl with no association. In contrast, the bands of *trans*-II and *trans*-III are somewhat irregular and the maxima, for dilute solutions, appear at 1721 cm.⁻¹, confirming the existence of some weak residual association.

In the *cis*-isomers, the absorption maxima are found at 1715 cm.⁻¹, which is low for a free ester carbonyl, confirming the existence of intramolecular association between the

⁴ Cf. S. J. Angyal and C. G. McDonald, *J.*, 1952, 686.

[1964]

Bryant, Hassall, and Weatherston.

4941

hydroxyl and the carbonyl and that the prevailing conformation resembles (IV). However, all show a second peak at 1736—1739 cm^{-1} , which is higher than that of the free carbonyl band of the *trans*-isomer of the cyclopentane series and can be explained by the presence of a second type of conformation (V) in which the double-bond character of the carbonyl grouping should be enhanced.

These results are in agreement with previous conclusions that the normal mode of hydrogen-bonding between alcohols and esters involves the carbonyl rather than the alcoholic oxygen of the ester group,⁵ the latter being involved only to a minor extent,⁶ except in favoured situations.⁷

DEPARTAMENTO DE QUÍMICA ORGÁNICA DE BARCELONA,
PATRONATO " JUAN DE LA CIERVA " (C.S.I.C.),
UNIVERSIDAD DE BARCELONA, ESPAÑA.

[Received, December 28th, 1963.]

⁵ Cf. F. Dalton, J. I. McDougall, and G. D. Meakins, *J.*, 1963, 4068.

⁶ A. R. H. Cole and (Miss) G. T. A. Müller, *J.*, 1959, 1224.

⁷ H. B. Henbest and B. J. Lovell, *J.*, 1957, 1965.
