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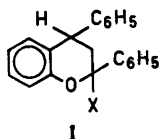
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The NMR Spectra of Some Chroman Derivatives

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Some years ago, 2,4-diphenyl-2-methylchroman (I a) was synthesised in this laboratory and two isomers melting at 118–119° and 83.0–83.5° were isolated.¹ Because the molecule contains two asymmetric carbon atoms, it is evident that the isolated isomers were racemic mixtures in which the enantiomers of one mixture were diastereomers of those of the other mixture. The configurations of the substances were not established at that time. The NMR spectra of the substances, however, make it possible to determine these configurations.



- X = (a) CH₃
(b) C₆H₅
(c) OC₂H₅

In order to obtain more information, the NMR spectra of 2,2,4-triphenylchroman (I b) and 2,4-diphenyl-2-ethoxychroman (I c) were taken in addition to those of the two 2,4-diphenyl-2-methylchroman isomers. In all cases, the three non-aromatic hydrogen atoms formed an ABX system from which the chemical shifts of these atoms could be derived.² The results are collected in Table 1, which also contains

information on chemical shifts of the other protons excluding the aromatic protons. It is evident from the chemical shifts that the A and B protons are the hydrogen atoms at position 3 and the X protons the hydrogen atoms at position 4. Important features of the spectra are the small difference between the shifts of the A and B protons of the low-melting 2,4-diphenyl-2-methylchroman and the positions of the X proton shifts. An interpretation of the spectra is most easily achieved by an analysis of the possible conformations.

A chromane derivative most likely exists in a half-chair or a half-boat conformation. In Fig. 1, the half-chair con-

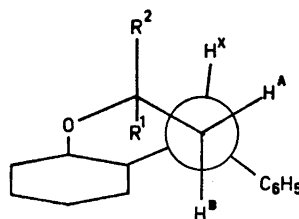


Fig. 1. Half-chair conformation of chromane derivative projected on a plane perpendicular to the bond between C(3) and C(4).

formation is projected on a plane perpendicular to the bond between the carbon atoms in positions 3 and 4. If the phenyl group in position 4 occupies the semi-equatorial position, the coupling constants J_{BX} and J_{AX} should be of the order of 10–15 and 5 Hz, respectively, according to the Karplus rule. If the phenyl group is in the semi-axial position, the two coupling constants should be almost equal and of the order of about 5 Hz. A similar discussion of the half-boat conformation leads to almost identical results. Because the experimentally determined coupling constants are about 13 and 5 Hz, the phenyl group in position 4 occupies the semi-equatorial position.

If the pyran rings exist in the half-chair conformation and a phenyl group in position 2 is in the *trans* position relative to the phenyl group in position 4, the former phenyl group should be in the axial position (R^2 in Fig. 1). An examination of Stuart scale models of such molecules shows that the phenyl group in position 2 turns its positively shielding sector³ towards the X proton. A phenyl group in the *cis* position

Table 1. Chemical shifts^a and coupling constants in the NMR spectra of the chroman derivatives.

Chroman derivative	M.p.	Chemical shifts (τ)					Coupling constants		
		A	B	X	CH ₃	OCH ₂	J_{AB}	J_{AX}	J_{BX}
I a	118–119°	7.35	7.73	6.43	8.34		13.7	4.8	12.8
I a	83.0–83.5°	7.69	7.84	5.80	8.34		13.7	5.0	13.0
I b	162–163°	6.94	7.40	6.11			13.7	5.0	12.9
I c	125–126°	7.54	7.98	5.46	8.98	{6.61 6.55}	13.6	5.8	13.0

^a The chemical shifts of the aromatic protons (τ 2.2–3.3) are omitted.

as well as an ethoxy group causes deshielding of the X proton by anisotropy and inductive effects. This gives the following order for the X proton shifts beginning from the lowest τ value: 2,4-diphenyl-2-ethoxychroman, *cis*-2,4-diphenyl-2-methylchroman, 2,2,4-triphenylchroman, and *trans*-2,4-diphenyl-2-methylchroman.

If the pyran rings exist in the half-boat conformation, shielding of the X protons by the substituents does not seem to be possible. Because only deshielding effects would thus be operative, an arrangement of the four substances in the order of presumed X proton shifts is difficult. However, the two 2,4-diphenyl-2-methylchromans would have their X proton shifts rather close to each other and the X proton shift of 2,2,4-triphenylchroman would lie at a lower field than the just-mentioned shifts.

The experimental order of the X proton shifts beginning from the lowest τ values is: 2,4-diphenyl-2-ethoxychroman, the low-melting 2,4-diphenyl-2-methylchroman, 2,2,4-triphenylchroman, and the high-melting 2,4-diphenyl-2-methylchroman. The triphenyl derivative lies between the two isomers of the diphenylmethyl derivative as in the first of the cases analysed above. This implies that these chromans exist in the half-chair form and that the phenyl groups in the low-melting isomer of 2,4-diphenyl-2-methylchroman are in *cis* positions and those of the high-melting isomer in *trans* positions.

These conclusions are supported by the following facts. The low-melting isomer of 2,4-diphenyl-2-methylchroman and 2,4-diphenyl-2-ethoxychroman, in which the phenyl groups occupy the equatorial and semi-equatorial positions, have their A and B proton shifts centered around the same τ value (7.76 ppm). The difference be-

tween the A and B proton shifts is smallest in the case of the low-melting 2,4-diphenyl-2-methylchroman and indicates a highly symmetrical structure around the methylene group in position 3, a fact that easily is verified from Fig. 1 ($R^1 = C_6H_5$; $R^2 = CH_3$). Finally it appears that the phenyl groups of 2,4-diphenyl-2-ethoxychroman occupy equatorial and semi-equatorial positions because the compound is produced by ring closure of 3-(*o*-hydroxyphenyl)-3-phenylpropiofenone in acid ethanol.^{1,4}

The double chemical shift of the ether methylene group of the ethoxy derivative results in two superimposed quartets. Such cases have previously been reported for methylene groups near an asymmetric center.⁵

Experimental. The spectra of the substances dissolved in deuteriochloroform were taken on a Perkin-Elmer R 12 NMR spectrometer (60 MHz). The A, B, and X proton shifts were calculated by the method recommended by Banwell.² A good agreement with experimental data was obtained when the parameters in Table 1 were used for calculation of line frequencies and intensities of the ABX system.

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