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2-Polyfluoroalkylchromones

12.* Nitration of 5,7-dimethyl-2-polyhaloalkylchromones and complete assignment of signals in the ^{1}H and ^{13}C NMR spectra of 5,7-dimethyl-2-trifluoromethylchromone and its mono- and dinitro derivatives

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The nitration of 5,7-dimethyl-2-polyhaloalkylchromones affords either 5,7-dimethyl-6-nitro- or 5,7-dimethyl-6,8-dinitro-2-polyhaloalkylchromones, depending on the reaction conditions. Signals in the ^{1}H and ^{13}C NMR spectra of the sterically hindered chromones were completely assigned using the 2D NOESY, HETCOR, and COLOC spectra. The influence of nonplanar nitro groups on chemical shifts of carbon atoms was studied. Some spectral peculiarities of the *peri*-methyl group were revealed. The ^{1}H-^{1}H and ^{13}C-^{1}H spin-spin coupling constants, including the extreme six-bond long-range coupling between the protons of the Me(5) group and H(8), were determined.

Key words: 2-polyhaloalkylchroman-4-ones, 2-polyhaloalkylchromones, nitration, ^{1}H and ^{13}C NMR spectroscopy, spin-spin coupling constants, increments of substituent chemical shifts, *peri*-methyl group, sterically hindered nitro groups.

The condensation of 2-hydroxy-4,6-dimethylacetophenone with R^FCO_2Et ($R^F = CF_3, C_3F_7, C_5F_{11}, C_7F_{15}$) in the presence of NaH in Et_2O has previously[2] been found to afford 5,7-dimethyl-2-hydroxy-2-perfluoroalkylchroman-4-ones **1**, whose dehydration in an acidic medium produces 5,7-dimethyl-2-perfluoroalkylchromones **2**. We have recently[3] described the nitration of 5,7-dimethyl-2-trifluoromethylchromone (**2a**) and showed that at 75 °C it transformed into 5,7-dimethyl-6,8-dinitro-2-trifluoromethylchromone (**3a**) in ~100% yield. When studying the nitration of other 5,7-dimethyl-2-polyhaloalkylchromones **2b—e**, we revealed that under milder conditions the main product, which was the 6,8-dinitro derivative, contained an admixture of the mononitro derivative with the NO_2 group in position 6 or 8 of the benzene ring. We succeeded in isolation of the mononitration products upon nitration of chromones **2a**,**e** at 0—3 °C.

This work is devoted to the synthesis of novel 5,7-dimethyl-2-polyhaloalkylchromones, examination of their nitration, and ^{1}H and ^{13}C NMR study of chromone **2a** and its mono- and dinitro derivatives. These compounds contain bulky substituents in the *ortho*- and *peri*-positions and are of interest, in particular, for studying the influence of substituents on chemical shifts of atoms in sterically hindered molecules.

Results and Discussion

The condensation of 4,6-dimethyl-2-hydroxyacetophenone with R^FCO_2Et ($R^F = CF_3, CF_2H, (CF_2)_2H, (CF_2)_4H$) in the presence of LiH in THF afforded 5,7-dimethyl-2-hydroxy-2-polyfluoroalkylchroman-4-ones (**1a—d**), which upon boiling in AcOH with an addition of concentrated HCl were dehydrated to 5,7-dimethyl-2-polyfluoroalkylchromones (**2a—d**). 5,7-Dimethyl-2-trichloromethylchromone (**2e**) was synthesized from 4,6-dimethyl-2-hydroxyacetophenone and trichloroacetonitrile through the formation of 2-amino-5,7-dimethyl-2-trichloromethylchroman-4-one (**1e**).[4] 5,7-Dimethyl-6,8-dinitro-2-polyfluoroalkylchromones **3a—e** were obtained in 72—95% yields by the nitration of chromones **2a—e** with a nitrating mixture at 75 °C for 1 h. Chromone **3d**, according to the ^{1}H NMR spectrum, contained a ~10% admixture of compound **4d** with one nitro group. It is most probable that compound **4d** was the primary reaction product. The nitration of chromone **2e**

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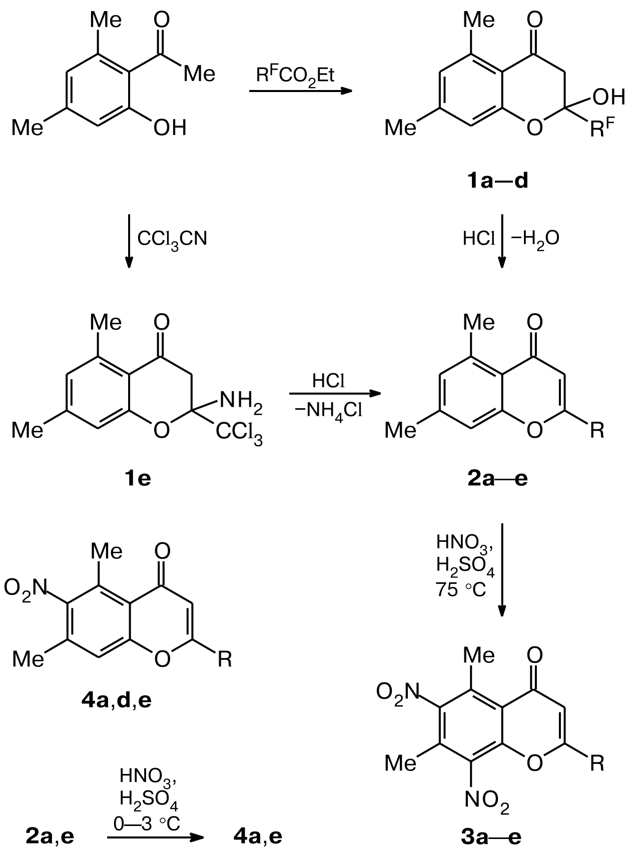
at 75 °C for 20 min with a smaller amount of concentrated H_2SO_4 produced a mixture of di- and mononitro derivatives in a ratio of 3 : 2. Mononitration products **4a**,**e** were selectively obtained from chromones **2a**,**e** when the reaction was carried out at 0—3 °C for 2 h (Scheme 1).

Scheme 1



R = CF_3 (**a**), CF_2H (**b**), $(CF_2)_2H$ (**c**), $(CF_2)_4H$ (**d**), CCl_3 (**e**)

Data on the nitration of 5,7-dimethylchromones are lacking, and we could not predict *a priori* the position (6 or 8) of the primary attack from the nitronium ion of the aromatic ring. To answer this question, we studied chromone **2a** and its mono- and dinitro derivatives by ^1H and ^{13}C NMR spectroscopy (400 and 100 MHz, respectively), the more so that, unlike coumarins,[5,6] quinolines,[7,8] and 2-quinolones,[9] ^1H and ^{13}C NMR spectroscopic data for chromones are fairly restricted.

^{1}H NMR spectra. Signals in the ^1H NMR spectra of 5,7-dimethyl-2-perfluoroalkylchromones (R^F = CF_3, C_3F_7, C_5F_{11}, C_7F_{15}), which were recorded for solutions in deuterioacetone, have previously[2] been assigned using an instrument with a working frequency of 90 MHz. Of two resonance signals from the methyl groups, the downfield signal (2.77—2.88 ppm) was ascribed to the *peri*-Me group at the C(5) atom (deshielding effect of the carbonyl group), and the upfield signal (2.57—2.59 ppm) was attributed to the Me group at the C(7) atom. The signal from the H(3) proton in this solvent was observed at 6.74—6.84 ppm, and two aromatic signals at 7.20—7.25 and 7.37—7.40 ppm were assigned to the H(6) and H(8) protons, respectively, without comment. The spin-spin coupling constant $^4J_{H,F} < 0.3$ Hz was indicated for H(3), and for H(6) and H(8) $^4J_{H(6),H(8)}$ was ~1 Hz. We found that in the spectra of chromones **2a—d** the chemical shifts (CS) of all signals, except signals from the *peri*-Me group, are displaced upfield ($\Delta\delta \sim -0.2$ ppm) on going from deuterioacetone to less polar deuteriochloroform (Table 1). The Gauss filtration procedure (narrowing of lines by the Gauss filter) revealed the fine structure of the aromatic and methyl protons but did not find even a weak coupling between the vinyl H(3) atom and the R^F group, which is usually observed in such cases ($^4J_{H,F}$ = 0.7—1.1 Hz). Moreover, in chromone **2b** the proton of the CF_2H group appears as a triplet of doublets with $^2J_{H,F}$ = 53.8 and $^4J_{H,H}$ = 0.5 Hz, and H(3) is manifested as a doublet with the same long-range ^1H-^1H coupling constant.

In the ^1H NMR spectrum of chromone **2a** aromatic protons appear as a septet and a doublet of quintets with the centers at 7.01 and 7.16 ppm, respectively (Fig. 1, *a*). Such a pattern is possible if these protons compose the AD part of the ADM_3X_3 spin system with $^4J_{AD}$ = 1.6 Hz (*meta*-constant), $^4J_{AM} = {}^4J_{AX}$ = 0.8 Hz (*ortho*-benzyl constant) for the upfield septet, and $^4J_{DM} = {}^6J_{DX}$ = 0.7 Hz (*ortho*- and *para*-benzyl constants) for the downfield doublet of quintets. The splitting observed in the spectrum is, in essence, a superposition of two septets, which look like quintets because their weakly intense edge lines are not seen against noise. The manifestation of the doublet nature of the downfield signal is related to a decrease in the averaged constant of the quartet of quartets due to the contribution from the smaller *para*-benzyl constant, which is inherent in H(8) only. This allows the assignment of a signal at 7.16 ppm to the H(8) proton and a signal at 7.01 ppm to H(6). This conclusion confirms that the previous[2] assignment was valid. Such an interpretation of the multiplicity of signals from H(6) and H(8) is also favored by the character of splitting of signals from the methyl groups, which are triplets with J = 0.7 Hz, in spite of the fact that the hydrogen atoms of the *peri*-methyl group are remote from H(8) at a distance of six bonds. A similar pattern was observed for chromones **2b—e** with an exception that the signals of both aromatic protons in the spectra of compounds **2c**,**d** look like septets and, hence, they cannot be distinguished by the character of splitting.

The 2D NOESY spectrum of chromone **2a** exhibits two cross peaks for the upfield signal from the methyl group (2.43 ppm) and two aromatic protons and one cross peak for the downfield signal from the methyl group

Table 1. ^{1}H NMR and IR spectra of chromanones **1a—d** and chromones **2a—e**, **3a—e**, and **4a**,**d**,**e**

Compound	^{1}H NMR (δ, J/Hz)							IR, ν/cm^{-1}
	C(5)Me	C(7)Me	CH$_2$/H(3)	H(6)	H(8)	R^F	OH	
1a	2.60 (t, ^4J = ^6J = 0.7)	2.32 (t, ^4J = 0.7)	3.00[a,b] (Δδ = 0.12, J_{AB} = 16.2)	6.74 (d.sept, J_m = 1.7, ^4J = 0.8)	6.73 (d.sept, J_m = 1.7, ^4J = ^6J = 0.7)		3.88 s	3300, 1670, 1620, 1570
1b	2.60 (t, ^4J = ^6J = 0.7)	2.32 (t, ^4J = 0.7)	2.92[a,c] (Δδ = 0.13, J_{AB} = 16.3)	6.72 (d.sept, J_m = 1.6, ^4J = 0.8)	6.70 (d.sept, J_m = 1.6, ^4J = ^6J = 0.7)	5.80 (dd, $^2J_{H,F}$ = 55.3, $^2J_{H,F}$ =54.9)	3.51 s	3340, 1665, 1620, 1570
1c	2.59 (t, ^4J = ^6J = 0.7)	2.32 (t, ^4J = 0.7)	3.04[a] (Δδ = 0.22, J_{AB} = 16.3)	6.74 (d.sept, J_m = 1.6, ^4J = 0.8)	6.70 (d.sept, J_m = 1.6, ^4J = ^6J = 0.7)	6.23 (tdd, $^2J_{H,F}$ = 52.7, $^3J_{H,F}$ = 6.3, $^3J_{H,F}$ = 5.4)	3.97 s	3260, 1675, 1620, 1570
1d	2.59 (t, ^4J = ^6J = 0.6)	2.32 (t, ^4J = 0.7)	3.06[a] (Δδ = 0.18, J_{AB} = 16.3)	6.75 (d.sept, J_m = 1.6, ^4J = 0.8)	6.72 (d.sept, J_m = 1.6, ^4J = ^6J = 0.7)	6.12 (tt, $^2J_{H,F}$ = 52.0, $^3J_{H,F}$ = 5.4)	3.86 s	3270, 1680, 1625, 1575
2a	2.79 (t, ^4J = ^6J = 0.7)	2.43 (t, ^4J = 0.7)	6.58 s	7.01 (d.sept, J_m = 1.6, ^4J = 0.8)	7.16 (d.sept, J_m = 1.6, ^4J = ^6J = 0.7)			1675, 1650, 1620, 1565
2b	2.80 (t, ^4J = ^6J = 0.8)	2.42 (t, ^4J = 0.7)	6.47 (d, $^4J_{H,H}$ = 0.5)	6.99 (d.sept, J_m = 1.6, ^4J = 0.8)	7.13 (d.sept, J_m = 1.6, ^4J = ^6J = 0.7)	6.39 (td, $^2J_{H,F}$ = 53.8, $^4J_{H,H}$ = 0.5)		1670, 1635, 1620, 1570
2c	2.80 (t, ^4J = ^6J = 0.7)	2.43 (t, ^4J = 0.7)	6.60 s	7.01 (d.sept, J_m = 1.6, ^4J = 0.8)	7.14 (d.sept, J_m = 1.6, ^4J = ^6J = 0.8)	6.10 (tt, $^2J_{H,F}$ = 53.0, $^3J_{H,F}$ = 3.7)		1670, 1620, 1570
2d	2.80 (t, ^4J = ^6J = 0.7)	2.43 (t, ^4J = 0.7)	6.63 s	7.02 (d.sept, J_m = 1.6, ^4J = 0.8)	7.16 (d.sept, J_m = 1.6, ^4J = ^6J = 0.8)	6.08 (tt, $^2J_{H,F}$ = 51.9, $^3J_{H,F}$ = 5.3)		1670, 1640, 1625, 1570
2e	2.80 (t, ^4J = ^6J = 0.8)	2.44 (t, ^4J = 0.7)	6.86 s	7.01 (d.sept, J_m = 1.6, ^4J = 0.8)	7.22 (d.sept, J_m = 1.6, ^4J = ^6J = 0.7)			1660, 1635, 1620
3a	2.79 s	2.39 s	6.76 s					1685, 1620, 1545
3b	2.79 s	2.38 s	6.64 s			6.43 (t, $^2J_{H,F}$ = 53.3)		1680, 1620, 1545
3c	2.79 s	2.39 s	6.76 s			6.06 (tt, $^2J_{H,F}$ = 52.8, $^3J_{H,F}$ = 3.5)		1675, 1615, 1535
3d	2.79 s	2.39 s	6.79 s			6.07 (tt, $^2J_{H,F}$ = 51.8, $^3J_{H,F}$ = 5.2)		1675, 1620, 1545
3e	2.80 s	2.40 s	7.00 s					1670, 1620, 1545
4a	2.74 (d, ^6J = 0.6)	2.42 (d, ^4J = 0.9)	6.65 s		7.35 (sept, ^4J = ^6J = 0.7)			1680, 1625, 1535
4d[d]	2.75 s	2.42 s	6.69 s		7.33 s	[e]		
4e	2.76 (d, ^6J = 0.7)	2.43 (d, ^4J = 0.9)	6.92 s		7.41 (sept, ^4J = ^6J = 0.7)			1660, 1620, 1535

[a] Center of the AB system.

[b] Each signal of the upfield part is split into a quartet with J = 0.7 Hz.

[c] Each signal of the upfield part is split into a doublet of doublets with J = 1.3 and 0.4 Hz.

[d] As an admixture in **3d**.

[e] Disguised by the signal from the proton of the $(CF_2)_2H$ group in compound **3d**.

(2.79 ppm) and the upfield signal from the aromatic proton. This proves finally and unambiguously that the peak at 7.01 ppm belongs to the H(6) atom and confirms that the assignment of the methyl and aromatic protons made from analysis of the multiplicity of their signals was valid (see the 2D HETCOR spectrum). Note that for 5,7-di-

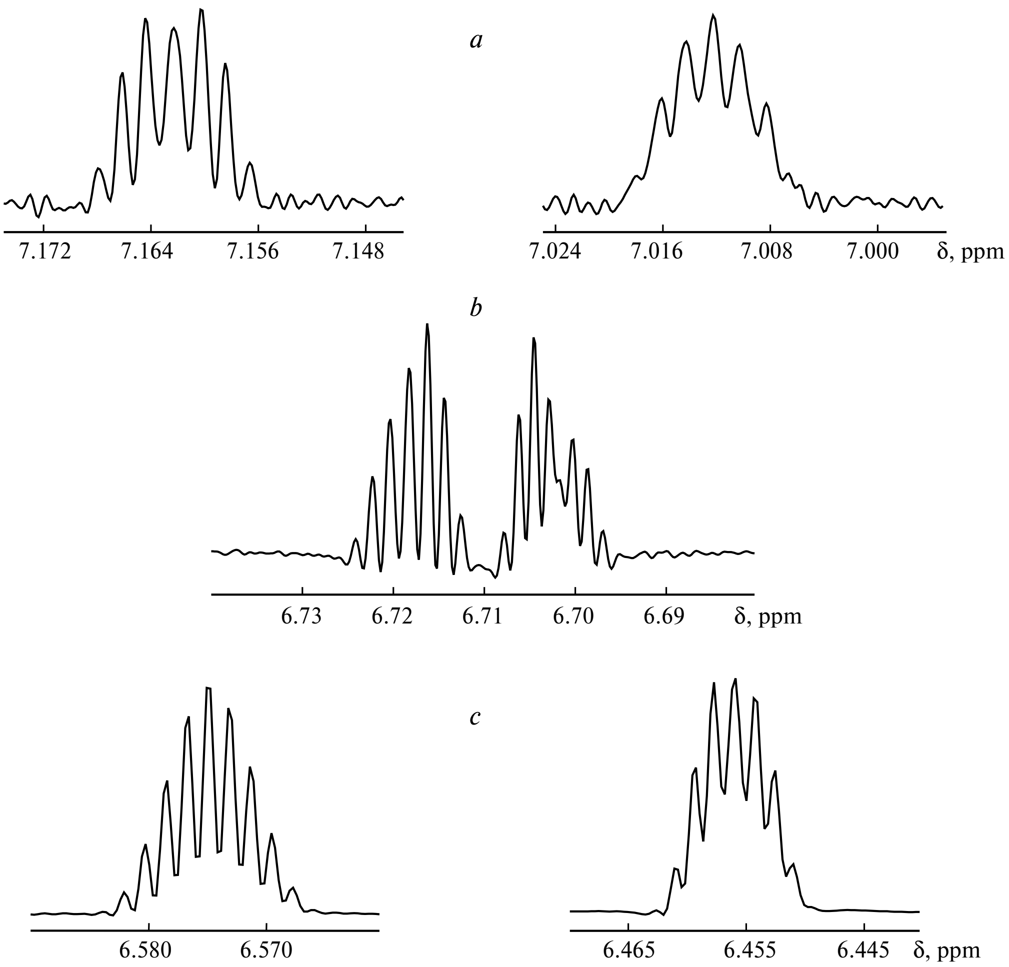


Fig. 1. Regions of aromatic protons in chromone **2a** (*a*), chromanone **1b** (*b*), and 3,5-dimethylphenol (*c*).

hydroxyflavones the signal from H(6) is more upfield than that from H(8).[10]

Analysis of the ^1H NMR spectra of chromanones **1a—d**, which are precursors of chromones **2a—d**, shows that in these compounds, unlike **2a—d**, the upfield signal is referred to the H(8) proton. The H(6) and H(8) protons in 5,7-dimethyl-2-hydroxy-2-perfluoroalkylchroman-4-ones (R^F = CF_3, C_3F_7, C_5F_{11}, C_7F_{15}) have previously[2] been described as one singlet. However, under our conditions they appeared as individual, closely arranged signals, which are split due to the long-range spin-spin coupling with the methyl groups. For example, in the spectrum of chromanone **1b** two triplets with $J = 0.7$ Hz are observed at 2.32 and 2.60 ppm corresponding to the Me groups at the C(7) and C(5) atoms, respectively, along with the AB system of the CH_2 group, whose upfield part represents a doublet of doublets of doublets ($J = 16.3$, 1.3, 0.4 Hz) due to the spin-spin coupling between the nonequivalent fluorine atoms of the CF_2H group and the methylene proton. The signal from the aromatic protons can be interpreted as the AB part of the ABM_3X_3 spin system with $^4J_{AB} = 1.6$ Hz (*meta*-constant), whose downfield half looks like a nonsymmetric (skewed) septet with $^4J_{AM} = {}^4J_{AX} = 0.8\ \text{Hz} = 0.5\,{}^4J_{AB}$, and the upfield half looks like the same doublet of quintets because $^4J_{BM} = {}^6J_{BX} = 0.7\ \text{Hz} < 0.5\,{}^4J_{AB}$ (Fig. 1, *b*). As in the case of chromone **2a**, both multiplets represent a superposition of two septets, and the doublet character of the signal at 6.70 ppm indicates that it belongs to the H(8) proton, which is slightly more shielded than H(6), whose signal is observed at 6.72 ppm. A similar pattern was observed in the spectra of compounds **1a**,**c**,**d**. Thus, as should be expected, the deshielding effect of the γ-pyrone system affects, to a greater extent, the adjacent aromatic H(8) atom, whose signal exhibits the downfield shift by 0.43—0.44 ppm on going from chromanones **1a—d** to chromones **2a—d**, while that of H(6) shifts by 0.27 ppm only.

At first glance, the product of mononitration of chromone **2a**, according to its ^1H NMR spectrum, can be taken for 5,7-dimethyl-8-nitro-2-trifluoromethylchromone. In fact, in addition to the singlet of the vinyl H(3) proton, the spectrum contains two doublets from the 5-Me and 7-Me groups with $J = 0.64$ and 0.88 Hz, respectively, and a distinct septet of the aromatic proton at 7.35 ppm with J = 0.75 Hz. This can lead to the invalid conclusion that the H atom is located in position 6. This signal cannot be assigned using the rule of additivity of substituent effects, which is based on the assumption that substituents are independent of each other when affecting the CS of the atom under study,[11] due to steric hindrances appeared in the mononitro derivative of chromone **2a** regardless of the nitration position. However, the 2D NOESY experiment for the mononitro derivative of chromone **2a** revealed only one cross peak between the signals at 2.42 and 7.35 ppm, indicating that the aromatic proton is situated near the 7-Me group. This proton cannot be situated in position 6 because two cross peaks with the 5-Me and 7-Me groups would be observed in this case. Thus, in the nitration of chromone **2a** the C(6) atom is first to undergo the electrophilic attack, due to which 5,7-dimethyl-6-nitro-2-trifluoromethylchromone (**4a**) is formed. In the ^{1}H NMR spectrum of this compound, the septet signal belongs to the H(8) proton, which interacts with the protons of the 7-Me and 5-Me groups having the close *ortho*- and *para*-benzyl constants ^4J = 0.88 and ^6J = 0.64 Hz. An analogous conclusion can be drawn for the structure of monodinitro derivative **4e** obtained from chromone **2e** and minor product **4d**. In these compounds, the NO_2 group deviates from the plane of the molecule due to steric reasons and, hence, the aromatic ring is deactivated to a less extent due to a decrease in the −M effect and can undergo the secondary attack from the nucleophile. This fact and the electron-releasing effect of the methyl groups explain the easiness of formation of dinitro derivatives **3a—e**.

By analogy to the well-studied *ortho*-benzyl constant[12,13] describing the long-range interaction between protons of the sp^3-hybridized carbon atom and *ortho*-protons of the aromatic system through four bonds ($^4J_{Me,H}$), the extreme long-range interaction through six bonds with the *para*-proton can be named the *para*-benzyl constant ($^6J_{Me,H}$). Previously[14] flavones exhibited the extreme long-range constant $^7J_{H(7),H(3)}$ = 0.27—0.52 Hz, which was accounted for the high planarity of the benzopyrone system. We found the $^6J_{Me,H}$ coupling in the compounds studied and account its appearance for the specificity of the methyl group in the *peri*-position to the carbonyl group. However, it turned out that this phenomenon is more general and also observed in compounds used as initial in the synthesis of chromanones **1a—e** and chromones **2a—e**. For example, in the spectrum of 4,6-dimethyl-2-hydroxyacetophenone, the 4-Me and 6-Me groups are manifested as triplets with J = 0.7 Hz at 2.27 and 2.56 ppm, and the H(3) and H(5) protons appear as doublets of septets with J_m = 1.9 and $^4J_{Me,H} = {}^6J_{Me,H}$ = 0.7 Hz at 6.54 and 6.66 ppm, *i.e.*, despite the different arrangements with respect to the Me groups, they look quite equally, which does not allow their assignment without additional experiments. The spectrum of 3,5-dimethylphenol, in which the aromatic and methyl protons form the $AA'MX_3X'_3$ spin system, is shown in Fig. 1, *c*. Due to the approximate equality (within the measurement accuracy) of the coupling constants of the *ortho*- and *para*-protons with the protons of the CH_3 groups $^4J_{AX} \sim {}^6J_{AX'} \sim 0.7$ Hz, this system is degenerated to the A_2MX_6 spectrum of the first order. The shape of spin multiplets is further simplified because of the multiplicity of the constants $^4J_{AX} = {}^4J_{MX} \sim 0.5{}^4J_{AM}$, due to which the H(2) and H(6) protons are observed as a doublet of septets with the center at 6.46 ppm, the H(4) proton is observed as a triplet of septets at 6.58 ppm, and the methyl groups appear as a quartet at 2.26 ppm. It should be mentioned that the aromatic protons in 3,5-dimethylphenol have previously[15] been described as broadened singlets, and the signal of the methyl groups has been described as a singlet. The measurements were carried out on an NMR spectrometer with a working frequency of 400 MHz.

The CS value of the H(3) proton in chromones is mainly affected by substituents at the C(2) atom and, to a less extent, by substituents in the aromatic ring. The CS of the H(3) atoms in 2-R- and 2-R^F-chromones unsubstituted at the benzene ring are presented in Table 2 to demonstrate the deshielding effect of the R^F and CCl_3 groups on the H(3) proton compared to such substituents as H, Me, Ph, and CO_2Et. These data show that, unlike the Me group, which shields the H(3) proton by −0.18 ppm compared to the hydrogen atom, the Ph and CF_3 groups shift $\delta_{H(3)}$ by 0.53 and 0.40 ppm, whereas the CO_2Et and CCl_3 groups demonstrate the downfield shifts by 0.81 and 0.68 ppm, respectively, *i.e.*, the CF_3 group is close to the phenyl group and CCl_3 is close to the ethoxycarbonyl group by the deshielding influence. It is also noteworthy that the CF_2H group has the smallest deshielding effect of all fluoroalkyl substituents presented in Table 2, and the increase in the number of fluorine atoms from 3 to 7 only insignificantly (~0.05 ppm) affects the CS of the H(3) atom.

Similar regularities are observed for all chromones **2a—e** and their mono- and dinitro derivatives **4a,d,e** and **3a—e**. The data in Table 1 show that the spectra of compounds **2c,d** containing the R^F = $(CF_2)_2H$ and $(CF_2)_4H$ groups are completely identical, except for $^3J_{H,F}$ = 3.7 Hz

Table 2. Chemical shifts of the H(3) proton in 2-R- and 2-R^F-chromones ($CDCl_3$, δ, ppm)

R	$\delta_{H(3)}$	Ref.	R^F	$\delta_{H(3)}$	Ref.
H	6.32	16	CF_2H	6.57	20
Me	6.14	16	CF_3	6.72	19
Ph	6.85	17	$(CF_2)_2H$	6.71	21
CO_2Et	7.13	18	C_2F_5	6.78	22
CCl_3	7.00	19	C_3F_7	6.77	22

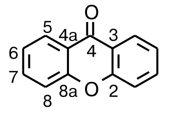
for **2c** and 5.3 Hz for **2d**. It has recently[23] been shown that the $^3J_{H,F}$ constant of the $(CF_2)_2H$ group, unlike the constants of the $(CF_2)_nH$ groups with n = 1, 3, and 4, differs substantially, depending on the nearest environment of the carbon atom bonded to this group. The $^3J_{H,F}$ = 3.0—3.8 Hz values were given[23] for 6-substituted 2-(1,1,2,2-tetrafluoroethyl)chromones, which allows the tetrafluoroethyl substituent to be easily distinguished from other polyfluoroalkyl groups with the terminal hydrogen atom. Note that the appearance of two methyl groups in positions 5 and 7 in 2-CF_3- and 2-CCl_3-chromones leads to shielding of the H(3) proton by ~–0.15 ppm, and the nitro groups in positions 6 and 8 have an opposite effect and return the proton signal to its former position. It is of interest that the NO_2 groups only insignificantly (within 0.05 ppm) change the CS of the protons of the adjacent methyl groups (Table 1).

^{13}C NMR spectra. The data of the ^{13}C NMR spectra of chromones **2a—4a** recorded without proton decoupling are presented in Table 3 together with the proton decoupling spectra of xanthone (**5**), chromone (**6a**), flavone (**6b**), and 2-trifluoromethylchromone (**6c**). The comparison of the spectra of compounds **6a** and **6c** shows that the replacement of the hydrogen atom by the CF_3 group affects slightly the CS of aromatic hydrocarbons but shields the C(2) and C(3) atoms of the pyrone ring by 2.8 and 2.3 ppm, respectively. On going from **6b** to **6c**, the C(2) atom is shielded by 10.3 ppm and the C(3) atom is deshielded by 3.5 ppm. A similar effect was observed for 5-CF_3-isoxazoles when the phenyl group was replaced by the trifluoromethyl group.[21] The signal from the carbonyl C(4) atom, unlike those from C(2) and C(3), is almost independent of the nature of the substituent in position 2 but exhibits a downfield shift by 1.8 ppm in chromone **2a** and is remarkably shielded (–1.0 and –1.8 ppm) when the nitro groups are consecutively introduced into positions 6 and 8 (compounds **4a** and **3a**). The C(3) atom in compound **3a** is deshielded by 1.1 ppm with respect to **2a**, and its CS becomes the same as that in unsubstituted chromone **6a** (112.7 ppm). The carbonyl carbon atom in chromone **4a** looks like a triplet with a constant of 1.5 Hz, and that in compound **3a** looks like a doublet with the same constant to indicate the two- and four-bond spin-spin interaction between the carbon atom of the carbonyl group and the H(3) and H(8) protons. In chromone **2a** this signal represents a multiplet due to the additional unresolved interaction with the H(6) atom.

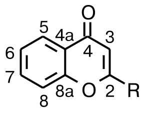
The $^nJ_{C,F}$ (n = 1—3) spin-spin coupling constants in chromones **6c** and **2a—4a** depend slightly on substituents in the aromatic ring: $^1J_{C,F}$ = 273.8—274.5 Hz, $^2J_{C,F}$ = 38.9—40.7 Hz, and $^3J_{C,F}$ = 2.7—2.8 Hz, and the latter constant corresponds to the minimum value of those indicated earlier for compounds with the H—C=C—CF_3 *cis*-fragment (2.8—7.1 Hz).[24,25] The appearance of the CF_3 group in position 2 of the chromone system increases the direct $^1J_{C(3),H(3)}$ constant, which is 168.5 Hz for 2-methylchromones,[26] 167—169 Hz for flavones,[10,14] and 172.5 Hz for chromone **2a**. The introduction of the electron-withdrawing nitro groups into the aromatic ring of chromone **2a** is accompanied by the further increase in the constant to 175.8 Hz. The trifluoromethyl group is presented in the spectra of these compounds as a quartet of doublets due to the additional splitting of the carbon atom on the vicinal hydrogen with $^3J_{CF_3,H(3)}$ = 3.4 Hz. The $^3J_{CF_3,H}$ = 1.8—8.0 Hz values have previously[25] been indicated for the compounds with the *cis*-arrangement of the H atom and CF_3 group.

Let us consider the signals from the carbon atoms of the benzene ring and its methyl groups in chromones **6c** and **2a—4a**. The signals from the aromatic carbon atoms in 2-trifluoromethylchromone (**6c**) were assigned on the basis of the published data for xanthone (**5**),[27] chromone (**6a**),[28] and flavone (**6b**)[14,17,28] (Table 3). The upfield spectral region of chromone **2a** contains two signals: a quartet of doublets at 22.38 ppm and a quartet of triplets at 21.51 ppm belonging to the carbon atoms of the methyl groups. The character of splitting of these signals allows an unambiguous assignment of the first of them to the Me group at the C(5) atom, and the second signal can be assigned to the Me group at the C(7) atom, because the character of splitting indicates the number of protons in the *ortho*-position with respect to these groups.[29] Although one of the methyl groups is in the *peri*-position to the carbonyl group, they differ slightly in CS ($\Delta\delta$ = 0.87 ppm), but the direct constant of the methyl group in position 5 is higher by 1.5 Hz than that of the 7-situated methyl group. Note that only one value of ^1J = 126.9 Hz was given in the series of methylated 2-quinolones for the methyl groups in positions 5 and 7.[9] The appearance of a quartet of triplets with ^3J = 4.5 Hz in the spectrum is associated with the close values of the $^3J_{Me(7),H(6)}$ and $^3J_{Me(7),H(8)}$ constants, which are 4.3 and 4.9 Hz, respectively, in 2-quinolones.[9] In nitrochromone **4a**, the $^3J_{Me(7),H(8)}$ constant also equals 4.9 Hz. The value of $^3J_{Me(5),H(6)}$ = 4.9 Hz was reported for 5-methyl- and 5,7-dimethyl-2-quinolones,[9] being 0.5 Hz lower than that in chromone **2a**. Since the ^1J and ^3J constants for 7-Me correlate well with analogous constants in methylated 2-quinolones, it can be assumed that an increase in $^1J_{Me(5)}$ to 129.0 and in $^3J_{Me(5),H(6)}$ to 5.4 Hz in **2a** reflects the *peri*-arrangement of the carbonyl and 5-Me groups. The $^2J_{C(5),Me}$ value in compounds **2a—4a**, which is 0.2—0.3 Hz higher than $^2J_{C(7),Me}$ (Table 3), also favors the fact that the increase in the $^1J_{C,H}$ and $^3J_{C,H}$ constants related to the *peri*-methyl group is not accidental.

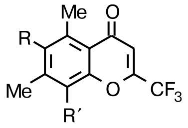
In the aromatic region of chromone **2a** spectrum, two most upfield signals at 116.04 and 120.15 ppm refer to the C(8) and C(4a) atoms in the *ortho*- and *para*-positions with respect to the electron-releasing substituents, and the most downfield signal at 157.22 ppm is attributed to



5a



6a—c



2a—4a

Table 3. ^{13}C NMR spectra of xanthone **5a** and chromones **6a—c** and **2a—4a** (CDCl$_3$, δ, ppm, J/Hz)

Atom	**5a**^{a}	**6a** (R = H)^b	**6b** (R = Ph)	**6c** (R = CF$_3$)	**2a** (R = R´ = H)	**4a** (R = NO$_2$, R´ = H)	**3a** (R = R´ = NO$_2$)
C(2)	155.52	155.0	163.0,^{b} 163.4,^{c} 162.50^d	152.21 (q, ^2J_F = 38.9)	150.64 (qd, ^2J_F = 38.9, $^2J_{H(3)}$ = 4.3)	151.04 (qd, ^2J_F = 39.6, $^2J_{H(3)}$ = 4.3)	150.93 (qd, ^2J_F = 40.7, $^2J_{H(3)}$ = 4.6)
C(3)	121.06	112.7	107.3,^{b} 107.5,^{c} 106.89^d	110.41 (q, ^3J_F = 2.8)	111.57 (dq, ^1J_H = 172.5, ^3J_F = 2.7)	111.93 (dq, ^1J_H = 174.1, ^3J_F = 2.7)	112.68 (dq, ^1J_H = 175.8, ^3J_F = 2.7)
C(4)	175.91	177.1	178.0,^{b} 178.4,^{c} 177.01^d	176.77	178.53 m	177.53 (t, $^2J_{H(3)}$ = $^4J_{H(8)}$ = 1.5)	175.66 (d, $^2J_{H(3)}$ = 1.5)
CF$_3$				118.51 (q, ^1J_F = 274.3)	118.66 (qd, ^1J_F = 273.8, $^3J_{H(3)}$ = 3.4)	118.34 (qd, ^1J_F = 274.1, $^3J_{H(3)}$ = 3.4)	117.82 (qd, ^1J_F = 274.5, $^3J_{H(3)}$ = 3.4)
C(4a)	121.06	124.6	123.7,^{b} 125.2,^{c} 123.28^d	123.88	120.15 (sept, $^3J_{H(3)}$ = $^3J_{H(6)}$ = $^3J_{H(8)}$ = $^3J_{Me}$ = 3.7)	120.81 (d.quint, $^3J_{H(8)}$ = 4.5, $^3J_{H(3)}$ = $^3J_{Me}$ = 3.6)	121.58 (quint.q, $^3J_{H(3)}$ = $^3J_{Me}$ = 3.7, $^5J_{Me}$ = 0.7)
C(5)	125.90	125.5	125.4,^{b} 125.6,^{c} 124.71^d	126.68	141.07 (q, $^2J_{Me}$ = 6.3)	132.85 (qt, $^2J_{Me}$ = 6.3, $^4J_{H(3)}$ = $^4J_{H(8)}$ = 1.0)	135.19 (q, $^2J_{Me}$ = 6.4)
C(6)	124.29	124.9	124.9,^{b} 125.2,^{c} 125.51^d	125.84	130.11 (d.quint.q, ^1J_H = 159.0, ^3J_H = 5.8)	150.77 m	149.77 (sept, $^3J_{Me}$ = 5.3)
C(7)	135.46	133.4	133.5,^{b} 133.8,^{c} 134.18^d	134.93	145.21 (q, $^2J_{Me}$ = 6.0)	136.45 (qd, $^2J_{Me}$ = 6.1, $^2J_{H(8)}$ = 0.7)	129.02 (q, $^2J_{Me}$ = 6.2)
C(8)	118.10	117.9	117.9,^{b} 118.0,^{c} 118.43^d	118.28	116.04 (d.quint.q, ^1J_H = 163.9, $^3J_{H(6)}$ = $^3J_{Me}$ = 5.9, $^5J_{Me}$ = 0.8)	118.57 (dqq, ^1J_H = 168.3, $^3J_{Me}$ = 5.3, $^5J_{Me}$ = 0.8)	139.45 m
C(8a)	155.52	156.2	156.0,^{b} 156.2,^{c} 155.72^d	155.55	157.22 (d, $^2J_{H(8)}$ = 3.3)	156.38 (d, $^2J_{H(8)}$ = 3.7)	147.58 s
Me(5)					22.38 (qd, ^1J_H = 129.0, $^3J_{H(6)}$ = 5.4)	15.81 (q, ^1J_H = 131.3)	16.10 (q, ^1J_H = 132.1)
Me(7)					21.51 (qt, ^1J_H = 127.5, $^3J_{H(6)}$ = $^3J_{H(8)}$ = 4.5)	17.80 (qd, ^1J_H = 129.9, $^3J_{H(8)}$ = 4.9)	13.50 (q, ^1J_H = 132.2)

[a] In a solution of DMSO-d$_6$,[27] for convenience of comparison the atoms are numerated as in chromones.

[b] In a solution of CDCl$_3$.[28]

[c] In a solution of CDCl$_3$.[17]

[d] In a solution of DMSO-d$_6$.[14]

the nodal C(8a) atom bonded to the oxygen atom. A comparison of the spectra of compounds **6a**, **6c**, and **2a** shows that the appearance of the CF$_3$ group has virtually no effect on the chemical shifts of the C(8), C(4a), and C(8a) atoms, while the introduction of the methyl groups results in shielding of the first two atoms (−2.2 and −3.7 ppm, respectively) and deshielding of the latter (1.7 ppm). Analysis of the multiplicity of these atoms shows that the chromones are very close to the well-studied coumarins and 2-quinolones by the values of the $^nJ_{C,H}$ (n = 1—3) constants, but differ from 2-quinolones by the doublet of the nodal C(8a) atom with $^2J_{C(8a),H(8)}$ =

3.3 Hz. It has previously been found that in 2-quinolones[9] this constant does not appear at all and in coumarins[5,6] it equals 2.8—3.0 Hz and increases to 4.9 Hz when hydroxy or alkoxy groups are introduced into position 7. This reflects, most likely, the general regularity of decreasing ${}^{1-3}J_{C,H}$ when replacing the oxygen atom by the nitrogen atom[9] but, nevertheless, all ${}^{3}J_{C,H}$ constants in chromone **2a** correlate well with both the coumarin and 2-quinolone systems. For example, a half of the symmetric doublet (${}^{1}J$ = 163.9 Hz) of the protonated C(8) atom is a quintet due to the equality of the constants ${}^{3}J_{C(8),Me(7)} = {}^{3}J_{C(8),H(6)}$ = 5.9 Hz, which agrees with the published data with account for decreasing the ${}^{3}J_{C(8),H(6)}$ constant from 7.0—7.5 Hz for unsubstituted coumarin and 2-quinolone[30] to 5.5—6.1 Hz for the compounds with the methyl group in position 7.[6,9] When H(6) is substituted by the NO_2 group, the doublet of quintets of the C(8) atom in **2a** is transformed into a doublet of quartets with ${}^{3}J_{C(8),Me(7)}$ = 5.4 Hz in **4a** (in 7-methyl-2-quinolone ${}^{3}J_{C(8),Me(7)}$ = 5.5 Hz[9]), and the ${}^{1}J$ value increases by 4.4 Hz. The specific feature of the system considered is the five-bond (between the C(8) atom and the protons of the 5-Me group) long-range spin-spin coupling resulting, in the case of chromone **2a**, in splitting of each peak of the quintet into a quartet with ${}^{5}J_{C(8),Me(5)}$ = 0.8 Hz, which is observed even for the quaternary C(4a) atom. The latter interacts through three bonds with six protons (Me(5), H(3), H(6), H(8)) with different constants (within 3—6 Hz) and appears as a multiplet.

The most complicated mutiplicity in the spectrum of chromone **2a** is observed for the protonated C(6) atom at 130.11 ppm, whose spin-spin interaction through 1 and 3 bonds with 8 protons (H(6), H(8), 5-Me, 7-Me) leads to a doublet of multiplets with ${}^{1}J$ = 159.0 Hz (moving away from the heteroatom and the methyl group in the *ortho*-position decrease the direct constant), each of which consists of eight main components (${}^{3}J \sim 5.8$ Hz) with their own finer splittings. Two quartets with ${}^{2}J$ = 6.3 and 6.0 Hz at 141.07 and 145.21 ppm, the first of which also demonstrates an interaction with the protons of the remote Me group, are attributed to the C(5) and C(7) atoms, respectively. The absence of the two-bond spin-spin coupling of these atoms with the H(6) and H(8) hydrogen atoms, which was not either observed in the earlier described spectra of coumarins[5] and 2-quinolones,[9] impedes the assignment of the C(5) and C(7) atoms using only the multiplicity of these signals. Moreover, as already mentioned above, the use of the additivity rule for the calculation of CS of atoms from substituent effects in the case of sterically hindered molecules usually provides inaccurate results and requires the introduction of correction increments, which take into account the mutual influence of the closely arranged groups. The spectra of compounds **6c** and **2a** show that the CS of the *ortho*-C(6) atom is downfield by 4.27 ppm, and those of the *ipso*-C(5) and *ipso*-C(7) atoms are shifted by 14.39 and 10.28 ppm, respectively. These values deviate from the standard increments of the methyl group (9.3 ppm for *ipso*-C and 0.6 ppm for *ortho*-C)[11] due to the *peri*-effect observed for different classes of organic substances.[6,31,32] For example, for 1-methyl-9-acridanone the *ipso*- and *ortho*-increments of the methyl group are 14.5 and 2.4—2.5 ppm.[32] Taking into account that in 3-methyl-9-acridanone the C(2) atom is deshielded by 1.8 ppm with respect to that in 9-acridanone, its total *ortho*-increment is 4.3 ppm, which was observed for the C(6) atom of chromone **2a**. Thus, with account for the *peri*-effect, the chemical shifts of the aromatic carbon atoms in **2a** agree well with the expected values, and this confirms that the assignment was valid.

As shown above, the product of mononitration of chromone **2a** has the structure of 6-nitro derivative **4a**. The conclusion finds many corroborations in the ${}^{13}C$ NMR spectra. First, compared to chromone **2a**, in nitrochromone **4a** the signals from the C(6) and C(8) atoms are shifted downfield by 20.66 and 2.53 ppm and in dinitrochromone **3a** they are shifted by 19.66 and 23.41 ppm, respectively. Second, in chromone **2a** the signal from C(8) forms a doublet of quintets, in **4a** it forms a doublet of quartets, and in **3a** this signal is a lowly intense multiplet of the quaternary atom. Third, in chromones **2a** and **4a** the signal from C(8a) represents a doublet with the constants ${}^{2}J$ = 3.3 and 3.7 Hz, respectively, due to the splitting on the H(8) atom, while in **3a** this signal is a singlet. Fourth, the signals from the methyl carbon atoms in **4a** look like a quartet and a quartet of doublets, which is provided only by the substitution of the H(6) atom. The character of splitting of these signals allows the rigorous assignment of the upfield quartet to the 5-Me group, and the downfield quartet can strictly be assigned to the 7-Me group. Fifth, the introduction of the first nitro group substantially shields both Me groups, whereas the introduction of the second nitro group shields only one of them. Shielding of carbon atoms of methyl groups by the *ortho*-nitro group is a well-known fact,[33—35] which allows the reliable assignment of the downfield quartet in the spectrum of **3a** to the 5-Me group, and the upfield quartet can be assigned to the 7-Me group situated between two NO_2 groups. Note that in 1,3-dimethyl-2-nitrobenzene[33] the carbon atoms of the methyl substituents are shield by −4.0 ppm compared to *m*-xylene, and in 3,5-dimethyl-4-nitrophenol and 3,5-dimethyl-4-nitroanizole[35] they are shielded by ~−3.0 ppm with respect to 3,5-dimethylphenol and 3,5-dimethylanisole. In our case, on going from **2a** to **4a**, the *peri*-Me group is shielded much more strongly than the 7-Me group (−6.57 and −3.71 ppm, respectively). Sixth, the introduction of the first NO_2 substituent is accompanied by an increase in the direct constant by 2.3—2.4 Hz for both methyl groups, while the introduction of the second NO_2 substituent increases the corresponding constant only for one of the Me groups. This observation confirms that the quartet signals from the methyl groups in **3a** were correctly assigned.

In the spectrum of nitrochromone **4a**, the quaternary C(5) and C(7) atoms form two quartets with broadened peaks (due to the interaction with the protons of the remote Me group) at 132.85 and 136.45 ppm with $^2J = 6.3$ and 6.1 Hz, respectively. Since their assignment on the basis of only the higher $^2J_{C(5),Me}$ value would insufficiently be correct and the $^2J_{C(7),H(8)}$ constant, like in chromone **2a**, is not manifested, we recorded the spectrum with selective proton decoupling for the protons of the downfield methyl group. In this spectrum, the upfield signal looks like a quartet of triplets, which allowed us to ascribe it to the C(5) atom with $^4J_{C(5),H(3)} = {}^4J_{C(5),H(8)} =$ 1.0 Hz. The doublet of quartets of the C(8) atom was simultaneously transformed into a doublet of quartets with $^5J_{C(8),Me(5)} = 0.8$ Hz, and the signal from the C(4a) became a doublet of quintets with the constants $^3J = 4.5$ and 3.6 Hz from the sextet with broadened peaks. Since on going from **4a** to **3a** the doublet of quintets becomes a quintet with $^3J_{C(4a),Me(5)} = {}^3J_{C(4a),H(3)} = 3.7$ Hz and coumarin has the constant $^3J_{C(4a),H(8)} = 4.6$ Hz,[5] we assume that in **4a** $^3J_{C(4a),H(8)} > {}^3J_{C(4a),H(3)}$ and equals 4.5 Hz.

In the spectrum of dinitrochromone **3a**, the signals from the C(5) and C(7) atoms are also manifested as quartets with broadened peaks at 135.19 and 129.02 ppm with $^2J = 6.4$ and 6.2 Hz, respectively. Assigning these spectra in the initial stage of their processing, we took into account that in the two former cases the higher ^2J constants belonged to the *peri*-Me group and, hence, we ascribed the downfield signal to this group, although in **2a** and **4a** it was more upfield than the 7-Me group. The subsequent analysis of the chemical shifts with account for the substituent effects showed that the assignment was valid.

When evaluating the substituent effect on chemical shifts of atoms in sterically overcrowded (*ortho*- and *peri*-substituted) aromatic and heteroaromatic compounds, one should take into account both the *peri*-effect mentioned above and the *ortho*-effect.[11,36] The latter also induces deviations from the additivity rule and manifests itself when the *ortho*-position has substituents with high steric requirements, such as Me and NO_2 groups. Unfavorable interactions with the side methyl substituents force the NO_2 group to turn about the C—N bond and to deviate from the benzene ring plane, as it occurs in the case of nitromesitylene where the torsion angle is equal to 66°.[37] It has previously been shown for substituted nitronaphthalenes[38] and *o*-nitroanisoles[34] that both the magnetic anisotropy of the nitro group and its conjugation with the π-electrons of the aromatic ring change in the nonplanar conformation appeared. The change in the anisotropic component mainly affects the adjacent carbon atoms, whereas the decrease in the −M effect, which is related to the deviation of the NO_2 group from the plane of the molecule, influences on the CS of both the *ortho*- and *para*-carbon atoms to shift their signals upfield with respect to the planar (sterically non-hindered) NO_2 group. The *ipso*-C and *m*-C atoms simultaneously experience the downfield shift, which was explained by an enhanced −I effect of the nonplanar (sterically hindered) NO_2 group.[34] To illustrate these regularities, the first two rows in Table 4 present the increments of the nonplanar NO_2 group in 1,3-dimethyl-2-nitrobenzene (**7d**) and the planar NO_2 group in nitrobenzene (**7b**). The difference between these increments (°Δ) shows that the deviation of the NO_2 group from the plane of the molecule is accompanied by shielding of *o*-C (−2.6 ppm) and especially *p*-C (−4.7 ppm), while the *m*-C atoms are deshielded (1.9 ppm).[33]

Since nitrochromones **4a** and **3a** are sterically hindered molecules with bulky *ortho*-substituents, it was of interest to reveal to which extent they would manifest the deviations from additivity observed previously.[33,34,38] For lack of data for 6-nitro-, 8-nitro-, and 6,8-dinitro-2-trifluoromethylchromones, we compared the Δδ values of the NO_2 groups in chromones **4a** and **3a** and in related 2-nitro-, 4-nitro-, and 2,4-dinitroxanthones (**5b—d**)[27] (Table 4). One should give the prior attention to the fairly well comparable Δδ values in compounds **7b** and **5b**,**c**. This allows us to consider the NO_2 groups in **5b**,**c** close to planarity (except for the increments for the nodal C(8a) atom bonded to the oxygen atom and reflecting most strikingly the specificity of the chromone system). Table 4 contains the deviations from the expected Δδ values caused by the nonplanarity of the 6-nitro-($^1Δ$) and 8-nitro-($^2Δ$) groups in **4a** and **3a** compared to the planar NO_2 groups in **5b** and **5c**. The comparison of $^1Δ$ and $^2Δ$ with the °Δ standard deviations for the NO_2 group in **7d** shows a fairly good correlation of their values and suggests that both the 6-NO_2 and 8-NO_2 groups are nonplanar. Among the *ortho*-C atoms, the *peri*-C(5) atom is most strongly shielded and the nodal C(8a) atom is least shielded. Perhaps, the lower $^2Δ$ values for the *ortho*- and *para*-carbon atoms in **3a** are related to a smaller turning angle of the 8-NO_2 group relative to the plane of the molecule compared to the 6-NO_2 group.

It was especially interesting to establish the combined influence of two sterically hindered nitro groups on CS of aromatic carbon atoms because such systems were not studied earlier. 2,4-Dinitroxanthone (**5d**), for which the additivity rule with a correction for the C(8a) atom is well fulfilled,[27] was taken as a model compound with two planar NO_2 groups. A comparison of the total increments of the nonplanar and planar nitro groups in **3a** and **5d** shows that the difference between them ($^3Δ$) for the carbon atoms in the *ortho*- and *para*-positions is ~−5.4 ppm, whereas it is ~2.6 ppm for the *ipso*-atoms. The calculated CS deviations of these atoms ($^1Δ + {}^2Δ$) coincide within 1 ppm for C(7), C(4a), and C(8a) and within 2 ppm for

Table 4. Increments of chemical shifts (Δδ, ppm) in the ^{13}C NMR spectra for the nonplanar and planar NO_2 groups in chromones **3a** and **4a** and xanthones **5b—d**

Increment[a]	Δδ, ppm					
	ortho-		*meta-*		*para-*	*ipso-*
δ(**7d**)—δ(**7c**)[b] [33]	−7.9		2.7		1.3	
δ(**7b**)—δ(**7a**)[11]	−5.3		0.8		6.0	19.6
°Δ[c]	−2.6		1.9		−4.7	
δ(**4a**)—δ(**2a**)	−8.22 (C(5))	−8.76 (C(7))	0.66 (C(4a))	2.53 (C(8))	−0.84 (C(8a))	20.66 (C(6)
δ(**5b**)—δ(**5a**)[27]	−4.12 (C(5))	−6.29 (C(7))	−0.18 (C(4a))	2.03 (C(8))	3.08 (C(8a))	19.01 (C(6)
¹Δ[c]	−4.10	−2.47	0.84	0.50	−3.92	1.65
δ(**3a**)—δ(**4a**)	−7.43 (C(7))	−8.80 (C(8a))	−1.00 (C(6))	0.77 (C(4a))	2.34 (C(5))	20.88 (C(8)
δ(**5c**)—δ(**5a**)[27]	−5.01 (C(7))	−7.97 (C(8a))	−0.44 (C(6))	1.69 (C(4a))	5.43 (C(5))	20.30 (C(8)
²Δ[c]	−2.42	−0.83	−0.56	−0.92	−3.09	0.58
		ortho-, *para-*			*meta-*, *ipso-*	
δ(**3a**)—δ(**2a**)	−5.88 (C(5))	−16.19 (C(7))	−9.64 (C(8a))	1.43 (C(4a))	19.66 (C6))	23.41 (C(8)
δ(**5d**)—δ(**5a**)[27]	−0.37 (C(5))	−10.59 (C(7))	−4.56 (C(8a))	2.15 (C(4a))	17.30 (C6))	20.50 (C(8)
³Δ[c]	−5.51	−5.60	−5.08	−0.72	2.36	2.91

[a] Increments of the nonplanar and planar groups were obtained from the spectra of the compounds by subtraction of the chemical shifts of the corresponding carbon atoms.

[b] The *ipso*-increment is not indicated.

[c] Δ = (increments of nonplanar NO_2) – (increments of planar NO_2).

Note. **5a** is xanthone, **5b** is 2-nitroxanthone, **5c** is 4-nitroxanthone, **5d** is 2,4-dinitroxanthone, **7a** is benzene, **7b** is nitrobenzene, **7c** is *m*-xylene, and **7d** is 1,3-dimethyl-2-nitrobenzene. ¹Δ + ²Δ: −7.19 (C(5)), −4.89 (C(7)),−4.75 (C(8a)), −0.08 (C(4a)), 1.09 ((C(6)), 1.08 (C(8)).

peri-C(5), *ipso*-C(6), and *ipso*-C(8). This indicates a good additivity of the Δδ values found for the nonplanar NO_2 group in the chromone system.

The heteronuclear 2D HETCOR spectra of chromones **2a** and **4a** exhibited five and four cross peaks, respectively, between the directly bound ^{1}H and ^{13}C atoms. The spectra are shown in Fig. 2, *a*, *b*, and all correlations are presented in Table 5. The data in Table 5 show that the protons and directly bound to them carbon atoms were correctly assigned on the basis of analysis of the chemical shifts and the character of signal splitting. Note that in the spectrum of **2a** the signal from the C(6) atom is more downfield than the signal from C(8), and the signal from the H(6) proton is more upfield than the signal from H(8). A similar situation takes place in **4a** for the 5-Me and 7-Me groups. In addition, the 2D COLOC experiment for chromone **4a** revealed the ^{1}H-^{13}C long-range heteronuclear correlations and confirmed the conclusions of analysis of the multiplet signals.

Thus, in this work we described the synthesis and nitration of a series of new 5,7-dimethyl-2-polyhaloalkylchromones, established the structures of the related mononitro derivatives, and for the first time examined in detail the ^{1}H and ^{13}C NMR spectra of the chromone system in comparison with the spectra of related compounds. The influence of the sterically hindered nitro groups on the chemical shifts of the aromatic carbon atoms was studied, and some spectral peculiarities of the methyl group situated in the *peri*-position to the carbon atom of the carbonyl group were revealed.

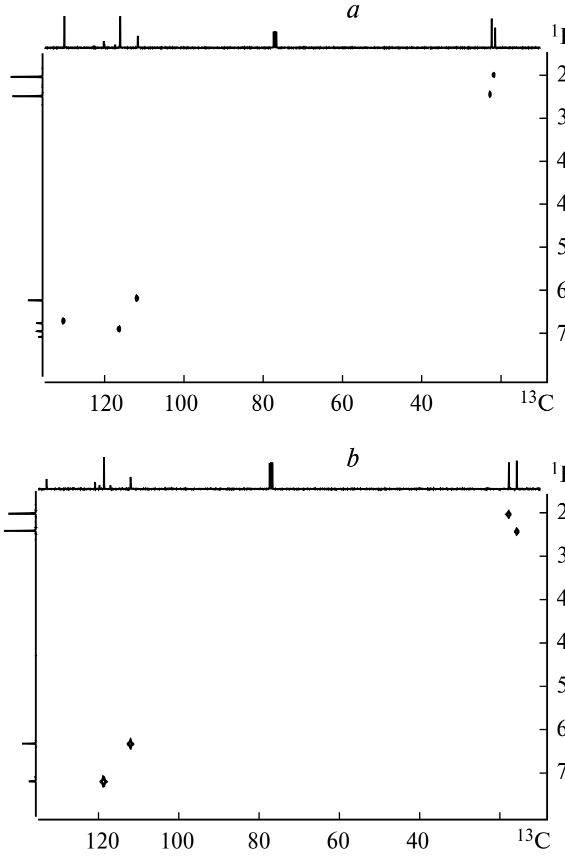


Fig. 2. 2D HETCOR spectra of chromone **2a** (*a*) and nitrochromone **4a** (*b*).

Table 5. Correlation between the ^{1}H and ^{13}C signals in the 2D HETCOR spectra of chromones **2a** and **4a**

Compound	C	H	Assignment
Chromone **2a**	21.51	2.43	Me(7)
	22.38	2.79	Me(5)
	111.57	6.58	C(3), H(3)
	116.04	7.16	C(8), H(8)
	130.11	7.01	C(6), H(6)
Nitrochromone **4a**	15.81	2.74	Me(5)
	17.80	2.42	Me(7)
	111.93	6.65	C(3), H(3)
	118.57	7.35	C(8), H(8)

Experimental

IR spectra were recorded on an IKS-29 instrument in Nujol. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer with working frequencies of 400.13 and 100.62 MHz, respectively, for solutions in $CDCl_3$. 2D NMR experiments were carried out using standard pulse sequences from the Bruker NMR Suite 2.6 software. The internal standard for ^{1}H and ^{13}C NMR spectra was Me_4Si.

Chromanones **1a**—**d**, chromones **2a**—**d**, and dinitrochromones **3a**—**d** were synthesized using described procedures,[3,39] and the syntheses of compounds **1e** и **2e** were described in Ref. 4. The data of the ^{1}H NMR and IR spectra of compounds **1a**—**d**, **2a**—**e**, **3a**—**e**, and **4a**,**d**,**e** are presented in Table 1. The ^{13}C NMR spectroscopic data for chromones **2a**—**4a** are presented in Table 3. The yields, melting points, and elemental analysis data for the synthesized compounds are presented in Table 6. Compounds **1a**,**e**, **2a**,**e**, and **3a** were described earlier.[2—4]

Table 6. Main characteristics of chromanones **1b**—**d** and chromones **2b**—**d**, **3b**—**e**, and **4a**,**e**

Compound	Yield (%)	M.p. /°C	Molecular formula	Found / Calculated (%)		
				C	H	N
1b	81	99—100	$C_{12}H_{12}F_2O_3$	59.75	5.16	—
				59.50	4.99	
1c	87	134—135	$C_{13}H_{12}F_4O_3$	53.40	4.34	—
				53.43	4.14	
1d	68	101—102	$C_{15}H_{12}F_8O_3$	45.88	3.27	—
				45.93	3.08	
2b	85	107—108	$C_{12}H_{10}F_2O_2$	64.41	4.54	—
				64.29	4.50	
2c	92	106—107	$C_{13}H_{10}F_4O_2$	57.06	3.43	—
				56.94	3.68	
2d	91	85—86	$C_{15}H_{10}F_8O_2$	47.86	2.82	—
				48.14	2.69	
3b	93	145—146	$C_{12}H_8F_2N_2O_6$	46.15	2.46	9.01
				45.87	2.57	8.92
3c	72	108—109	$C_{13}H_8F_4N_2O_6$	42.76	2.16	7.71
				42.87	2.21	7.69
3d	95	123—124	$C_{15}H_8F_8N_2O_6$	38.83	1.70	6.08
				38.81	1.74	6.03
3e	95	187—188	$C_{12}H_7Cl_3N_2O_6$	37.68	1.81	7.34
				37.78	1.85	7.34
4a	56	127—128	$C_{12}H_8F_3NO_4$	50.06	2.97	4.70
				50.19	2.81	4.88
4e	35	179—180	$C_{12}H_8Cl_3NO_4$	43.00	2.39	4.24
				42.83	2.40	4.16

5,7-Dimethyl-6,8-dinitro-2-trichloromethylchromone (3e) was synthesized using a procedure described[3] for the synthesis of 6-nitro-2-trifluoromethylchromone (75 °C, 1 h, 2.0 mL of concentrated H_2SO_4 per 0.5 g of chromone **2e**). A decrease in the amount of concentrated H_2SO_4 to 0.5 mL and shortening of the duration of the reaction to 20 min resulted in the isolation of a mixture consisting of 60% dinitrochromone **3e** and 40% 5,7-dimethyl-6-nitro-2-trichloromethylchromone (**4e**).

5,7-Dimethyl-6-nitro-2-trifluoromethylchromone (4a). A mixture of concentrated H_2SO_4 (0.5 mL) and 70% HNO_3 (0.5 mL) was added to a solution of chromone **2a** (0.5 g, 2.1 mmol) in concentrated H_2SO_4 (2.0 mL) on cooling with water and ice. The reaction mixture was left at 0—3 °C for 2 h, after which it was diluted with an ice-cold water, and the precipitate was filtered off and recrystallized from hexane. An increase in the reaction duration to 8 h produced a mixture of the mono- and dinitro derivatives. 5,7-Dimethyl-6-nitro-2-trichloromethylchromone (**4e**) was synthesized under similar conditions.

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