FREQUENCIES AND INTENSITIES OF THE CARBONYL IR ABSORPTION BANDS AND STRUCTURES OF CYCLOPENTA[b]CHROMENE DERIVATIVES

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The integral intensities of the absorption bands of the carbonyl groups ($A_{C=O}$) of 2-phenylcyclopenta[b]chromene derivatives were determined. The $A_{C=O}$ values and the $\nu_{C=O}$ frequencies are proposed as criteria for the determination of the positions of the aldehyde and ketone groups in cyclopenta[b]chromenes. The applicability of these criteria was confirmed by ^{13}C NMR spectroscopy of the carbonyl bonds. A qualitative relationship between the $A_{C=O}$ values and the ^{13}C chemical shifts of the bonds of a number of carbonyl-containing compounds was found.

A characteristic feature of the IR absorption spectra of carbonyl derivatives of nonbenzenoid aromatic hydrocarbons (azulene, pseudoazulenes, and fulvene) is the considerable decrease in the frequencies of the stretching vibrations of the ketone or aldehyde groups [1-6]. For example, the frequency of the C=O vibrations in the IR spectrum of 1,3-diacetylazulene in solution in CCl_4 is 1638 cm^{-1}, whereas it is 1707 and 1690 cm^{-1}, respectively, in the spectra of benzaldehyde and acetophenone [2, 3]. Since the frequencies of the aromatic C=C and C=O bonds in the IR spectra of carbonyl-containing pseudoazulenes of the cyclopenta[b]chromene ring are overlapped (Fig. 1), they cannot be used as a spectral criterion of the presence of C=O bonds. Proceeding from the assumption of additivity of the IR absorption bands, the use of the integral intensities of the vibrational bands of the C=C and C=O bonds may be regarded as promising for the solution of this problem. The ^{13}C resonance signals in the NMR spectra can be used as an additional criterion for the determination of the types of C=O bonds.

The aim of the present report was to obtain the spectral characteristics of 2-phenylcyclopenta[b]chromene and its derivatives, to establish the spectral criteria of the presence and location of functional groups such as aldehyde and ketone groups, and to establish correlations between the spectral parameters and the peculiarities of the structures of the molecules.

A. Frequencies and Intensities of the Bands of the Vibrations of the Carbon Skeleton Above 1600 cm^{-1}

Two bands (1632-1642 cm^{-1}) are observed in the IR spectra of 2-phenylcyclopenta[b]chromene and its derivatives in KBr pellets and in solutions in chloroform (Table 1 and Fig. 1). The integral intensities of the bands in the spectra of I-III in solution in chloroform range from 1.1 to 1.6 practical units (10^{-4} liter·mole^{-1}·cm^{-2}). The retention of the vibrational frequency over the narrow range of 1632-1642 cm^{-1} for a large number of 2-phenylcyclopenta[b]chromene derivatives may constitute evidence for a slight change in the form of the normal vibrations corresponding to this band. The intensity of this band increases to 3.0 to 3.5 units when strong electron-acceptor substituents such as carbonyl groups are introduced in the aromatic system of the investigated pseudoazulenes (VI and VII, Table 1).

B. Frequencies and Intensities of Carbonyl Groups

The assignment of the bands at 1632-1642 cm^{-1} in the IR absorption spectra of the pseudoazulenes of the 2-phenylcyclopenta[b]chromene series that contain carbonyl groups in the 1 position was based on indirect factors, viz., on the chemical evidence for the presence of a carbonyl group [7]. Direct arguments in favor of the assignment of the band at 1632-1642 cm^{-1} to the $\nu_{C=O}$ stretching vibrations must be adduced.

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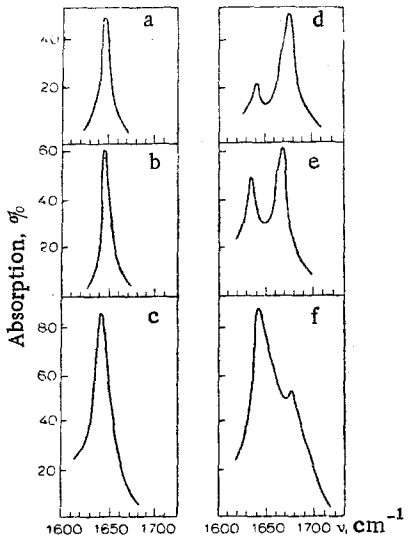
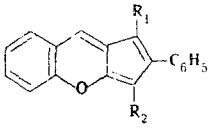
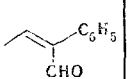
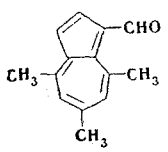
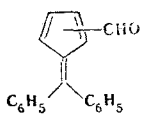


Fig. 1. IR absorption spectra in $CHCl_3$ at 1600-1700 cm^{-1}: a) 2-phenyl- (I); b) 1,2,3-triphenyl- (III); c) 1-formyl-2-phenyl- (IV); d) 1,2-diphenyl-3-formylstyryl- (VIII); e) 1,2-diphenyl-3-formyl- (VI); f) 1,3-diformyl-2-phenylcyclopenta[b]chromene (IX).

TABLE 1. Frequencies and Integral Intensities of Some IR Absorption Bands of 2-Phenylcyclopenta[b]chromene Derivatives (in $CHCl_3$)



Compound	Substituents		C=C		C=O	
	R_1	R_2	Frequency, ν, cm^{-1}	Intensity, $A \cdot 10^{-4}$ liter·mole^{-1}·cm^{-2}	Frequency ν, cm^{-1}	Intensity, $A \cdot 10^{-4}$ liter·mole^{-1}·cm^2
I	H	H	1642	1,1	—	—
II	Ph	H	1642	1,4	—	—
III	Ph	Ph	1642	1,6	—	—
IV	CHO	H	1636*	~	1636	Σ(C=O+C=C) = =7,45
V	$COCH_3$	H	1632*	~	1632	Σ(C=O+C=C) = =6,11
VI	Ph	CHO	1638	3,5	1668	3,8
VII	Ph	$COCH_3$	1640	3,0	1659	3,9
VIII	Ph		1640	2,2	1672	4,6
IX	CHO	CHO	~1640	~	1640) 1669)	Σ(C=O+C=C) = =11,6
X			—	—	1628	6,3
XI			—	—	1660	4,5
XII	Ph—CO—Ph		—	—	1663	2,46

*The C=O band is overlapped with the C=C band.
†The band of the C=C vibration is overlapped with the band of the C=O group.

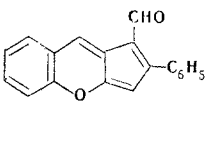
The measured intensity of the absorption band at 1632-1642 cm^{-1} in the spectra of 1-formyl- (IV) and 1-acetyl-2-phenylcyclopenta[b]chromenes (V) ranges from 6 to 7 units (Table 1). It was demonstrated above that the intensity of the C=C band of the skeletal vibrations in this region in the spectra of phenyl-substituted pseudoazulenes I-III is ~1.6 units. Consequently, the contribution of absorption of the carbonyl group to this band is ≈4.5-6.0 units. This is in agreement with the measured intensities of the carbonyl bands at 1659-1672 cm^{-1} in the IR spectra of VI-VIII of ≈3.8-4.6 units.

Two absorption bands are observed in the spectrum of IX (Fig. 1); the high-frequency band was assigned to the vibrations of a carbonyl group in the 3 position, while the low-frequency band was assigned to the vibrations of the C=C bond of the skeleton and a C=O group in the 1 position. In fact, as demonstrated above, the intensity of one C=O band ($A_{C=O}$) ≈ 4.5-6.0 units, the $A_{C=C}$ intensity is 1.6 units, and the overall intensity, with allowance for two carbonyl groups and C=C bonds of the skeleton, is 10.5-12 units.

To prove the presence of carbonyl groups in 1-carbonyl-containing pseudoazulenes we used a second independent method, viz., ^{13}C NMR spectroscopy. It is apparent from Fig. 2 that a resonance signal with a chemical shift of 185.66 ppm is observed in the ^{13}C NMR spectrum of 1-formyl-2-phenylcyclopenta[b]chromene (IV). No doubts are raised regarding the assignment of this signal to the carbon atom of the formyl group, since other signals are not expected in this region. Two signals at 186.61 and 183.77 ppm corresponding to the carbon atoms of two formyl groups are observed in the spectrum of 1,3-diformyl-2-phenylcyclopenta[b]-chromene (IX) in this region. Like the $\nu_{C=O}$ frequencies in the IR spectra of 1,3-diformyl-pseudoazulene (IX), the resonance signals of the ^{13}C chemical shifts indicate nonequivalence of the formyl groups in the 1 and 3 positions. The spin–spin splitting (Fig. 2b) of the ^{13}C signals at 183-187 ppm is in agreement with the fact of the presence of two formyl groups in these compounds.

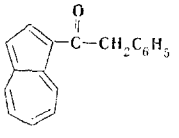
C. Relationship between the Spectral Characteristics and the Structures

The explanation for the anomalously low $\nu_{C=O}$ frequency of the formyl or ketone groups in the 1 or 3 position of the azulene ring and in the 1 position of the cyclopent[b]chromene system as compared with the $\nu_{C=O}$ values of these groups in the 2 position of azulene or the 3 position of cyclopentachromene may be as follows. The 1 and 3 positions in the 2-phenyl-cyclopenta[b]chromene system with fixed double bonds in the fulvene part correspond to the α and β positions of fulvene. In this connection, the frequencies of the vibrations of the carbonyl groups in 1-formyl-2-phenylcyclopenta[b]chromene IV and 1-ω-phenylacetylazulene XIII are, respectively, 1636 and 1640 cm^{-1}, i.e., they are low-frequency values [6]. On the other hand, in 1,2-diphenyl-3-formylcyclopenta[b]chromene VI and in 2-ω-phenylacetylazulene XIV the frequencies of the vibrations of the carbonyl groups in the aldehyde and ketone groups, which



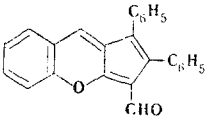
IV

$\nu_{C=O}$ 1636 cm^{-1},



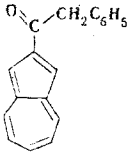
XIII

$\nu_{C=O}$ 1640 cm^{-1};



VI

$\nu_{C=O}$ 1668 cm^{-1},



XIV

$\nu_{C=O}$ 1675 cm^{-1}

are known to be in the β position, have the higher-frequency values of 1668 and 1675 cm^{-1}, respectively.

Many authors feel that the aldehyde and ketone groups in azulenes and pseudoazulenes are strongly polarized; however, outside of the $\nu_{C=O}$ frequencies, data in favor of polarization have not been presented. The $\nu_{C=O}$ value, however, depends in a complicated manner on a number of factors of the molecular structure, and it is therefore unreliable. The chemical shifts of the ^{13}C atoms of the ketone and aldehyde groups and the integral intensities of the absorption bands of the stretching vibrations of these groups are more reliable for this purpose. The chemical shift (δ) of the ^{13}C nucleus depends linearly on the electronic shielding, and the lower δ values correspond to greater shielding, while the intensity of the absorption band of the carbonyl group is symbatic to the dipole moment of the molecule [8-10]. According to the data in [8], the δ values for the aldehyde and ketone groups range from 183 to 204 ppm: acetone (XV, 204.1), acetophenone (XVI, 196.9), benzophenone (XVII, 194.8), benzaldehyde

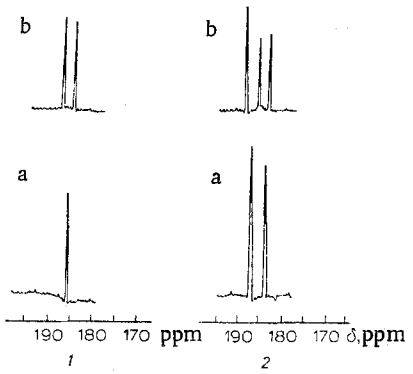


Fig. 2. ^{13}C NMR spectra in $CDCl_3$: 1) 1-formyl-2-phenyl- (IV); 2) 1,3-diformyl-2-phenylcyclopenta[b]chromene; a) in the case of complete suppression of spin–spin coupling; b) in the case of incomplete suppression of spin–spin coupling.

(XVIII, 190.7), and dibenzo[a,d]tropone (XIX, 191.36 ppm). A value of 185.66 was found for 1-formyl-2-phenylcyclopenta[b]chromene (IV), while 183.77 and 186.61 ppm were found for 1,3-diformyl-2-phenylcyclopenta[b]chromene (IX). The shift of the resonance signal of the ^{13}C chemical shift of the keto group to strong field constitutes evidence for a significant increase in the electron density on the carbon atom of the C=O group. The integral intensities of the bands of the C=O stretching vibrations ($A_{C=O}$) in the IR spectra of this series of carbonyl-containing compounds [10-14] also have a tendency to increase from formaldehyde to 1,3-diformyl-2-phenylcyclopenta[b]chromene. This qualitative relationship between $\delta^{13}C$ values of the C=O group and $A_{C=O}$ confirms the validity of the approach set forth above. Consequently, it follows from a comparative analysis of the ^{13}C chemical shifts of the aldehyde groups in the NMR spectra and the integral intensities of the absorption bands of the stretching vibrations of the C=O groups in the IR spectra that the aldehyde groups in the 1 and 3 positions of azulene and cyclopenta[b]chromene are strongly polarized in a manner comparable to the polarization of the C=O group in benzotropones [10, 15]. This is manifested in the chemical properties of 1-acetylazulene, which does not give a hydrazone when it is heated with hydrazine.

EXPERIMENTAL

The compounds were synthesized by known methods [7, 16-19]. The IR spectra of KBr pellets and solutions of the compounds in chloroform were recorded with a UR-20 spectrometer. The integral intensities of the absorption bands (A_{XY}) of the stretching vibrations of the C=C and C=O bonds of the aldehyde and ketone groups were measured by the Ramsay method [20], while the intensities of the bands were calculated from the formula

$$A_{XY} = \frac{\pi}{2} \cdot \frac{I}{c \cdot l} \cdot \Delta\nu_{1/2^a} \cdot \ln\left(\frac{T_0}{T}\right)_{max},$$

where c is the concentration in moles per liter, l is the layer thickness in centimeters, and $\Delta\nu_{1/2}{}^{a}$ is the half-width of the band in reciprocal centimeters.

The intensities of the bands (A_{XY}) are given in practical units (10^{-4} liter·mole^{-1}·cm^{-2}). The accuracy in the measurement of the narrow bands at 1500-1700 cm^{-1} was ±2 cm^{-1}, while the accuracy in the measurement of the intensities was ±7%. The A_{XY} values presented in Table 1 were obtained by averaging two to three measurements.

The ^{13}C NMR spectra of the compounds in $CDCl_3$ were recorded with Varian XL-100-15 (25.16 MHz) and CFT-20 (20 MHz) spectrometers under pulse conditions of accumulation with Fourier transformation. The chemical shifts were measured with an accuracy of 0.04 ppm relative to the internal signal of the solvent.

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LITERATURE CITED

1. K. Hafner, Angew. Chem., 70, 419 (1958).
2. A. G. Andersonand W. F. Harrison, J Am. Chem. Soc., 86, 708 (1964).
3. W. Treibs and W. Schroth, Ann., 642, 82 (1961).
4. G. V. Boyd and E. W. Clark, J.Chem. Soc., C, No. 9, 859 (1966).
5. A. G. Anderson, J. Org. Chem., 37, 3499 (1972).
6. Yu. N. Porshnev, N. A. Andronova, E. M. Tereshchenko, and K. Z. Ogorodnik, Zh. Org. Khim., 10, 2602 (1974).
7. Yu. N. Porshnev, V. A. Churkina, and V. V. Titov, Khim. Geterotsikl. Soedin., No. 10, 1324 (1978).
8. G. C. Levy and G.L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, New York (1972).
9. V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, Dipole Moments in Organic Chemistry [in Russian], Khimiya, Leningrad (1968), p. 195.
10. B. E. Zaitsev, Yu. N. Sheinker, and Yu. D. Koreshkov, Dokl. Akad. Nauk SSSR, 136, 1090 (1961).
11. C. M. Barrow, J. Chem. Phys., 21, 2008 (1953).
12. L. B. Archibald and A. D. Pullin, Spectrochim. Acta, 12, 34 (1958).
13. H. W. Thompson and D. J. Jewell, Spectrochim. Acta, 13, 254 (1958).
14. H. W. Thompson and D. A. Jameson, Spectrochim. Acta, 13, 236 (1958).
15. A. J. Jones, P. D. Gardner, D. M. Grant, W. M. Litchman, and V. Boekelheide, J. Am. Chem. Soc., 92, 2395 (1970).
16. Yu. N. Porshnev, V. A. Churkina, and M. I. Cherkashin, Khim. Geterotsikl. Soedin., No. 6, 751 (1976).
17. Yu. N. Porshnev, V. A. Churkina, N. A. Andrionova, and V. V. Titov, Khim. Geterotsikl. Soedin., No. 7, 902 (1977).
18. K. Hafner and C. Bernhard, Angew. Chem., 69, 533 (1957).
19. K. Hafner and K.-H. Vöpel, Angew. Chem., 71, 672 (1959).
20. D. A. Ramsay, J. Am. Chem. Soc., 74, 72 (1952).

PHOTO- AND THERMOCHROMIC 2-AMINO-2H-CHROMENES*

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A number of N-aryl- and N-alkylimines of 2-hydroxy-5,6-benzocinnamaldehyde were synthesized. The cyclic 2-amino-2H-chromene structure in nonpolar solvents was established for them by IR, UV, and PMR spectroscopy. It is shown that the transition to polar solvents leads to the establishment of a tautomeric ring-chain equilibrium. The equilibrium thermal transformations and phototransformations of some N-aryl- and N-alkylimines were studied.

We have previously established that the N-arylimines of 2-hydroxy-5,6-benzocinnamaldehyde exist in the crystalline state and in solutions in nonpolar solvents in cyclic 2H-chromene form A [2]. In the present research we studied the equilibrium thermal transformations and phototransformations of N-aryl- and N-alkylimines of this aldehyde and also synthesized some new aldimines.

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