

INFRARED SPECTRA OF SUBSTITUTED 5-PHENYL-2-FURALDEHYDES AND TRANSMISSION OF SUBSTITUENT EFFECTS BY THE FURAN RING

A. PERJÉSSY^a, R. FRIMM^b and P. HRNČIAR^a

^a Department of Organic Chemistry, Komenský University,

^b Department of Organic Chemistry, Slovak Institute of Technology, Bratislava

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The C=O stretching frequencies of a series of substituted 5-phenyl-2-furaldehydes were studied and compared with analogous data for a series of substituted benzaldehydes. In both series a linear correlation exists between the C=O stretching frequency and σ substituent constants. Using these correlations, the transmissive factor of substituent effects for furan ring was found to be 0.65 ± 0.12 in tetrachloromethane and 0.48 ± 0.06 in chloroform, in agreement with previously reported data.

Hammett dependence of the C=O stretching frequency of organic compounds containing bridge atom or group between the carbonyl group and substituted aromatic nucleus can be used in quantitative study of transmission of substituent effects by this bridge¹⁻⁵. In a previous work⁶ we have determined the transmissive factor of substituent effects for furan ring, using the observed linear relationships between the arithmetic mean of the symmetrical and asymmetrical C=O stretching frequencies in series of 2-(5-phenyl-2-furfurylidene)-1,3-indanediones and 2-benzylidene-1,3-indandiones and σ substituent constants.

In the present work we have utilized the linear relationship between the C=O stretching frequency and σ constants for series of substituted 5-phenyl-2-furaldehydes (I) and benzaldehydes (II) in quantitative study of the transmission of substituent effects by the furan ring with the aim to verify as well as to give precision to the previously reported results⁶.

EXPERIMENTAL

Compounds studied. Substituted 5-phenyl-2-furaldehydes (I) were prepared according to literature⁷⁻¹². All the compounds were purified prior to measurements by repeated crystallization from an appropriate solvent or by repeated distillation. Substituted benzaldehydes (II) were commercially available products which, shortly prior to use, were freed from the products of spontaneous oxidation, benzenecarboxylic acids, by shaking with saturated KHCO₃ solution, followed by crystallization or distillation, until single absorption bands were obtained in the region of C=O vibrations.

IR spectra measurements. The IR spectra were recorded with Zeiss, Model UR-20 spectrophotometer in the 1800–1600 cm⁻¹ region. The wavenumber scale of the instrument was calibrated with the use of standard spectrum of the indene-camphor-cyclohexanone mixture¹³.

The frequencies were read with the accuracy of $\pm 1 \text{ cm}^{-1}$. The measurements were carried out with solution of the compounds in tetrachloromethane and in chloroform in the 0.25 cm or 0.1 cm thick cells. The compounds were used in concentrations which ensured that the absorption in the studied region amounted to 70–75%. The analytical purity solvents were dried and purified in the usual way prior to use.

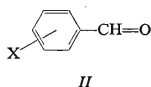
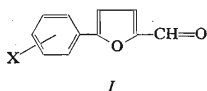
Statistic treatment of data. The values of σ substituent constants were those reported by McDaniel and Brown¹⁴, except for the value for 3,4-O₂CH₂ which was taken from the work¹⁵. Statistic parameters of linear correlations were calculated on Gier digital computer, using non-approximated relations¹⁶.

RESULTS AND DISCUSSION

Data presented in Table I show that on going from tetrachloromethane to chloroform the C=O stretching frequencies of all the substituted 5-phenyl-2-furaldehydes (*I*) increase by 10–13 cm^{-1} . The C=O stretching frequencies of the series of substituted benzaldehydes (*II*) measured in the same solvents and given in Table II agree well with the data reported¹⁷, with the exception of 4-methoxy and 4-chloro derivatives, the frequencies of which were found to be by 6–7 cm^{-1} higher. This difference can be due to rapid oxidation of some of the substituted benzaldehydes. Difficulties in obtaining pure compounds have also been mentioned in the work¹⁷. In the present study benzenecarboxylic acids were thoroughly removed. On changing the solvent, similar changes of the C=O stretching frequencies as in the previous case can again be observed, amounting here to 4–19 cm^{-1} . As follows from comparison of the frequencies given in Table I and II the insertion of the furan ring between the aldehyde group and the benzene ring brings about a decrease in the C=O stretching frequencies which equals to 20–24 cm^{-1} in tetrachloromethane and to 17–30 cm^{-1} in chloroform. This fact, similarly as in the case of 2-(5-phenyl-2-furfurylidene)-1,3-indandiones¹, indicates an extended conjugation of C=O bonds in the system of furaldehydes *I*.

TABLE I
C=O Stretching Frequencies in Substituted 5-Phenyl-2-furaldehydes *I* and Substituent Constants

Subst.	$\nu(\text{C=O}), \text{cm}^{-1}$		σ	Subst.	$\nu(\text{C=O}), \text{cm}^{-1}$		σ
	CCl ₄	CHCl ₃			CCl ₄	CHCl ₃	
4-OCH ₃	1 685	1 672	-0.27	3-F	1 692	1 679	0.34
4-CH ₃	1 687	1 674	-0.17	3-Cl	1 692	1 680	0.37
H	1 689	1 676	0.00	3-Br	1 693	1 680	0.39
4-Br	1 690	1 678	0.23	3-NO ₂	1 694	1 684	0.71
4-Cl	1 690	1 678	0.23	4-NO ₂	1 695	1 685	0.78



We have found that in both series a good linear correlation exists between the C=O stretching frequency and σ (Fig. 1). Statistic parameters of these correlations (Table III) show that the dependence for the series of compounds *I* is more significant. The errors in the determined slopes are however approximately the same (c. 10%), which allows us to compare both these slopes. If the transmission factor of substituent

TABLE II
C=O Stretching Frequencies in Substituted Benzaldehydes *II* and σ Substituent Constants

Subst.	$\nu(\text{C}=\text{O}), \text{cm}^{-1}$		σ	Subst.	$\nu(\text{C}=\text{O}), \text{cm}^{-1}$		σ
	CCl_4	CHCl_3			CCl_4	CHCl_3	
4-N(CH ₃) ₂	1 695	1 677	-0.83	H	1 711	1 702	0.00
4-NH ₂	— ^a	1 682	-0.66	4-F	1 711	1 705	0.06
4-OCH ₃	1 705	1 690	-0.27	3-OCH ₃	1 712	1 707	0.12
4-CH ₃	1 710	1 691	-0.17	4-Cl	1 714	1 708	0.23
3,4-O ₂ CH ₂ ^b	1 699	1 693	-0.16	4-CN	1 717	1 713	0.66
3-NH ₂	— ^a	1 699	-0.16	4-NO ₂	1 718	1 714	0.78

^a The spectra were not measured because of low solubility of the compounds in tetrachloromethane. ^b Included for the sake of simplicity, even though general formula *II* is not valid for the substance (3,4-dioxymethylenebenzaldehyde).

TABLE III
Statistic Parameters of Linear Correlations of C=O Stretching Frequencies with σ for Substituted 5-Phenyl-2-furaldehydes *I* and Benzaldehydes *II*

Symbols used: q and s slope and its error, q and s_q frequency for the unsubstituted derivative and the error, s standard deviation, and r correlation coefficient.

Series (No of members)	Solvent	q (s_q)	q (s_q)	s	r
<i>I</i> (10)	CCl_4	8.97 (0.70)	1 688.4 (0.6)	0.72	0.977
<i>I</i> (10)	CHCl_3	11.80 (0.36)	1 675.5 (0.3)	0.37	0.996
<i>II</i> (9)	CCl_4	13.75 (1.53)	1 709.4 (0.3)	2.10	0.959
<i>II</i> (12)	CHCl_3	24.52 (2.35)	1 699.2 (0.3)	3.62	0.957

effects for the furan ring (more strictly for 2,5-furylene bridge) are calculated according to relation (1),

$$\pi'(\text{Fu}) = \varrho_I / \varrho_{II}, \quad (1)$$

where ϱ_I and ϱ_{II} are the slopes of corresponding linear correlations for compounds *I* and *II*, respectively, the following values are obtained: $\pi'(\text{Fu}) = 0.65 \pm 0.12$ in tetrachloromethane, and $\pi'(\text{Fu}) = 0.48 \pm 0.06$ in chloroform. These values agree well with those determined with the use of linear $\bar{\nu}(\text{C}=\text{O})$ σ^+ - dependence in series of substituted 2-(5-phenyl-2-furfurylidene)-1,3-indandiones and 2-benzylidene-1,3-indandiones⁶ (0.68 ± 0.12 in tetrachloromethane and 0.46 ± 0.03 in chloroform). As follows from the comparison of $\pi'(\text{Fu})$ for both solvents substituent effects are better transmitted in tetrachloromethane than in chloroform solutions. This phenomenon has previously been attributed⁶ to the formation of hydrogen bonds between the oxygen atom of furan ring and chloroform molecules. The value of transmissive factor $\pi'(\text{Fu}) = 0.47$ calculated⁶ from relation (2),

$$\pi'(\text{Fu}) = \varepsilon^4(\text{C}_{sp^2}) + \varepsilon^2(\text{C}_{sp^2}) \varepsilon(\text{O}), \quad (2)$$

where $\varepsilon(\text{C}_{sp^2})$ and $\varepsilon(\text{O})$ are the transmissive factors of substituent effects for sp^2 -hybridized carbon atom and oxygen atom respectively (reported by Bowden¹⁸), is also in harmony with the experimental value obtained in chloroform (0.48 ± 0.06). Similar results have also been obtained in a previous work⁶. Also here substituent effects

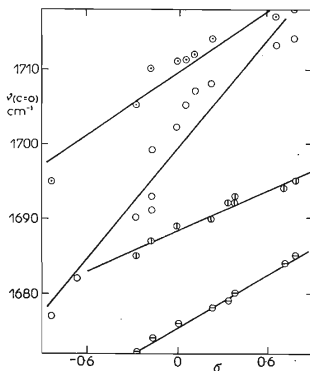


FIG. 1

The Plot of C=O Stretching Frequencies vs σ for Series of 5-Phenyl-2-furaldehydes *I* (CCl_4 ◻, CHCl_3 ◻) and Benzaldehydes *II* (CCl_4 ○, CHCl_3 ○)

are transmitted by furan ring roughly two times better than are by benzene ring¹⁹⁻²¹ (i.e. through 1,4-phenylene bridge).

When taking into account the results of the present and the previous work⁶, the transmissive factors for furan ring can be expressed by the following average values: 0.665 ± 0.120 in tetrachloromethane and 0.470 ± 0.055 in chloroform solutions.

REFERENCES

1. Perjéssy A., Hrnčiar P.: This Journal 35, 1120 (1970).
2. Perjéssy A., Láčová M.: This Journal 36, 2956 (1971).
3. Perjéssy A., Láčová M., Hrnčiar P.: This Journal 36, 2775 (1971).
4. Perjéssy A., Vida M., Láčová M.: This Journal 37, 1319 (1972).
5. Perjéssy A., Hrnčiar P.: This Journal 37, 1707 (1972).
6. Perjéssy A., Hrnčiar P., Krutošiková A.: Tetrahedron 28, 1025 (1972).
7. Akashi H., Oda R.: Rept. Inst. Chem. Res. Kyoto Univ. 19, 93 (1949).
8. Malinowski S.: Roczniki Chem. 27, 54 (1953).
9. Frimm R., Kováč J., Závodská E.: Collection of Communications, Section Chemistry, p. 41. Slovak Institute of Technology, Bratislava 1967.
10. Frimm R., Kováč J., Jurášek A.: Collection of Communications, Section Chemistry, p. 35. Slovak Institute of Technology, Bratislava 1967.
11. Brit. pat. 1 139 164 (1969).
12. Snyder H. R., Davis C. S., Bickerton R. K., Halliday R. P.: J. Med. Chem. 10, 807 (1967).
13. Jones R. N., Fauer P. K., Zacharias W.: Rev. Univ. Mines 15, 417 (1959).
14. McDaniel D. M., Brown H. C.: J. Org. Chem. 23, 420 (1958).
15. Jaffé H. H.: Chem. Rev. 53, 191 (1953).
16. Eichler J.: Chem. listy 60, 1203 (1966).
17. Thompson H. W., Needham R. W., Jameson D.: Spectrochim. Acta 9, 208 (1957).
18. Bowden K.: Can. J. Chem. 41, 2781 (1963).
19. Parnes Z. N., Ždanovič V. I., Kursanov D. N.: Dokl. Akad. Nauk SSSR 132, 1322 (1960).
20. Bezuglij V. D., Dmitrijeva V. N., Škodina I. A., Melnik L. A.: Ž. Obšč. Chim. 34, 376 (1964).
21. Zuman P.: Chem. listy 48, 94 (1954).

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