

ELECTRONIC STRUCTURE OF THE ROTATIONAL ISOMERS OF FURFURAL

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(Received in the UK 14 April 1971; Accepted for publication 10 May 1971)

Abstract—The electronic structures of the two planar rotational isomers of furfural are discussed. Calculations by PPP-CI and Del Re methods demonstrate that definite differences should be observed between the properties of the possible rotamers. On the basis of theoretical calculations and observed properties of both isomers it is possible to establish their relative content in equilibrium mixtures.

TWO PLANAR isomers of furfural, A and B, obtained by rotation of the formyl group in relation to the furan ring have been assumed to exist because of two carbonyl absorption bands in the IR spectrum.¹



Later, on the basis of dipole moment calculations by the group moments method it has been assumed² that the two isomers should possess significantly different dipole moments and that their equilibrium mixture at room temperature should contain mainly the A form. At sufficiently low temperature both isomers of furfural may be discerned on the basis of their NMR spectra.³ The proton chemical shifts of rotamers have been assigned by qualitative considerations of the deshielding effects of electronegative carbonyl oxygen atoms.³ The ratio of intensities of the signals of the two isomers shows that in the solvent used, $(\text{CH}_3)_2\text{O}$, at low temperatures the B form is energetically preferred.³

The data from the IR spectra of furfural⁴ have been interpreted in the sense that at room temperature the A form prevails in an equilibrium mixture in CCl_4 . This interpretation has been stated to be consistent with previous calculations of dipole moments.² On the basis of the ratio of intensities of $\tilde{\nu}_{\text{C=O}}$ -bands and their temperature dependence the higher frequency C=O -absorption band has been assigned to the A form.⁴

The present study is devoted to the examination of possibilities for a theoretical description of the experimentally established differences of the quoted physical properties of furfural and related molecules. Two methods, PPP-CI^{5, 6} and the method due to Del Re^{7, 8} were utilized for the quantum chemical calculations of both furfural isomers.

It has been shown recently that the electronic spectra of furan may be reproduced satisfactorily using various sets of parameters in the PPP approximation.^{9, 10, 11} At the

same time it has been shown that considerable difficulties arise in the choice of parameters reproducing the ground state of the same compound (dipole moment, electronic densities $P_{O=O}$ and $P_{C=O}$).^{9, 10, 12} In general it has been found that a high value of the one-center coulomb integral W_O and a low value of the two-center resonance integral β_{CO} should be adopted^{9, 10, 13} so as to obtain a satisfactory correspondence between calculated and experimentally established atomic net charges.^{13, 14, 15} We have used parameters according to the requirements quoted above.¹⁶ All singly excited singlet π -electronic configurations were considered. The furfural geometry was chosen according to the data for furan¹⁷ and furan-2-carboxylic acid.¹⁸

RESULTS AND DISCUSSION

Values calculated by us are compared to the experimental data in Tables 1 and 2. Table 1 presents the calculated π -bond orders $P_{O=O}$ for both A and B forms. We can see that the rotamer A to which the $\tilde{\nu}_{C=O}$ -band at higher frequency is attributed⁴ actually possesses a higher C=O bond order. Thus, a qualitative accordance with the experimental assignment is observed. The difference between the bond orders $P_{C=O}$ of both rotamers seems however relatively small to explain the experimentally observed difference of the $\tilde{\nu}_{C=O}$ absorption frequencies of the rotamers.

Both PPP and Del Re methods were used to calculate dipole moments, 4.11 D for rotamer A, and 3.24 D for rotamer B, respectively. The experimentally found values of

TABLE 1. GROUND STATE ELECTRONIC INDICES AND OBSERVED IR AND NMR CHARACTERISTICS FOR THE TWO ROTAMERS OF FURFURAL

Compound	$P_{C=O}$	$\tilde{\nu}_{C=O}$ cm^{-1}	atom no.	$q\pi$	$q\sigma$	$\sqrt{q\sigma + \pi}$	PMR ^a	
							157°K	303°K
Furfural A	0.8812	1700 ^b 1699(CCl ₄)	1	+0.1129	-0.2432	-0.1303		
			2	-0.0345	+0.0922	+0.0577		
			3	+0.0176	-0.0364	-0.0188	7.42	7.23
			4	-0.0417	-0.0410	-0.0827	6.79	6.58
			5	+0.0331	+0.0483	+0.0814	8.04	7.73
			6	+0.2592	+0.0264	+0.2856	9.74	9.61
			7	-0.3466	-0.0748	-0.4214		
Furfural B	0.8798	1681 ^b 1682(CCl ₄)	1	+0.1083	-0.2432	-0.1349		
			2	-0.0430	+0.0922	+0.0492		
			3	+0.0369	-0.0364	+0.0005	7.57	7.23
			4	-0.0376	-0.0410	-0.0786	6.79	6.58
			5	+0.0256	+0.0483	+0.0739	8.04	7.73
			6	+0.2530	+0.0264	+0.2794	9.56	9.61
			7	-0.3432	-0.0748	-0.4180		
Furan ^c	—	—	1	+0.1120	-0.2467	-0.1347		
			2	-0.0165	+0.0499	+0.0344	7.36 ^d	
			3	-0.0395	-0.0408	-0.0803	6.28 ^d	

^a ref. 3

^b ref. 4.

^c calculated dipole moment $\mu=0.48$ D; experimental—00.6 D, ref. 17; 0.70 D, ref. 15

^d ref. 22

the dipole moments for the equilibrium mixture of isomers at 25° are 3.56 D (C_6H_6), 3.60 D (dioxan)² and 3.63 D.¹² The differences in dipole moments of both forms calculated by us and with the aid of the group moments method² are qualitatively consistent (3.48 D for rotamer A and 2.33 D for rotamer B²). The values of dipole moments found by us however provide no reason to state, as it has been previously,^{2,4} that the A form of furfural prevails at room temperature in solution.

We endeavoured to find a correlation between NMR chemical shifts and $\sigma + \pi$ charges of carbon atoms adjacent to the corresponding protons. σ -Charges were taken into consideration in order to estimate the short distance effects of the polarization of the σ -core caused by heteroatoms. This approach provides the possibility of establishing a

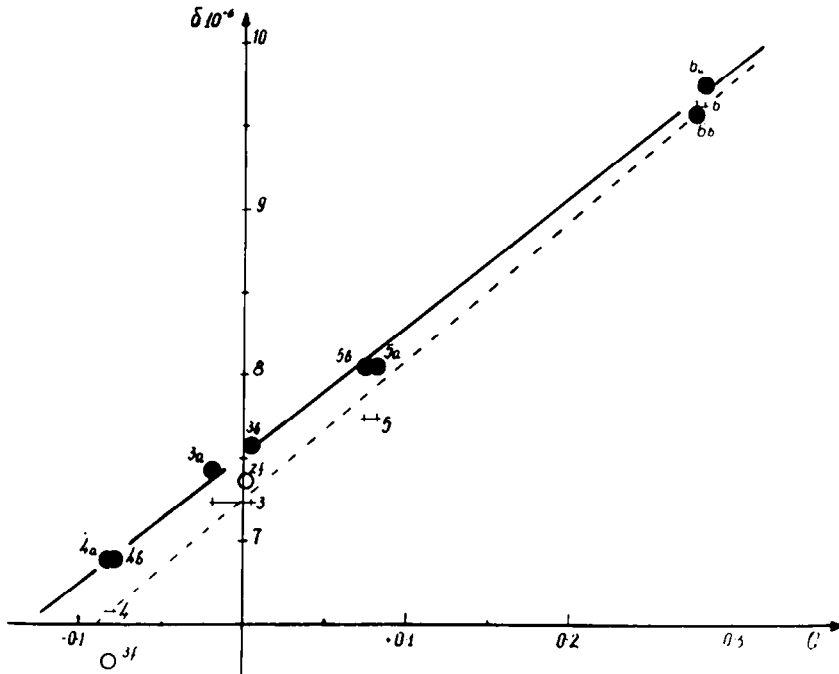


FIG 1. Plot of PMR chemical shifts vs. total $\sigma + \pi$ charges Q of the two rotamers of furfural (full line -157°K ; dotted line -303°K). 2f and 3f—the chemical shifts of furan protons.

general correlation for all protons including these in close vicinity to heteroatoms. Such an approach has been quantitatively substantiated by Pople¹⁹ and more recently it has been shown that a quantitative relation exists between the total charge and the diamagnetic component in the proton shielding.²⁰ A simple correlation $\delta = k \cdot Q$ was found for vinyl ethers.²⁰

The calculated σ , π and $\sigma + \pi$ charges compared to corresponding NMR shifts of both rotamers of furfural are also presented in Table 1. As may be seen from Table 1 and Fig. 1 a linear correlation with a slope 8.65 p.p.m./e exists between the above quantities. The slope of the correlation observed is in a good accordance with the slopes of similar correlations 7–13.5 p.p.m./e known from the literature.²¹ In conformity with the previous interpretation³ the formyl proton of the A form should be deshielded as compared to that

of the B form. Further, the proton H-3 of A should be subject to larger shielding than that of B. This result is also in accordance with the qualitative interpretation.³ On the basis of our calculations it may be stated that between the chemical shifts of the H-4 and H-5 protons of both rotamers there should also exist a definite though slight difference, less than that observed for the formyl and the H-3 protons. These differences obviously have not been observed because of instrumental difficulties. It should be noted that with the aid of total $\sigma + \pi$ charges it is possible to predict correctly the order of the chemical shifts for the H-3 and H-5 protons, in contrast to the case using only the π -charges. The correlation with the total charges is also applicable to furan chemical shifts,²² Fig. 1, neglecting the eventual role of circular diamagnetic currents in the furan ring.

Some conflicting statements have been made as to whether the ring current in furan is much less than that in benzene²³ or comparable.²⁴ Actually, the neglect of the polarization of the σ -core of furan and the resulting magnetic anisotropy of the atomic environment requires the assumption of a diamagnetic ring current in order to explain the observed proton shieldings.^{14, 25}

Adopting the alternative approach—neglecting the ring currents and taking into account the differential effect of the polarization of the σ -core we succeed in obtaining a correlation for furan derivatives equivalent to those in the literature.^{14, 15} There are some indications for the correctness of this approach such as the formyl protons correlate with the $\sigma + \pi$ charge, Fig. 1. If ring currents were actually present, this correlation should fail because of the different shielding constants for the ring protons from those for the formyl protons. On the basis of the above results we are inclined to agree that the ring currents in furan derivatives are negligible.

The total π -energies for rotamers of furfural were calculated as -258.22 eV for isomer A and -257.04 eV for isomer B. We have also calculated the difference in the coulombic energy of the point charges of both isomers²⁶ and the difference in the Van der Waals

TABLE 2. CALCULATED AND OBSERVED ELECTRONIC TRANSITION ENERGIES AND OSCILLATOR STRENGTHS

Compound	E_{calc} eV	f	E_{exp} eV (ref. 28)	$\log \epsilon$
Furfural A	4.597	0.576		
	5.801	0.433		
			3.68 ($n - \pi^*$)	1.80
			4.62	4.25
		5.83 ^a (?)		
Furfural B	4.604	0.634		
	5.792	0.174		

^a J. Bielecki, V. Henri, *Ber. Dtsch. Chem. Ges.* **47**, 1690 (1914)

energies of conformations as well.²⁷ The latter values are at least an order smaller than the difference in the π -energy, i.e. they are negligible in the considerations of the stability of rotamers. There is a discrepancy between our result and the result obtained from the investigation of the NMR spectrum of furfural,³ which is apparently due to solvation effects. An indication of the significance of these factors is the observation that the ratio of intensities of $\tilde{\nu}_{\text{C=O}}$ in the IR spectra is subject of considerable change with change of

solvent. In CCl_4 the $\tilde{\nu}_{\text{C=O}}$ -band at higher frequency is more intensive, while in CHCl_3 the $\tilde{\nu}_{\text{C=O}}$ -band is more intensive at lower frequency.

Calculated PPP-CI transition energies and oscillator strengths for both rotamers of furfural are given in Table 2. The conformity of these results to the experimental data²⁸ is entirely satisfactory. The fact that the lowest transition energies for both isomers are practically equal should be emphasized. An estimate of the relative content of rotamers in the equilibrium mixture might be obtained on the basis of the intensity of the second π - π^* transition since for this transition considerable differences are calculated between the oscillator strengths of both rotamers, Table 2. Unfortunately, at present comprehensive data on this transition in the spectrum of furfural is lacking.

CONCLUSIONS

The calculation of the electronic structure of furfural by the PPP-CI method, combined with the method of Del Re provides an explanation of the differences in some physical properties of the two existing rotational isomers. Qualitative agreement between the calculated $P_{\text{C=O}}$ bond orders and observed $\tilde{\nu}_{\text{C=O}}$ stretching frequencies was found. The results concerning dipole moments, NMR and electronic spectra show an entirely satisfactory agreement with experimental values.

A good linear correlation between observed NMR shifts of both rotamers and calculated $\sigma + \pi$ atomic net charges of the adjacent carbon atoms was obtained. This result serves to show that the diamagnetic ring currents in furan and furfural are negligible.

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