STRUCTURE AND BASICITY OF ω-SUBSTITUTED ETHYNYL 2-THIENYL KETONES

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By a comparison of the calculated and experimental dipole moments of ethynyl 2-thienyl ketones, it was shown that the S,O-cis conformation is the most probable one. The basicities of these compounds were estimated by means of IR spectroscopy from the shift of the band of the phenolic OH stretching vibration. The correlation relationships between the dipole moments of the ketones, their basicities, and the association constants of propiolic acids that have identical substituents attached to the triple bond were established. It is noted that the experimental characteristics found do not correlate with the different sorts of σ substituent constants; this provides evidence for a difference in the mechanism of the interaction of the atomic groups in a number of acetylenic and aromatic molecules.

The structure of molecules of thienyl alkynyl ketones makes it possible to assume the possibility of the existence of these compounds in the form of two planar conformations (Fig. 1).

TABLE 1. Experimental and Calculated Dipole Moments of $C_4H_3SCO-C{\equiv}C-R$

R	μ_{exp}, D	μ_{calc}, D	
		s,o-cis	*s,o*-trans
C_4H_9	4,33	3,67	1,25
H	3,49	3,80	1,57
Br	3,37	3,80	1,42
C_6H_5	4,30	3,66	1,38
C_4H_3S	4,14	3,49	1,52

TABLE 2. Spectral Characteristics of Thienyl Alkynyl Ketones $C_4H_3SCO-C{\equiv}C-R$

Compound	R	$\nu_{C=O}$, cm^{-1}	$A_{C=O} \cdot 10^{-4}$ $mole^{-1} \cdot liter \cdot cm^{-2}$	$\Delta\nu_{OH}$, cm^{-1}
I	C_4H_9	1636	2,42	190
II	CH_3	1637	2,38	188
III	C_3H_7	1637	2,40	187
IV	$Si(CH_3)_3$	1636	2,48	175
V	Br	1640	2,51	152
VI	C_6H_5	1634	2,80	185
VII	H	1640	2,62	155
VIII	C_4H_3S	1632	3,25	176

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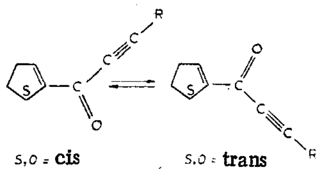

Fig. 1. Conformation of the investigated ketones.

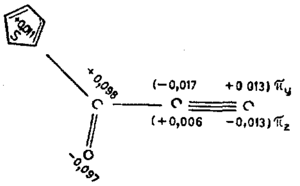

Fig. 2. Diagram of the distribution of the π-electron charges.

TABLE 3. Dissociation Constants (pK_a) of Propiolic Acids

No.	Acid	pK_a
I	$CH_3C{\equiv}CCOOH$	7,46
II	$C_6H_5C{\equiv}CCOOH$	7,32
III	$Si(CH_3)_3C{\equiv}CCOOH$	7,21
IV	$HC{\equiv}CCOOH$	6,84
V	$BrC{\equiv}CCOOH$	6,78

It has been shown by comparison of the calculated and experimental dipole moments that 2-formyl- and 2-acetylthiophenes [1, 2] and thiophene analogs of chalcones [3] are characterized by planar conformations with a cis orientation of the sulfur of the heteroring and the oxygen of the carbonyl groups.

Our comparison of the calculated and experimental dipole moments of thienyl alkynyl ketones shows (Table 1) that a structure in which the oxygen atom of the carbonyl group and the sulfur atom of the heteroring are on the same side of the single C−C bond (S,O-cis isomers) is most favorable for them.

ω-Substituted ethynyl 2-thienyl ketones are convenient objects for the study of the transmission of the effect of substituents (R) through the triple bond. From this point of view, an analysis of the spectroscopic characteristics of the carbonyl group is of great interest. However, the frequencies of the stretching vibrations and the intensity of the absorption bands of the C=O group in the IR spectrum of the investigated ketones change only slightly as the substituents are varied (Table 2). It follows from the results presented in Table 2 that the basicity of the carbonyl group, which we estimated from the shift in the band of the phenolic OH stretching vibration ($\Delta\nu_{OH}$), is the most sensitive parameter to the change in the electron distribution under the influence of substituents R. The substituents are arranged in the following order with respect to the degree of their effect on the basicity of the ketones:

$$Alk > Ph > Si(CH_3)_3 \simeq C_4H_3S > H \simeq Br.$$

It is quite apparent that the observed order does not correspond to the inductive effect of radicals R. This follows from both the high basicity of ketone VI as compared with VII and from the reduced basicity of ketone IV, the inductive constant of the $Si(CH_3)_3$ grouping of which requires the highest basicity in the investigated series of ketones. At the same time, it is known [4] that the basicities of alkynylamines $RCH_2C{\equiv}CH_2NH_2$ and the magnitude of the quadrupole splitting in the Mössbauer spectra of alkynyltin compounds $RCH_2C{\equiv}CSnR_3$ [5] are described by the Taft induction constants. Consequently, it can be assumed that the reason for the above change in the basicities of ethynyl 2-thienyl ketones is conjugation of substituents R with the triple bond. Thus the lower basicity of ketone IV as compared with ketones I-III can be explained by the acceptor properties of the $Si(CH_3)_3$ group. Further analysis shows that neither the relative magnitudes of the basicities nor the dipole moments of the investigated ketones correlate with the different sorts of σ substituent constants (σ_I, σ_p, σ_c^+, σ_c^0) found on the basis of aromatic compounds [6].

The absence of a correlation between the σ constants and the quadrupole splittings in the Mössbauer spectra of alkynyltin compounds $Alk_3SnC{\equiv}C{-}R$ and their dipole movements was also established for a large number of substituents by Zavgorodnii and co-workers [7, 8]. They assume that the σ constants of the aromatic series do not adequately reflect the intraelectronic interaction in the acetylenic systems. All of these results are most likely explained by qualitative and quantitative changes in the mechanism of the mutual effect of substituents attached to the triple bond. To a certain degree, the results obtained may be due to the change in the overlap integrals of the AO of the substituent and the carbon of the triple bond as a consequence of shortening of $C_{sp}{-}R$ bond length with respect to the $C_{sp^2}{-}R$ bond length.

We would like to direct the readers' attention to the results of a calculation of the π-electron system of the ketone (Fig. 2) within the Pople approximation, which show the possibility of counterpolarization of the π_z and π_y systems of the triple bond. The effect may lead to a certain peculiarity in the transmission of the effect of the atoms through the triple bond. In particular, if the π-electron systems of two substituents attached to the triple bond are oriented in mutually perpendicular planes, the counterpolarization of the π-electron clouds of the C≡C bond can, in principle, lead to a change in the sign of the effect, i.e., a donor substituent may "force" the triple bond to be an electron acceptor with respect to the second substituent (it may reinforce its acceptor properties).

The problem of the applicability of the σ constants to acetylenic reaction series was previously examined by Charton [9]. The satisfactory correlation between the ionization constants of 3-substituted propiolic acids as the dipole moments of acetylenic compounds and the Hammett σ_p constants that Charton found is probably determined by the limited set of substituents attached to the acetylenic bond [CH_3, C_2H_5, C_4H_9, $C(CH_3)_3$, C_6H_5 and COOH].

In order to obtain additional information regarding the interaction of nonbonded atomic groups in acetylenic derivatives, we measured the dissociation constants of 3-substituted propiolic acids with substituents attached to triple bonds that are analogous to the ketones under examination (Table 3). The dissociation constants of the propiolic (IV) and bromopropiolic (V) acids are practically identical. This fact and the data on the basicities of the analogous ketones can apparently be explained by compensation of the −I and +M effects of the bromine atom attached directly to the triple bond.

A linear dependence expressed by the following equation exists between the $\Delta\nu_{OH}$ and pK_a values found:

$$\Delta\nu_{OH}=57.23\ pK_a-236\ (r=0.996;\ s_0=1.6).$$

The existence of the linear relationship $\Delta\nu_{OH} = f(pK_a)$ and the absence of a relationship between the relative basicities of the ketones and the Hammett σ_p constants also exclude the possibility of a correlation between the dissociation constants of 3-substituted propiolic acids and the Hammett σ_p constants. The same can be said relative to the dipole moments of the ketones, which are linearly related to $\Delta\nu_{OH}$:

$$\Delta\nu_{OH}=36.9\mu+28\ (r=0.99;\ s_0=2.9).$$

An increase in the electron density on the oxygen atom of the carbonyl group leads to an increase in the basicity and to an increase in the dipole moments of the ketones, inasmuch as μ is primarily determined by polarization of the C=O group, as shown by the calculations.

Thus the results obtained with respect to the relative basicities and dipole moments of thienyl alkynyl ketones and the acidities of 3-substituted propiolic acids attest to substantial differences in the electronic interactions in a number of acetylenic and aromatic molecules.

EXPERIMENTAL

The IR spectra of CCl_4 solutions of the thienyl alkynyl ketones were recorded with a UR-20 spectrometer. The intensities of the absorption bands were calculated by the Iogansen method [10]. The shifts of the frequencies of the phenolic OH stretching vibration ($\Delta\nu_{OH}$) during its interaction with ketones were measured in CCl_4 (the concentration of the investigated ketone was 0.1 mole/liter and the concentration of the phenol was 0.02 mole/liter). The $\Delta\nu_{OH}$ value was determined as the average of five to six measurements. Treatment of the data by the method of mathematical statistics showed that the absolute error in the measurement of $\Delta\nu_{OH}$ was $\pm 3\ cm^{-1}$ with a confidence probability of 0.95.

The dipole moments of the ketones were measured with a Dipol' precision dielecometer by the method of dilute solutions at 1 MHz and 25° in benzene. The molecular polarization at infinite dilution ($P_{2\infty}$) was found by the Hedestrand method.

The dissociation constants of the acids were determined in methanol by potentiometric titration. Benzoic acid, the dissociation constant of which is 9.4 pK_a units, was used as the standard.

LITERATURE CITED

1. H. Iumbroso and P. Pastour, Comptes Rend., 261, 1279 (1965).
2. V. I. Minkin, Yu. A. Zhdanov, and E. N. Malysheva, Teor. i Éksperim. Khim., 7, 180 (1972).
3. V. I. Savin, S. A. Flegontov, and Yu. P. Kitaev, Khim. Geterotsikl. Soedin., 1188 (1970).
4. R. I. Kruglikova and G. R. Kalinina, Zh. Organ. Khim., 7, 857 (1971).
5. B. I. Rogozev, V. S. Zavgorodnii, L. M. Krizhanskii, and A. A. Petrov, Zh. Obshch. Khim., 38, 2064 (1968).
6. Yu. A. Zhdanov and V. I. Minkin, Correlation Analysis in Organic Chemistry [in Russian], Izd. Rostovsk. Univ. (1966).

7. V. S. Zavgorodnii, B. I. Rogozev, É. S. Sivenkov, and A. A. Petrov, Zh. Obshch. Khim., 41, 2237 (1971).
8. V. S. Zavgorodnii, B. I. Rogozev, É. S. Sivenkov, K. S. Mingaleva, and A. A. Petrov, Zh. Obshch., Khim., 41, 2241 (1971).
9. M. Charton, J. Org. Chem., 26, 735 (1961).
10. A. V. Iogansen, Opt. i Spektrosk., 16, 813 (1964).