

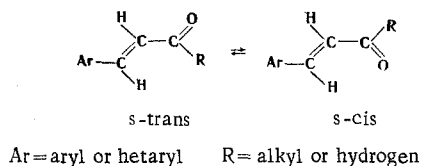
STEREOCHEMISTRY AND DIPOLE MOMENTS  
OF  $\alpha,\beta$ -UNSATURATED HETEROCYCLIC KETONES\*

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UDC 547.722.733:541.67.634:543.422.4

The dipole moments of eight  $\alpha,\beta$ -unsaturated aromatic and heterocyclic aldehydes and ketones in dioxane solution were measured. The moments of the syn and anti conformations were calculated by vector-additivity schemes. The effect of the conformation on the moment of the C=O group was taken into account. The charge distribution was calculated by the Pariser-Parr-Pople method in order to estimate the polarization of the C=C bond.

Conjugation of the double bonds through a single bond in  $\alpha,\beta$ -unsaturated carbonyl compounds leads to a considerable increase in the double-bond character of the single bond and an increase of 10-15 kcal/mole in the energy barrier to rotation relative to the single bond. This results in the development of s-trans-cis isomers [2] relative to the single bond; these isomers can be readily identified by means of, for example, IR spectroscopy [3, 4]. The position of the s-trans  $\rightleftharpoons$  s-cis conformational equilibrium for aromatic  $\alpha,\beta$ -unsaturated ketones depends on the "volume" of the substituent (R) attached to the carbon atom of the carbonyl group [1]. If R=H the molecule exists mainly in the s-trans conformation. When R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or iso-C<sub>3</sub>H<sub>7</sub>, the IR spectrum shows a doublet of bands of carbonyl absorption caused by the existence of the s-trans  $\rightleftharpoons$  s-cis conformational equilibrium in these compounds. Moreover, the conformational equilibrium is shifted to favor the s-cis isomer on passing to a bulkier substituent. When R=tert-butyl, the molecule exists in the s-cis conformation.



Since s-trans-cis isomers differ appreciably with respect to their polar properties, the method of dipole moments has frequently been used to study their structures [5-8]. If the magnitude of the polariza-

\* Communication II of the series " $\alpha,\beta$ -Unsaturated Carbonyl Compounds and Their Derivatives." See [1] for communication I.

TABLE 1. Dipole Moments and Conformer Ratios of  $\alpha,\beta$ -Unsaturated Aromatic Carbonyl Compounds

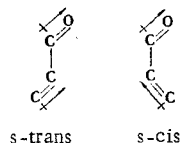
Compound	$\mu_{\text{exp}}$ , D	Conformer present [1], %	
		s-trans	s-cis
C <sub>6</sub> H <sub>5</sub> CH=CHCHO	3,71 <sup>16</sup>	~ 100	~ 0
C <sub>6</sub> H <sub>5</sub> CH=CHCOCH <sub>3</sub>	3,31 <sup>11</sup>	57	43
C <sub>6</sub> H <sub>5</sub> CH=CHCOCH <sub>2</sub> CH <sub>3</sub>	3,13	31	69
C <sub>6</sub> H <sub>5</sub> CH=CHCOCH(CH <sub>3</sub> ) <sub>2</sub>	3,06	14	86
C <sub>6</sub> H <sub>5</sub> CH=CHCOC(CH <sub>3</sub> ) <sub>3</sub>	2,87 <sup>11</sup>	0	100

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR, Kazan. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 10, pp. 1331-1335, October, 1972. Original article submitted September 17, 1971.

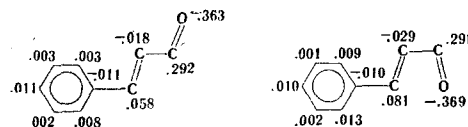
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tion of the C=C bond in the C=C-C=O chromophore was disregarded in calculations made from vector-additivity schemes, the *s-cis* and *s-trans* conformations of an unsaturated carbonyl compound could not be differentiated [6-8]. On the other hand, the conformations of several  $\alpha,\beta$ -unsaturated carbonyl compounds could be established when the polarization of the C=C bond was taken into account by means of bond moments [5].

Taking the polarization of the C=C bond into account by this or another method is of fundamental significance in calculations of *s-cis-trans* conformations. The directions of the moments of the C=C and C=O bonds coincide in the *s-trans* conformation, while in the *s-cis* conformation the angle between the moments, which are directed to different sides, is 120°. All other conditions being equal, the *s-trans* isomer will have a larger dipole moment than the *s-cis* isomer.



The *s-cis* double bond will have a larger induced dipole than the *s-trans* double bond because of the direct effect of the field of the carbonyl group. According to the method in [9], the dipole induction of the carbonyl group on the *s-cis* C=C bond was estimated to be four times that on the *s-trans* C=C bond [3]. The charge distribution on the atoms, found with the  $\pi$  approximation of the Pariser-Parr-Pople method, also confirms that the dipole of the carbonyl group in the *s-cis* conformation polarizes the double bond more strongly than in the *s-trans* conformation.



The dipole moment of cinnamaldehyde is 3.71 D. Benzalacetone has a lower dipole moment of 3.31 D. Replacement of the methyl group by ethyl and isopropyl groups leads to a further decrease in the dipole moment (Table 1), while tert-butyl styryl ketone has the minimum dipole moment (2.87 D). The difference between the moment of acetone (2.71 D [10]) and pinacolone (2.79 D [10]) is 0.08 D, from which it can be concluded that the difference (0.44 D) between the moments of benzalacetone and tert-butyl styryl ketone is due to the different position of the *s-trans*  $\rightleftharpoons$  *s-cis* conformational equilibrium of each of these compounds [11]. From these data it can be approximately estimated that the *s-cis* isomer of benzalacetone has a moment that is 1 D lower than that of the *s-trans* isomer.

According to the PMR data, the substituents attached to the double bond of  $\beta$ -( $\alpha$ -thienyl)acrolein (I) and  $\beta$ -( $\alpha$ -furyl)acrolein (II) are *trans* oriented, which is indicated by the spin-spin coupling constant of the olefinic protons: for I,  $\delta$  6.43 ( $\alpha$ -H), 7.53 ppm ( $\beta$ -H),  $J=16$  Hz; for II,  $\delta$  6.57 ( $\alpha$ -H), 7.20 ppm ( $\beta$ -H),  $J=16$  Hz. The absorption bands of the C=O group in the IR spectra of I and II are more intense than those of the C=C bond (for I,  $\nu_{C=O}$  1688  $\text{cm}^{-1}$ ,  $\nu_{C=C}$  1619  $\text{cm}^{-1}$ , and the intensity ratio is 2.0; for II,  $\nu_{C=O}$  1688  $\text{cm}^{-1}$ ,  $\nu_{C=C}$  1634  $\text{cm}^{-1}$ , and the intensity ratio is 2.5). This sort of intensity ratio is characteristic for the *s-trans* conformers of  $\alpha,\beta$ -unsaturated carbonyl compounds [3, 4]. In addition to the bands at 1619 and 1634  $\text{cm}^{-1}$  of the C=C stretching vibrations of the *s-trans* conformer, the spectra of I and II contain bands at 1595 and 1609  $\text{cm}^{-1}$ , which, in analogy with the band at 1611  $\text{cm}^{-1}$  of cinnamaldehyde [1], can be assigned to the presence of the *s-cis* isomer of I and II in solution.

Unsymmetrical thiophene and furan substituents presuppose yet another form of isomerism, which we have arbitrarily designated as *syn* and *anti* (Table 2). We used a vector scheme to calculate the dipole moments of the planar *syn-trans-s-trans* conformations of I and II. In view of its low concentration, the admixed *s-cis* isomer was not taken into account in the calculations. The moment of  $\alpha$ -substituted thiophene (1.01 D) was calculated from the moment of thiophene (0.54 D [12]). This moment forms an angle of 40° with the axis of symmetry of the thiophene ring. The moment of  $\alpha$ -substituted furan (0.98 D), which forms an angle of 42° with the axis of symmetry of the furan ring, was calculated from the moment of furan (0.71 D [13]). In the calculations, the furan and thiophene molecules were considered to be regular pentagons, and the moments (0.71 and 0.54 D, respectively) were directed from the center of the ring toward the heteroatom [14, 15]. A moment of 2.89 D, calculated from the *trans-s-trans* conformation

TABLE 2. Dipole Moments and Conformations of  $\alpha,\beta$ -Unsaturated Heterocyclic Carbonyl Compounds

Compound	X	$\mu_{\text{exp}}$ , D	$\mu_{\text{calc}}$ , D	
			syn	anti
I	S	4.00	3.50	2.61
II	O	4.44	4.09	3.27
III	S	3.40	3.70	2.73
IV	O	2.99	3.42	2.59
V	S	3.27	3.59	2.69
VI	O	3.36	3.55	2.73

of cinnamaldehyde (3.71 D [16]) and a  $C_{\text{sp}^2} \leftarrow H$  moment of 0.7 D, was selected for the carbonyl group. In comparing the experimental values of the dipole moments with the moments calculated for the syn and anti conformations of I and II, one should prefer the syn conformation in both cases (Table 2).

According to the PMR data, 1-( $\alpha$ -thienyl)-3-tert-butyl-1-propen-3-one (III) and 1-( $\alpha$ -furyl)-3-tert-butyl-1-propen-3-one (IV) have a trans orientation of the substituents attached to the double bond: for III,  $\delta$  6.83 ( $\alpha$ -H), 7.70 ppm ( $\beta$ -H), and  $J=15$  Hz; for IV,  $\delta$  7.12 ( $\alpha$ -H), 7.36 ppm ( $\beta$ -H), and  $J=16$  Hz. The IR spectra of III and IV in the region of the stretching vibrations of the C=O and C=C bonds are characteristic for s-cis- $\alpha,\beta$ -unsaturated ketones: the stretching vibrations of the C=C bonds surpass the C=O stretching vibrations in intensity (for III,  $\nu_{\text{C}=\text{O}}$  1685  $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}}$  1595  $\text{cm}^{-1}$ , and the intensity ratio is 0.5; for IV,  $\nu_{\text{C}=\text{O}}$  1684  $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}}$  1614  $\text{cm}^{-1}$ , and the intensity ratio is 0.3). The dipole moments of the syn- and anti-trans-s-cis conformations (Table 2) were calculated for III and IV using the above-mentioned moments of the furan and thiophene substituents, a carbonyl-group moment of 2.0 D, calculated from the moment (2.87 D) of trans-s-cis-benzalpinacolone [11], and a  $(\text{CH}_3)_3\text{C} \rightarrow \text{C}$  moment of 1.0 D.

The dipole moments of the syn and anti conformations were similarly calculated for 1-( $\alpha$ -thienyl)-3-phenyl-1-propen-3-one (V) and 1-( $\alpha$ -furyl)-3-phenyl-1-propen-3-one (VI), which, according to the IR-spectroscopic data, exist in the trans-s-cis conformation [17, 18]. The carbonyl-group moment for the calculation of these compounds was calculated from the dipole moment of trans-s-cis-benzalacetophenone (3.05 D [16]) and was found to be 2.35 D. The phenyl-group moment was selected as 0.7 D.

The experimental values of the dipole moments for ketones III-VI are intermediate between the calculated values of the syn and anti conformations. The expression  $\mu^2 = (1-x)\mu_1^2 + x\mu_2^2$  gives the following mole fractions of the syn conformer: 0.7 III, 0.5 IV, 0.6 V, and 0.7 VI. The fact that the syn conformation is preferable both for the s-trans (I-II) and the s-cis (III-VI) carbonyl compounds can be explained by the dipole-dipole interaction of the heteroring and the carbonyl group.

## EXPERIMENTAL

$\beta$ -( $\alpha$ -Thienyl)acrolein (I) [bp 106-108° (4 mm)] was obtained by the condensation of  $\alpha$ -formylthiophene and acetaldehyde via the method in [19].  $\beta$ -( $\alpha$ -Furyl)acrolein (II) [mp 49° (from hexane)] was obtained by the condensation of furfural and acetaldehyde via the method in [20]. 1-( $\alpha$ -Thienyl)-3-phenyl-1-propen-3-one (V) [mp 58° (from ethanol)] and 1-( $\alpha$ -furyl)-3-phenyl-1-propen-3-one (VI) [mp 26° (from

hexane)] were synthesized by the condensation of  $\alpha$ -formylthiophene and furfural with acetophenone via the method in [17, 20]. The synthesis of ethyl styryl ketone and isopropyl styryl ketone was previously described in [1].

1-( $\alpha$ -Thienyl)-3-tert-butyl-1-propen-3-one (III). A 0.22-mole sample of  $\alpha$ -formylthiophene and 0.22 mole of pinacolone were mixed in 50 ml of ethanol in the presence of 1 ml of 20% aqueous KOH solution. The mixture was held at 20° for 24 h and was then poured into 150 ml of water. The aqueous mixture was extracted with ether, and the ether layer was dried. The ether was removed, and the residue was vacuum-distilled to give 89% of a product with bp 133° (4 mm) and mp 112° (from hexane). Found: C 67.9; H 7.2%.  $C_{11}H_{14}OS$ . Calculated: C 67.9; H 7.3%.

1-( $\alpha$ -Furyl)-3-tert-butyl-1-propen-3-one (IV). This compound was similarly obtained in 91% yield and had bp 122° (3 mm). Found: C 74.2; H 7.9%.  $C_{11}H_{14}O_2$ . Calculated: C 74.1; H 7.9%.

The dielectric constants were measured on 0.1-0.05 M solutions in dioxane by the no-beat method with an IDM-1 device. The dioxane was purified by the method in [21]. The experimental dipole moments were calculated by the method in [22].

The IR spectra of  $CCl_4$  solutions (in a cuvette with a layer thickness of 0.4 mm) were recorded with a UR-20 spectrometer. The ratio of the areas of the  $\nu_{C=O}$  and  $\nu_{C=C}$  bands was calculated after the corresponding peaks were cut out and weighed.

The PMR spectra were recorded with a Varian HA-100 spectrometer; 0.5 M solutions in  $CCl_4$  were investigated with tetramethylsilane as the internal standard.

The theoretical quantum-chemical calculations were kindly given to us by V. V. Zverev, to whom we express our gratitude.

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