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We have measured the dipole moments of 23 azachalcones in benzene solution at 25°C. The experimentally determined values and those calculated using a vector additive scheme for the dipole moments are compared with the chemical structure of the azachalcones and suggestions are made about the most probable surface configuration of the ketones. For 1-pyridyl-3-arylpropenones-1, a correlational relationship is found between the values of μ , the intramolecular distances, and the σ -constant of Hammett for the constituents.

We have reported earlier the results of investigating the dipole moments of chalcones [1], and their furane [2], thiophene [3], selenophene [4], pyrrole [5], and quinoline [6] analogs. In extending these investigations to heterocyclic chalcones, we decided to determine the dipole moments of the isometric α , β -unsaturated ketones of the pyridine series (the azachalcones) of the type:



where R represents phenyl in cases (I-III), 4-tolyl in (IV-VI), 4-anisyl in (VII-IX), 4-fluorophenyl in (X-XII), 4chlorophenyl in (XIII-XV), 4-nitrophenyl in (XVI), 2-furyl in (XVII-XVIII), 2-thienyl in (XIX-XXI) and 2-selenienyl in (XXII, XXIII) (Table 1); and to compare the data so obtained with the chemical structure of these compounds. There are indications in the literature of the values of μ only for the most simple carbonyl derivatives of pyridine, namely the corresponding aldehydes [7, 8] and methyl ketones [7-11].

For all these compounds we have used the vector additive scheme to calculate the dipole moments for the possible coplanar conformations. In these calculations the moment of the pyridine ring was taken as equal to 2.22 D [12], while the angle bonds and the intradistances were taken from [13], and the remaining necessary data from this paper and also from [4-6].

EXPERIMENTAL*

The synthesis of azachalcones was carried out using crotonic condensation of 2-, 3-, and 4-acetyl pyridines with aromatic and heterocyclic aldehydes in an alkaline medium, as already described in [14].

Measurements of dipole moments were performed using the Debye dilute solution method in benzene solution at a temperature 25 ± 0.02 °C, in a similar way to that described in [3-5]. Errors in measurement did not exceed ± 0.03 D. The results are shown in Table 2.

DISCUSSION OF RESULTS

The azachalcones which we have investigated, from the method by which they were produced, represent trans-isomers with respect to the substituents at the aliphatic double bond. In investigations of chalcone [15] and its heterocyclic analog [2-6], it has been shown that the carbonyl group is in the s-cis-position in relation to the neighboring vinyl group. It is reasonable to suppose that in compound I-XXIII a similar configuration of the co-planar substituents will be found.

For azachalcones, in the molecules of which 2- and 3-pyridyl residues are found, we may imagine the existence of two planar conformations (Fig. 1), differing in the fact that the atoms of nitrogen and oxygen are located

* The student G. V. Kulachek participated in the experimental work.

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| R = pyridy1-4 | μ, D | accord. to Higashi | | 3,26 | 3,76 | 4,24 | 2,14 | 2,02 | 1 | 1 . | 3,5 3 | 1 |
|---------------|----------|--------------------------|--|---|--------------------|--------------------|---------------------|---------------------|--------------------|--|--|--|
| | | calc,* | | a) 2,42 | a) 2,81 | a) 3,66 | a) 0,92 | a) 0,77 | | l . | a) 2,66 b) 2,43 | 1 |
| | | meas. | | 3,27 | 3,77 | 4,23 | 2,10 | 1,95 | 1 | | 3,54 | |
| | Com- | punod | | III | Ν | IX | XII | Х٧ | ŀ | 1 | IXX | I |
| R = pyridy1-3 | μ, D | accord. to Higashí | | 2,88 | 3,29 | 3,59 | 2,19 | 2,26 | | 3,23 | 3,15 | 3,38 |
| | | calc.* | | $_{ m b}^{ m a}) \stackrel{4}{}_{ m 0}, 23$ | a) 4,60 b) 0,78 | a) 5,40 b) 1,54 | a) 2,42 b) 1,98 | a) 2,85 b) 2,04 | | a) 4,75 b) 0,37 c) 4,19 d) 0,50 | a) 4,56 b) 1,76 c) 4,25 d) 0,32 | a) 4,43 b) 1,62 c) 4,10 d) 0,20 |
| | | meas. | | 2,88 | 3,31 | 3,62 | 3,25 | 2, 22 | | 3,28 | 3,15 | 3,36 |
| | Com- | punod | | Π | > | VIII | IX | XIV | 1 | , XVIII | XX | IIIXX |
| | μ, D | accord. to Higashi | | 2,31 | 2,46 | 2,64 | 2,61 | 2,92 | 4,57 | 2,22 | 2,16 | 2,46 |
| - pyridy1-2 | | calc.* | | a) 4,89 b) 2,85 | a) 5,09 b) 2,26 | a) 5,63 b) 2,65 | a) 3,98 b) 2,47 | a) 4,32 b) 2,83 | a) 5,40 b) 5,24 | a) $5,59$ b) $3,16$ c) $4,50$ d) $2,09$ | a) 5,39 b) 3,04 c) 4,55 d) 2,58 | a) 5,45 b) 2,90 c) 4,42 d) 2,44 |
| R : | | meas. | | 2,31 | 2,47 | 2,64 | 2,61 | 2,93 | 4,68 | 2,23 | 2,13 | 2,40 |
| | Com- | punoď | | | IΛ | VII | X | IIIX | IVX | IIVX | XIX | ПХХ |
| | Rı | | | Phenyl | 4-tolyl | 4-anisyl | 4-fluoro- phenyl | 4-chloro- phenyl | 4-nitro- phenyl | 3-furyl | 2-thienyl | 2-selenienyl |

TABLE 1. Dipole Moments of Azachalcones R-CO-CH = CH-R₁

* For compounds I-XVI the values of μ were calculated for the syn- and anti-conformations (a and b) of the pyridine ring, while for compounds XVII-XXIII the calculation was carried out for the four forms: a) syn-, b) anti-, c) syn-anti-, and d) anti-syn-s-cis-forms.

| Com- pound | α | β | $P_{\infty}, \mathrm{cm}^{3}$ | <i>MR _D</i> ,cm ³ | Com- pound | α | β | $P_{\infty}, \mathrm{cm}^3$ | MR_D , cm ³ |
|---------------|-------|-------|-------------------------------|---|---------------|-------|------|-----------------------------|--------------------------|
| <u> </u> | | | | | | | | | |
| I | 7,8 | 0,53 | 170,48 | 61,57 | XIII | 12,49 | 0,54 | 242,46 | 66,44 |
| П | 12,1 | 0,62 | 231,22 | 61,57 | XIV | 7,45 | 0,83 | 167,23 | 66,44 |
| III | 15,53 | 0,63 | 280,43 | 61,57 | xv | 5,97 | 0,86 | 144,58 | 66,44 |
| IV | 8, 89 | 0, 56 | 189, 59 | 66, 19 | XVI | 30,39 | 0,82 | 516,91 | 64,18 |
| V | 15,78 | 0,58 | 290,17 | 66,19 | XVII | 7,18 | 0,62 | 155,09 | 53,68 |
| VI | 20,6 | 0,59 | 357,79 | 66,19 | XVIII | 15,31 | 0,62 | 273,93 | 53,68 |
| VII | 10,2 | 0,66 | 208,66 | 67,83 | XIX | 6,86 | 0,72 | 152,18 | 59,61 |
| VIII | 18,85 | 0,74 | 335,97 | 67,83 | XX | 14,50 | 0,77 | 262,94 | 59,61 |
| IX | 26,26 | 0,75 | 378,82 | 67,83 | XXI | 18,18 | 0,76 | 312,19 | 59,61 |
| x | 9,99 | 0,81 | 201,95 | 62,47 | XXII | 8,87 | 1,25 | 181,59 | 63,23 |
| XI | 7,00 | 0,65 | 175,84 | 62,47 | XXIII | 16,75 | 1,34 | 294,60 | 63,64 |
| XII | 6,73 | 0,75 | 153,33 | 62,47 | | | l | | |

TABLE 2. Results of Dipole Measurements *

* $\varepsilon_0 = 2.2725$; $\alpha_0 = 0.87368$; T = 298°; ε_0 is the dielectric constant of the solvent; P_{∞} is * complete polarization extrapolated to infinite dilution; MR = molecular refraction.



Fig. 1. The molecule of 1-(pyridy1-2)-3-pheny1propenone-1: a) syn-s-cis-form; b) anti-s-cisform.

on one (the syn-form) or on different (the anti-form) sides of the bond which links together the heterocyclic ring with the carbonyl group.

Comparison of the calculated values of μ for the syn- and anti-forms with the experimentally found values of μ for 1-(pyridyl-2)-3-aryl propinones-1 (I, IV, VII, X, XIII, and XVI) shows that in this case the anti-form is preferred. The negative value of the interaction moment observed for some ketones (I, VII, XVI), which represents the difference $\mu \exp - \mu$ calc. should presumably be attributed to the possible steric hindrances (see Fig. 1) which lead to a disruption of the coplanarity of the molecules.

For 1-(pyridy1-3-)-3-arylpropinones-1 (II, V, VII, XI, XIV), the existence for syn- and anti-conformations represents a statistical equilibrium, since the values found for μ do not differ appreciably from the half-sum of the calculated moments for the two forms. In the case of ketones representing derivatives of 4-pyridyl (III, VI, IX, XII, XV), the possibility of these existing in the syn- and anti-conformation is theoretically excluded, and the observed quite appreciably positive difference between the values of μ_{exp} and μ_{calc} (0.7-1.1 D) must be due basically to a conjugation effect.

Replacement of the phenyl series in the arylketones examined by 2-furyl, 2-thienyl and 2-selenienyl (XVII-XXIII) leads to the possibility of the appearance of two further coplanar conformational forms, owing to the fact that these five-membered heterocyclic radicals may in their turn be located in different ways on the plane in relation to the carbonyl group. However, taking into account the fact that it is doubtful whether substitution of aryl by a heterocycle would have any effect on the conformational position of the pyridine ring, we may draw the general conclusion from the data obtained that both forms (syn- and anti-) for furyl, thienyl, and selenienyl are possible in these compounds (XVII-XXIII). The same conclusion was reached in [2-4] from an investigation of analogous chalcones, in which instead of pyridyl the radical phenyl was employed. A consideration of the Brigleb-Stewart model for these ketones, in relation to the spacial effects, again indicates that it is not possible to arrive at preference for any of the forms. In addition to this, for the compound XIX it may be suggested that the thienyl is present in the cis-conformation in relation to the carbonyl group.

Attention should be paid to the fact that the dipole moments in the series of isomeric ketones containing electron-donor radicals (I, II, III, etc.) increase in the series of derivatives from 2-pyridyl to 3-pyridyl and 4-pyridyl. At the same time, in the series of isomeric pyridine aldehydes [7] and acetylpyridines [7-11], and also in the halogen-substituted pyridinic chalcones (X-XV), the reverse change of the dipole moments of the isomers is



Fig. 2. Relationship between the dipole moments of 1 - (pyridyl-2)-3 - arylpropinones - 1 and the σ -substitution constants.

observed: $\alpha > \beta > \gamma$. It is probable that this should be attributed to a difference in the conjugation effects for the compounds considered.

The introduction of electron-donor groups into the paraposition of the phenyl radical leads in all cases to an increase in μ (compounds I-III, IV-IX). Electron-acceptors (fluorine and chlorine) cause a reduction in μ (compounds XI, XII, XIV, XV), with the exception of ketones substituted by 2-pyridyl (X, XIII, XVI). The change in the values of the dipole moments under the influence of substituents, taking into account the intramolecular distances, gives a quite satisfactory correlation with the McDaniel and Brown σ -constants [16], from the formula composed by two of us in [6]:

$$\frac{\mu_{\rm R}-\mu_{\rm H}}{d_{\rm R}-d_{\rm H}}=\rho\sigma,$$

where μ_R is the dipole moment of the ketone possessing a substituent in the aromatic ring, μ_H the dipole moment of the ketone without the substituent, d_R the distance from the center of the aromatic nucleus to the center of charge of the substituent (selected from [17]), d_H the distance from the center of the aromatic nucleus to the hydrogen atom (2.48 Å), and ρ and σ are the constants of the Hammett equation. Figure 2 shows the correlation straight line for 1-(pyridyl-2)-3-arylpropinones-1, from which it is seen that this proceeds through the origin, and only the point for fluorine deviates from the correlation.

Table 1 also contains the value of μ calculated from the experimental data from the simplified Higashi equation [18]: $\mu = K\sqrt{\alpha}$. The value of K was taken as 0.828 [19]. The results obtained are in good agreement with calculations based upon the usual formulas [20]. By means of the equation given it is possible to calculate values of μ rapidly and with sufficient accuracy.

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