

**<sup>1</sup>H-NMR STUDY OF TRANSFER OF SUBSTITUENT EFFECTS  
IN 2-DIBENZOYLMETHYLENE-3-ETHYLBENZOTHIAZOLINES  
AND -SELENAZOLINES\***

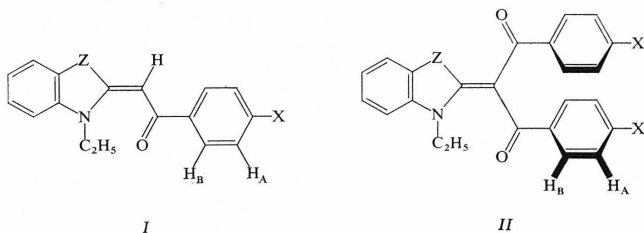
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<sup>1</sup>H-NMR spectra of *p*-substituted 2-mono- and -dibenzoylmethylene-3-ethylbenzothiazolines and -selenazolines have been measured. Conformation of carbonyl groups of the dibenzoyl derivatives is *s-cis*, *s-cis* with respect to the exocyclic double bond, and the both benzene rings are twisted out of the plane of the molecule. Effect of *para*-substituents in the benzoyl group on internal chemical shift of the ethyl group bound to heterocyclic nitrogen atom in the dibenzoyl derivatives is contrary to that in the planar monobenzoyl derivatives.

Recently we proved by means of SCF MO calculations and <sup>1</sup>H-NMR spectra<sup>1</sup> that diformylmethylene derivatives of benzthiazoline and benzoselenazoline are present predominantly in the energetically most favourable *s-cis*, *s-cis* conformation of the β-dicarbonyl grouping. If the dibenzoyl derivatives *II* exist in the same conformation, then, due to steric reasons, the benzene rings must be twisted out of the plane of the molecule, which results in weakening of conjugation of aromatic ring with carbonyl group. The aim of the present work was to prove this conformation and study



Z = S, Se

X = NH<sub>2</sub>, OCH<sub>3</sub>, H, I, NO<sub>2</sub>

\* Part III in the series Spectroscopic Investigations of β-Dicarbonyl Compounds; Part II: J. Mol. Struct. 27, 267 (1975).

transmission of substituent effects through such system with disturbed conjugation using  $^1\text{H-NMR}$  spectra. A set of monobenzoyl derivatives *I* was chosen for comparison, since they can be expected to be planar and exhibit perfect conjugation.

## EXPERIMENTAL

The studied compounds were prepared by the procedure described earlier<sup>2</sup>. The newly prepared substances 2-(4-iodobenzoylmethylene)-3-ethylbenzosenazoline (m.p. 210.5–211.5°C, ligroin–benzene 1 : 1) and 2-bis(4-iodobenzoyl)methylene-3-ethylbenzosenazoline (m.p. 198.5 to 199.5°C, ligroin–benzene 1 : 1) were identified by elemental analysis and  $^1\text{H-NMR}$  spectra,

The  $^1\text{H-NMR}$  spectra were measured with a Tesla BS 487C (80 MHz) and a Bruker WP 80 (80 MHz) spectrometers in deuteriochloroform (0.03M solutions). Tetramethylsilane, which was used as internal standard, served for stabilization of field-frequency lock in the spectrometer Tesla (CW mod). The stabilization was carried out on deuterium atoms of the solvent when working with the pulse spectrometer WP 80 (FTNMR). The chemical shifts for protons in benzoyl group were calculated for AA'BB' system from the computed frequencies of spectral lines with digital differentiation corresponding to an accuracy of  $\pm 0.0005$  ppm (spectral width 5 Hz/cm). Only in the case of the hydrogen atoms  $\text{H}_A$  and  $\text{H}_B$  ( $X = \text{H}$ ) the chemical shifts were estimated from spectrum with the accuracy of  $\pm 0.01$  ppm.

## RESULTS AND DISCUSSION

First of all, planarity of monobenzoyl derivatives was confirmed. Internal chemical shift  $\Delta_{\text{Et}}$  of ethyl group depends on electronegativity of the atom to which the ethyl group is bound<sup>3</sup>. Therefore, it is possible to determine from this shift whether and how much a substitution in the benzene ring will affect electron density in the heterocyclic part of the molecule. It was found that in the series of derivatives  $\Delta_{\text{Et}}$  gradually increases from amino to nitro derivative in accord with decrease of electron density at the heterocyclic nitrogen atom by the substituent effect. The  $\Delta_{\text{Et}}$  values can be correlated well with the Hammett  $\sigma_p$  constants<sup>4</sup>; slope of this correlation is positive, which indicates conjugation in the whole system (Table I). The same was confirmed also by a bathochromic shift (by 34 nm) in UV spectrum of the *para*-derivative as compared with the unsubstituted analogue<sup>2</sup>.

Conjugation of benzene ring with the adjacent carbonyl group can be proved by chemical shifts of proton signals of the *para*-disubstituted benzene ring. For this purpose it is necessary to estimate how much the rest of the molecule, *i.e.* 3-ethyl-2-benzthiazolinemethylenecarbonyl ( $\text{Y}_1$ ), contributes to shielding of the aromatic protons. This contribution, denoted as increment  $a_j$ , expresses the change of chemical shift of signals of individual hydrogen atoms caused by introduction of a substituent in the benzene ring as compared with the chemical shift of unsubstituted benzene<sup>5</sup> (*i.e.* 7.27 ppm). The influence of the substituent  $\text{Y}_1$  on individual *ortho* and *meta* positions can be obtained from chemical shifts of *para*-substituted monobenzoyl derivatives *I* ( $X = \text{NH}_2, \text{OCH}_3, \text{H}, \text{I}, \text{NO}_2$ ). For these substituents the increments  $a_i$

are known<sup>5</sup>. If the measured chemical shifts of the protons  $H_A$  and  $H_B$  are plotted against the corresponding increments  $a_i$ , two straight line are obtained, each of them being described by Eq. (1) (ref.<sup>6</sup>).

$$\delta = (7.27 + a_j) + a_i(1 + Ka_j). \quad (1)$$

The found values (Table II;  $a_j = a - 7.27$ ) are very close to the known values for methoxycarbonyl group<sup>5</sup>, which clearly indicates the influence of substituent  $Y_1$  on signals of the aromatic protons, the effect being similar to that of  $\text{COOCH}_3$  group *i.e.* conjugation and diamagnetic anisotropy of carbonyl group in planar arrangement.

The problem of configuration of the double bond in the monobenzoyl derivatives *I* remains to be solved. Only one isomer seems to be formed in the reaction, the other was never isolated neither was his presence proved in reaction mixture. Considerable difference between chemical shifts of signals of olefinic protons in thiazoles *I* ( $Z = S$ ) and selenazoles *I* ( $Z = Se$ ) seem to indicate that sulphur and selenium atoms are on the same side of the double bond as the olefinic proton. We intend to deal with this problem later.

The dibenzoyl derivatives *II* can assume (as in the case of the diformylmethylene derivatives<sup>1</sup>) four conformations differing in mutual orientation of carbonyl groups

TABLE I

Chemical Shifts<sup>a</sup> of Proton Signals of Monobenzoyl Derivatives *I* in  $\delta$  (ppm) and Correlation<sup>b</sup> of  $\Delta_{E1}$  with  $\sigma_p$  Constants

Substituent	$\sigma_p$	$\delta_{\text{CH}=\text{}}$		$\delta_{\text{CH}_2}$		$\delta_{\text{CH}_3}$		$\Delta_{E1}$	
		S	Se	S	Se	S	Se	S	Se
NH <sub>2</sub>	-0.660	6.511	—	4.168	—	1.435	—	2.733	—
OCH <sub>3</sub>	-0.268	6.536	6.845	4.191	4.247	1.447	1.463	2.744	2.784
H	0	6.580	6.891	4.213	4.272	1.458	1.474	2.755	2.798
I	0.180	6.509	6.814	4.209	4.264	1.451	1.467	2.758	2.797
NO <sub>2</sub>	0.778	6.568	6.871	4.271	4.322	1.490	1.501	2.781	2.821
<i>b</i>	—	—	—	—	—	—	—	0.033	0.034
<i>a</i>	—	—	—	—	—	—	—	2.754	2.794
<i>r</i>	—	—	—	—	—	—	—	0.9968	0.9810
<i>P</i>	—	—	—	—	—	—	—	99.9	98.0

<sup>a</sup> 0.03M solution in  $\text{CDCl}_3$ ; tetramethylsilane as internal standard; <sup>b</sup>  $\Delta_{E1} = a + b\sigma_p$ ; *r* correlation coefficient; *P* correlation significance in %.

and the exocyclic double bond. Conformation *s-trans*, *s-trans* (TT) can be excluded immediately. This conformation is strongly destabilized by dipole-dipole repulsion of parallel carbonyl groups; besides that such orientation would result in different chemical shifts of proton signals of the two benzene rings due to different heteroatoms in close vicinity of these rings. However, spectra of all the studied compounds *II* show that the both benzoyl substituents are "equivalent",\* and signals of the corresponding protons are isochronous.

If a random equivalence due to rapid equilibration of the *s-cis*, *s-trans* (CT) and *s-trans*, *s-cis* (TC) conformations were operating, then it would mean that one benzene ring would come close to further carbonyl group for a certain time and its protons would be considerably deshielded. However, the reverse is true, which supports the *s-cis*, *s-cis* conformation (CC). Signals of aromatic protons of the dibenzoyl derivatives *II* are shifted upfield ( $\Delta_B = -0.55$  and  $\Delta_A = -0.33$  ppm) due to prevented conjugation and lowered effect of diamagnetic anisotropy of carbonyl group, and due also to mutual shielding by ring currents in the neighbouring parallel benzene ring (similar situation as that in 1,8-diphenyl-naphthalene<sup>7</sup>,  $\Delta\delta = -0.53$  ppm).

TABLE II

Chemical Shifts<sup>a</sup> of Proton Signals of Monobenzoyl Derivatives *I* in  $\delta$  (ppm) and Correlation<sup>b</sup> with  $a_i$  Increments

Substituent	$a_{ortho}$	$\delta_A$		$a_{meta}$	$\delta_B$	
		S	Se		S	Se
NH <sub>2</sub>	-0.75	6.695	—	-0.25	7.871	—
OCH <sub>3</sub>	-0.48	6.953	6.964	-0.09	7.986	8.011
H	0	7.44	7.45	0	8.03	8.05
I	0.39	7.721	7.746	-0.21	7.789	7.800
NO <sub>2</sub>	0.95	8.128	8.152	0.26	8.288	8.298
<i>b</i>	—	0.846	0.823	—	0.908	1.006
<i>a</i>	—	7.369	7.396	—	8.044	8.049
<i>r</i>	—	0.9965	0.9962	—	0.9718	0.9825
<i>P</i>	—	99.9	99.9	—	99.5	98.0

See Table I; <sup>b</sup>  $\delta = a + ba_i$ ; *r* correlation coefficient; *P* correlation significance in %.

\* In fact, the two benzoyl groups are not equivalent even in *s-cis*, *s-cis* conformation due to different heteroatoms in the five-membered ring. Of course, in this conformation the heteroatoms are removed enough from the benzoyl protons (<0.5 nm), so that spatial influence on their shielding can be neglected<sup>1</sup>.

Chemical shift of the proton  $H_A$  (Table IV) is, due to this shielding, lower than in unsubstituted benzene. Therefore the dibenzoyl derivatives *II* exist predominantly in CC conformation having the two benzene rings mutually parallel but twisted (on the bond connecting benzene ring and carbonyl groups) from the plane of the molecule for steric reasons. The same result was obtained also from study of EPR spectra<sup>8</sup> of polarographically reduced nitro derivatives *II* ( $X = NO_2$ ); from this study it was possible to obtain also approximate angle of deviation  $57^\circ$ .

Hindered conjugation between the aromatic ring and heterocyclic part of the molecule makes itself felt also in the internal chemical shift of the ethyl group bonded to nitrogen. Lowered transmission of substituent effects results in decrease of slope of the correlation between  $\Delta_{Et}$  and  $\sigma_p$  constants. This slope decrease depends on cosine of the deviation angle, which was found in a study<sup>9</sup> of 4-ethyl-4'-substituted benzylideneanilines. For the case of the dibenzoyl derivatives *II* this means that for the angle about  $57^\circ$  the slope should be approximately half that of correlation in the monobenzoyl derivatives *I* series. If the both benzene rings were perpendicular to the heteroaromatic part of the molecule, then the transmission of the effect would be zero. In fact, however, nitro group shifts  $\Delta_{Et}$  towards lower values, whereas methoxy group shifts  $\Delta_{Et}$  to higher values, hence the correlation slope is negative (Table III). Therefore,  $\Delta_{Et}$  of the derivatives *II* is influenced by some other way — not only by the electronic effect of the substituent X.

TABLE III

Chemical Shifts<sup>a</sup> of Proton Signals of Dibenzoyl Derivatives *II* in  $\delta$  (ppm) and Correlation<sup>b</sup> of  $\Delta_{Et}$  with  $\sigma_p$  Constants

Substituent	$\sigma_p$	$\delta_{CH_2}$		$\delta_{CH_3}$		$\Delta_{Et}$	
		S	Se	S	Se	S	Se
OCH <sub>3</sub>	-0.268	4.380	4.089	1.529	1.197	2.851	2.892
H	0	4.073	4.089	1.245	1.236	2.828	2.953
I	0.180	4.044	4.047	1.233	1.219	2.811	2.828
NO <sub>2</sub>	0.778	4.123	4.084	1.314	1.275	2.809	2.809
<i>b</i>	—	—	—	—	—	-0.037	-0.075
<i>a</i>	—	—	—	—	—	2.831	2.858
<i>r</i>	—	—	—	—	—	-0.8400	-0.9222
<i>P</i>	—	—	—	—	—	80	80

<sup>a, b</sup> See Table I.

2-(Diacylmethylene)-1,3-dialkylimidazolidines were reported<sup>10</sup> to release their steric strain by twisting of the molecule about the exocyclic double bond. The dibenzoyl derivatives *II* have similar conformation, and, therefore, an analogous deformation of molecule can be expected with these compounds. Large internal chemical shift of ethyl group in these derivatives is due, to a certain extent, to the fact that hydrogen atoms of the CH<sub>2</sub> group lie near the plane of the carbonyl group<sup>1</sup> and, hence, are deshielded by diamagnetic anisotropy of the double bond. Decrease in  $\Delta_{Et}$  for the nitro derivatives *II* and increase in  $\Delta_{Et}$  for the methoxy derivatives *II* can thus be explained by change of this contribution to chemical shift. If nitro group lowers electron density at the exocyclic bond, it enables an easier and greater twisting of the molecule and, hence, a greater distance between CH<sub>2</sub> protons and C=O bond plane. On the contrary, increase of electron density at C=C bond by methoxy group contributes to coplanarity of this grouping and to increase of deshielding effect of diamagnetic anisotropy on CH<sub>2</sub> protons.

This hypothesis is confirmed also by results of correlation of chemical shifts of the protons B with  $a_{meta}$  increments (Table IV). The correlation slope is markedly different from unity, and the correlation coefficient is rather low, too. This finding, observed in other cases<sup>9,11</sup>, indicates a conformation change near the protons B caused by the substituent X.

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TABLE IV  
Chemical Shifts<sup>a</sup> of Proton Signals of Dibenzoyl Derivatives *II* in  $\delta$  (ppm) and Correlation<sup>b</sup> with  $a_i$  Increments

Substituent	$a_{ortho}$	$\delta_A$		$a_{meta}$	$\delta_B$	
		S	Se		S	Se
OCH <sub>3</sub>	-0.48	6.683	6.702	-0.09	7.581	7.585
H	0	7.17	7.18	0	7.53	7.53
I	0.39	7.550	7.563	-0.21	7.240	7.249
NO <sub>2</sub>	0.95	8.036	8.061	0.26	7.666	7.684
<i>b</i>	—	0.949	0.952	—	0.759	0.782
<i>a</i>	—	7.153	7.172	—	7.512	7.520
<i>r</i>	—	0.9993	0.9996	—	0.8192	0.8364
<i>P</i>	—	99.9	99.9	—	80	80

<sup>a, b</sup> See Table II.

## REFERENCES

1. Holík M., Skála V., Čiernik J.: *Chem. Zvesti* 29, 533 (1975).
2. Mistr A., Láznička V., Šimák B.: *This Journal* 38, 3616 (1973).
3. Cavanaugh J. R., Dailey B. P.: *J. Amer. Chem. Soc.* 77, 3977 (1955).
4. McDaniel D. H., Brown H. C.: *J. Org. Chem.* 23, 420 (1958).
5. Beeby J., Sternhell S., Hoffmann-Ostenhof T., Pretsch E., Simon W.: *Anal. Chem.* 45, 1571 (1973).
6. Holík M.: *Org. Magn. Resonance*, in press.
7. House H. O., Magin R. W., Thompson H. W.: *J. Org. Chem.* 28, 2403 (1963).
8. Komenda J., Huzlík J.: Unpublished results.
9. Holík M., Běluša J., Břicháček J.: *This Journal*, in press.
10. Sandström J., Wennerbeck I.: *Chem. Commun.* 1971, 1088.
11. Holík M., Potáček M., Švaříček J.: *This Journal*, in press.

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