Spectroscopic investigations of β-dicarbonyl compounds. I. The proton magnetic resonance and quantum chemical study of 2-diformylmethylene-3-ethylbenzothiazolines and benzoselenazolines

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From the p.m.r. spectra of 2-diformylmethylene-3-ethylbenzothiazoline, 2-diformylmethylene-3-ethylbenzoselenazoline, 2-diformylmethylene-3-ethyl-5-methoxybenzoselenazoline, and 2-diformylmethylene-3-ethyl-(1,2-d)-naphthothiazoline and from HMO and SCF MO calculations the conclusion was drawn on the dipolar structure of diformylmethylene derivatives and the *s-cis,s-cis* conformation of exocyclic C=C and carbonyl double bonds.

На основе измеренных ЯМР спектров 2-диформилметилен-3-этилбензотиазолина, 2-диформилметилен-3-этилбензоселеназолина, 2-диформилметилен-3-этил-5-метоксибензоселеназолина и 2-диформилметилен-3-этил-(1,2-d)-нафтотиазолина и МОХ и ССП МО рассчетов предполагается диполярная структура диформилметиленовых производных, а также *с-цис, с-цис* конформация эксоциклической связи C=C и карбонильных C=O связей.

Recently, 2-diformylmethylene-3-ethylbenzothiazoline *IIa* and 2-diformylmethylene-3-ethylbenzoselenazoline *IIb* were prepared from 2-methylbenzothiazole and 2-methylbenzoselenazole ethoiodides *Ia* and *Ib*, respectively [1]. The reaction was performed by formylation with fosgene in dimethylformamide followed by potassium carbonate hydrolysis. Using the same method, 2-diformylmethylene-3-ethyl-5-methoxybenzoselenazoline *IIc* and 2-diformylmethylene-3-ethyl-(1,2-d)-naphthothiazoline *IId* were prepared (Scheme 1).

Regarding the position of carbonyls with respect to the exocyclic double bond, theoretically, the nonenolizable β-dicarbonyl compounds *II* can exist in four conformations (Scheme 2). In this paper, quantum chemical calculations of the most favoured conformer confirmed by means of p.m.r. spectroscopy are presented.

Experimental

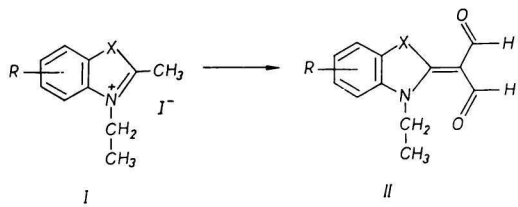
Preparations according to [1]:

2-Diformylmethylene-3-ethyl-5-methoxybenzoselenazoline *IIc*: yield 39%, m.p. 105–106°C (ethanol).

For $C_{13}H_{13}NO_3Se$ (310.21) calculated: 50.33% C, 4.22% H, 4.51% N; found: 50.12% C, 4.53% H, 4.86% N.

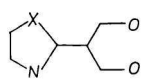
2-Diformylmethylene-3-ethyl-(1,2-d)-naphthothiazoline *IId*: yield 19%, m.p. 222–223°C (ethanol).

For $C_{16}H_{13}NO_2S$ (283.36) calculated: 67.82% C, 4.62% H, 4.94% N, 11.32% S; found: 68.08% C, 4.73% H, 4.70% N, 11.31% S.

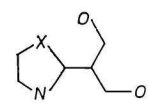


a) X = S, R = H;
b) X = Se, R = H;
c) X = Se, R = 5-CH_3O;
d) X = S, R = 4,5-benzo.

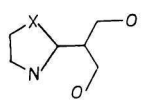
Scheme 1



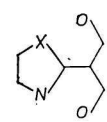
s-trans,s-trans (TT)
$E_\pi = -175.5963$ eV



s-cis,s-trans (CT)
$E_\pi = -175.8059$ eV



s-trans,s-cis (TC)
$E_\pi = -175.8194$ eV



s-cis,s-cis (CC)
$E_\pi = -175.9700$ eV

Scheme 2

Table 1

SCF parameters and resonance integrals*

Atom	Parameter (in eV) $-I$	A	Z	Bond	Resonance integral (in $\beta = -2.388$ eV)
C	11.42	0.58	3.25	C—C, C=C	1.0
O	13.80	2.20	3.95	C=O	1.0
N	27.50	9.20	2.67	C—N	0.8
X	20.00	9.16	3.25	C—X	0.7

* *The SCF MO program was elaborated by Mr J. Pancíř (Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague).*

Quantum chemical calculations

For SCF calculations of model structures (Scheme 2), simplified by neglecting the aromatic ring, we used parameters plotted in Table 1 and the following geometry: Heterocyclic ring was represented by a regular pentagon with bond length 1.4 A. The open-chain part of structures was defined by 120° bond angles and 1.4 A (C=C), 1.5 A (C—C), and 1.3 A (C=O) bond lengths. Orientation in the coordinate system was such one that the x axis was a prolongation of exocyclic C=C double bond and the origin was placed inside the heterocyclic ring in a 0.6 A distance from pentagon side perpendicular to the x axis. Variation of parameters and geometry did not show any substantial effect on either the order of energy levels or energy differences among them. HMO calculations of structure *II* (Scheme 3) were performed using the following empirical parameters: $h_N = 1.5$, $h_X = 2.0$, $h_O = 1.0$, $k_{CN} = k_{CX} = 0.8$, and $k_{CO} = 1.0$.

Proton magnetic resonance spectra

The p.m.r. spectra were recorded on Tesla BS 487C spectrometer (80 MHz) in deuteriochloroform (0.1 mole) using tetramethylsilane as an internal standard. Chemical shifts (Table 2) of aldehyde protons and ethyl group signals were determined by a stationary method using high quality audio generator, which was tuned manually until the top of signal was achieved. The frequency was read from frequency counter with an accuracy of ± 0.001 Hz. Chemical shift was then calculated as a mean of five measurements. Approximate ranges of aromatic multiplets were obtained from a precalibrated chart paper.

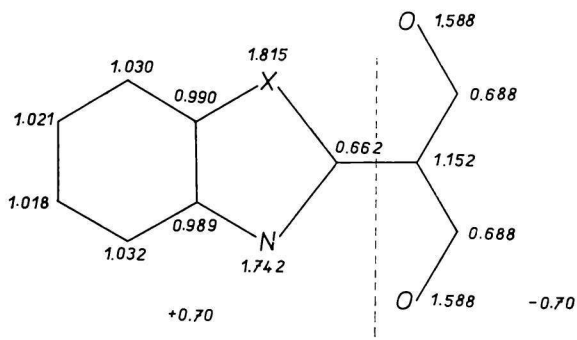
Results and discussion

SCF calculations of total π-electron energies (Scheme 2) clearly show the conformational preference of a CC arrangement. Energy difference between TT and CC conformers equals to 8.61 kcal mol^{-1} (1 eV = 23.03 kcal mol^{-1}) and, therefore, the TT conformation will be suppressed mainly owing to a dipole-dipole repulsion [2]. Also CT and TC conformers are destabilized by 3.78 and 3.47 kcal mol^{-1}, respectively, with respect to the CC arrangement.

The conformational preference for diformylmethylene derivatives *IIa—d* was confirmed experimentally by their p.m.r. spectra (Table 2).

Both aldehyde protons form one two-proton singlet, which does not change the shape in temperature range from −68 to +60°C. This fact suggests rather an "equivalency"* of both protons than their fast equilibration in CT and TC arrangements. The TT conformation is excluded due to a different environment of CHO protons. Furthermore, the chemical shift of aldehyde protons confirms the CC conformation. The proximity of another carbonyl in CT or TC arrangement would decrease chemical shift of the concerned CHO proton by an additional diamagnetic anisotropy contribution [3, 4].

Another interesting feature of the p.m.r. spectra of diformylmethylene derivatives *IIa—d* is a very low chemical shift of protons of CH_2 group from ethyl bonded to nitrogen. Extremely high values of internal chemical shift of ethyl group $\Delta_{CH_3\text{-}CH_2}$ calculated for our structures *IIa—d* may be partially attributed to the positive charge on nitrogen atom. From HMO quantum chemical calculation (Scheme 3) we have found not only that nitrogen possesses a partial positive charge (+0.258), but also that the molecule shows a dipolar character. The heteroaromatic part of molecule (to the left from dotted line in Scheme 3) is charged positively (+0.70) whereas along the β-dialdehyde chain a negative charge (−0.70) is delocalized.** However, a partial positive charge alone either on nitrogen or in the heteroaromatic part of molecule cannot explain such high values of $\Delta_{CH_3\text{-}CH_2}$ in *II*. The $\Delta_{CH_3\text{-}CH_2}$ value in 2-methylbenzothiazolium system was found to be lower (3.358) than in diformylmethylene derivatives *IIa—c* possessing similar heteroaromatic surroundings in spite of a higher calculated charge on nitrogen atom (+0.301).



Scheme 3

* As a matter of fact, these protons are nonequivalent also in CC conformation because of a different nature of N and X substituents. However, N and X are fairly distant from aldehyde protons and thus the contribution to their shielding is negligible.

** The same fact can be inferred from the HMO diagram of 2-dibenzoylmethylene-3-ethylbenzothiazoline [5].

Table 2

Chemical shifts in δ scale (p.p.m.)

Compound	CHO	Aromatic	CH_2	CH_3	$\Delta_{CH_3-CH_2}$
IIa	9.508	7.9–7.4	4.844	1.419	3.425
IIb	9.540	7.9–7.4	4.904	1.401	3.503
IIc	9.514	7.7–7.0	4.841	1.394	3.447
IId	9.555	8.5–7.6	5.016	1.170	3.846

Therefore, a conclusion has been drawn that in the deshielding of CH_2 group also a contribution of the neighbouring carbonyl must be taken into account which is possible only in TC and CC conformations. In *IId* derivative, due to the proximity of an additional aromatic ring to methylene hydrogen atoms, the aromatic ring still increases the deshielding of CH_2 group thus increasing the value of $\Delta_{CH_3-CH_2}$ to 3.846.

The deshielding of methylene group by carbonyl together with the before-mentioned "equivalency" of aldehyde protons confirms the conformational preference of CC arrangement in a full agreement with our SCF MO calculated prediction.

References

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