

## Quantum-chemical study of electronic properties of model spirooxazines

Victor M. Anisimov\*, Sergei M. Aldoshin

*Institute of Chemical Physics in Chernogolovka Russian Academy of Sciences, Chernogolovka, 142432, Russia*

Received 1 November 1996; accepted 5 February 1997

### Abstract

Model spirooxazines were studied via *ab initio* quantum-chemical calculations. An anomeric interaction between nitrogen lone pair and antibonding orbital of the C<sub>spiro</sub>–O bond has been considered by Hartree–Fock SCF level of theory with 3-21G basis set. The extent of the  $n_N-\sigma^*_{CO}$  interaction has been shown to depend on planarity of the nitrogen atom, being maximized with its planarity growth. Electronic properties and geometry parameters of model spirooxazines were considered by limited CI under 3-21G basis set. Excitation lengthens the C<sub>spiro</sub>–O bond and causes a significant polarization of total wave function, which results in increasing of the system dipole moment and transferring the electronic density from the O2 atom and the phenyl fragment onto the N13=C14 bond in the case of spirooxazine and onto the NO<sub>2</sub> group in the case of nitro-spirooxazine. Elongation of the C–O bond under excitation is due to the NO<sub>2</sub> interaction in spirooxazines. CI calculation of the excited singlet state of a model chromene does not show elongation of this bond. © 1997 Elsevier Science B.V.

**Keywords:** Model spirooxazines; Electronic properties; Spirooxazine; Ab initio; Anomeric interaction; Excited state

### 1. Introduction

Spiropyrans (SP) and spirooxazines (SO) are typical organic compounds exhibiting photochromism [1]. Upon ultraviolet irradiation the C<sub>spiro</sub>–O bond is broken to form the X-isomer which is then isomerized into a merocyanine form (Scheme 1).

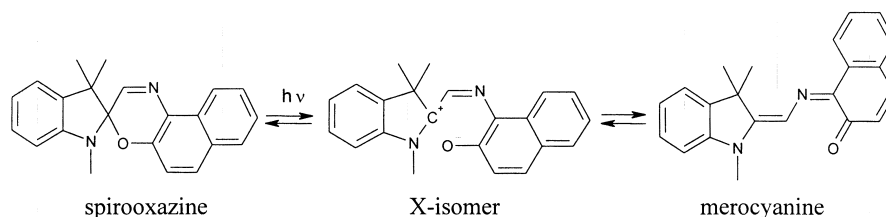
An electronic structure and geometry of SP and structural mechanism of the photochromism have been extensively studied by various authors (see review [2]). Recently photochromism of SO has been of the increased interest. Compared to SP, they show better fatigue resistance [3] which provides a possibility of their practical application. Thus,

detailed study of a mechanism of the bond cleavage and isomerization of the open form of SO is an important task.

Spectroscopic studies of spiropyrans show that the both first excited singlet and triplet can be involved in the conversion mechanism [4, 5]. In SP with the NO<sub>2</sub>-containing benzopyran moiety the bond rupture reaction occurs mainly via the triplet state, while in the NO<sub>2</sub>-free SP the photoreaction occurs via the singlet state.

This conversion has been extensively studied using various spectroscopic techniques [6, 7] and different quantum-chemical calculations [8, 9]. A femtosecond transient absorption spectroscopy study [6] of the spirooxazine revealed that the merocyanine is formed only from the first excited singlet.

\* Corresponding author.

Scheme 1. Breaking of the  $C_{\text{spiro}}\text{-O}$  bond in a spirooxazine under ultraviolet radiation.

Another interesting feature of SP and SO is an anomeric interaction between the nitrogen lone pair and an antibonding orbital of the  $C_{\text{spiro}}\text{-O}$  bond. There is much evidence [2, 10] that this interaction facilitates the ring opening reaction. The extent of this  $n_{\text{N}}\text{-}\sigma^*_{\text{CO}}$  interaction depends on the planarity of the nitrogen atom and is maximum when nitrogen lone pair is collinear to the  $C_{\text{spiro}}\text{-O}$  bond. This interaction results in shortening of the N–C bond and the corresponding elongation of the  $C_{\text{spiro}}\text{-O}$  bond. For example, a length of the C–O bond in six-membered oxygen-containing heterocycles is equal to 1.41–1.43 Å, while in 3,3-diphenylpyrano[5,6-f]quinoline it is 1.458 Å [11], and it is essentially elongated to 1.460–1.496 Å in SP [2, 10]. Thus, our objective was, using quantum-chemical calculations, to check whether this experimentally found elongation is due to the  $n_{\text{N}}\text{-}\sigma^*_{\text{CO}}$  interaction, and to study the role of this interaction in the geometry of the excited state.

## 2. Computational technique

All calculations were carried out non-empirically by GAMESS [12] program with 3-21G basis set on DEC Alpha 3000/600 computer. To reveal anomeric interaction, constraint geometry optimization of **1** has

been used, with a value of the dihedral angle  $W$  being changed step by step, while all the other coordinates were allowed to vary subject to energy minimization. The dihedral angles  $W$  were used for controlling the N3 atom planarity. Optimized geometries of **1** are summarized in Tables 1 and 2 with constraint parameter  $W_1(\text{C1-N3-C4-C5})$  and  $W_2(\text{H7-N3-C4-C5})$ , respectively. To check out planarity of N3 in each table we used a sum of the N3 atom valence angles,  $\Sigma(\text{N3}) = \{\text{C1-N3-C4} + \text{C4-N3-H7} + \text{C1-N3-H7}\}$ , and a dihedral angle  $W_{\text{pyr}}(\text{C4-N3-C6-C1})$ , which determines a degree of the pyran cycle bending.

The ground state ( $S_0$ ), the first ( $S_1$ ) and the second ( $S_2$ ) excited singlet states of **2**, **3** and **4** were computed under configuration interaction (CI) with a 3-21G basis set and frozen core approximation applied. Active space was constructed from three double occupied MOs, two independent MOs with alpha and beta spin, and three virtual molecular orbitals. Only the first-order excitations were considered. Thus we had 1764 configuration state functions (CSF) included in each CI calculation. Because of the program limitations, only partial geometry optimizations were carried out; all the rest of the parameters were kept from full geometry optimizations under single determinant Hartree–Fock SCF calculations with the same basis set.

Table 1  
Constraint optimization of **1** with fixed values of the  $W_1$  parameter

Parameter	$W_1 = 159.0^\circ$	$W_1 = 164.0^\circ$	$W_1 = 169.2^{\circ*}$	$W_1 = 174.0^\circ$
$W_{\text{pyr}}(\text{C4-N3-C6-C1}),^\circ$	155.1	158.5	162.5	166.8
$\Sigma(\text{N3}),^\circ$	353.4	355.2	357.0	358.5
C1–O2	1.4542	1.4554	1.4563	1.4566
C1–N3	1.4457	1.4442	1.4430	1.4420

\* Indicates equilibrium geometry.

Table 2  
Constraint optimization of **1** with fixed values of the  $W_2$  parameter

Parameter	$W_2 = 14.0^\circ$	$W_2 = 8.7^\circ$ *	$W_2 = 4.0^\circ$
$W_{\text{pyr}}(\text{C4-N3-C6-C1}),^\circ$	161.3	162.5	163.6
$\Sigma(\text{N3}),^\circ$	354.0	357.0	358.3
C1–O2	1.4560	1.4563	1.4566
C1–N3	1.4453	1.4430	1.4414

\* Indicates equilibrium geometry.

Table 3  
MOPAC 93 [13] calculation of  $\text{NH}_3$  molecule with different planarity of N atom

$n\text{LP-N-H}$ angle ( $^\circ$ ) <sup>a</sup>	$\Delta H$ (kcal mol <sup>-1</sup> )	Energy of HOMO (eV)	S(N) <sup>b</sup>	$P_z(\text{N})$ <sup>b</sup>	S(H) <sup>b</sup>
120.0	-1.02	-11.439	0.42	-0.83	-0.21
115.0	-5.91	-10.911	0.38	-0.87	-0.19
109.9 <sup>c</sup>	-7.29	-10.418	0.32	-0.91	-0.16
105.0	-6.51	-10.041	0.25	-0.94	-0.12
100.0	-4.91	-9.769	0.17	-0.97	-0.08
95.0	-3.56	-9.615	0.09	-0.99	-0.04
90.0	-3.05	-9.566	0.00	-1.00	0.00

<sup>a</sup>  $n\text{LP}$  is normal vector of nitrogen lone pair.

<sup>b</sup> Atomic orbital coefficients in HOMO.

<sup>c</sup> Equilibrium geometry.

### 3. Results and discussion

#### 3.1. Anomeric interaction

We have studied the efficiency of the anomeric interaction between the nitrogen lone pair and the antibonding orbital of the  $\text{C}_{\text{spiro}}\text{-O}$  bond by varying the planarity of the N3 atom. We suppose that an increase of the nitrogen planarity causes a rise of its lone pair energy and a decrease of an energy gap between the  $n(\text{N3})$  and  $\sigma^*(\text{C1-O2})$  orbitals, making their interaction stronger. In case of the anomeric interaction this will be followed by shortening of

C1–N3 and lengthening of C1–O2 bonds. Another behaviour of the length of these bonds depending the N3 planarity would disprove our supposition. To study the problem we used a model spirooxazine **1**.

According to  $W_{\text{pyr}}$  and  $\Sigma(\text{N2})$  values from Table 1 and 2, planarity of N3 increases from left to right. The C1–N3 and C1–O2 bonds are shortened and elongated, respectively. These results confirm that an increase of the N3 planarity leads to the increase of the anomeric interaction.

It can be supposed that changes of the anomeric interaction we have found are due rather to changes of the mutual orientation of the lone pair and antibonding orbital of the C–O bond than to the planarity changes of the N3 atom. Actually, it is very difficult to

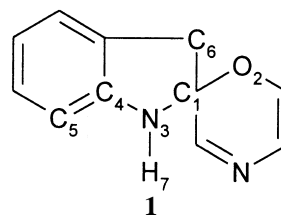
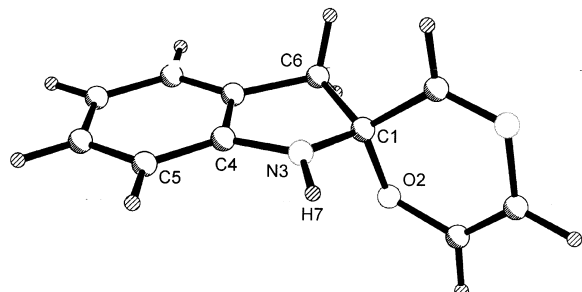


Table 4  
Results of CI calculation of **2**

$S_0$			$S_1$			$S_2^*$		
CSF	Coeff.	Population	CSF	Coeff.	Population	CSF	Coeff.	Population
15	0.9694	22220000	12	0.7651	12221000	5	0.8859	22121000
365	-0.1076	22200020	14	0.4136	22211000	9	-0.1889	21221000
1310	-0.0845	20220200	53	0.3600	12220001	522	-0.2230	21220100
<i>Total energy (hartree)</i>								
-641.56420991			-641.34348432			-641.32799545		
<i>Dipole moment D</i>								
X	-1.0405		-2.0806			-0.8136		
Y	-0.9557		-1.5909			-0.6087		
Z	-0.4517		0.0654			-3.4873		
Total	1.4833		2.6200			3.6323		

\* Expected photochemically active excited singlet state.

determine theoretically orientation of a normal vector of the nitrogen lone pair in the asymmetric environment to check out this hypothesis. Nevertheless, we suppose this effect to be insignificant. A simple example demonstrates how planarization raises an energy of the lone pair. Table 3 shows results of semi-empirical [13] calculation of the  $\text{NH}_3$  molecule with  $C_{3V}$  symmetry. In the planar structure of the  $\text{NH}_3$  molecule HOMO ( $n\text{LP}-\text{N}-\text{H} = 90^\circ$ ) is a pure nitrogen lone pair. Thus the HOMO energy has a linear dependence on the nitrogen atom planarity. This proves that the N3 lone pair energy in **1** will depend on planarity of this atom.

Table 5  
Results of CI calculation of **3**

$S_0$			$S_1^*$			$S_2$		
CSF	Coeff.	Population	CSF	Coeff.	Population	CSF	Coeff.	Population
15	0.9735	22220000	5	0.8976	22121000	9	0.6251	21221000
105	-0.1253	22200002	494	-0.1521	22021100	125	0.1667	22120010
1310	-0.0710	20220200	522	-0.2690	21220100	510	0.6121	22120100
<i>Total energy (hartree)</i>								
-805.03486598			-804.80993183			-804.80125624		
<i>Dipole moment, D</i>								
X	-6.4958		-13.4786			-9.1303		
Y	-2.8244		-5.4002			-3.6994		
Z	1.7427		5.8062			2.2941		
Total	7.2945		15.6380			10.1149		

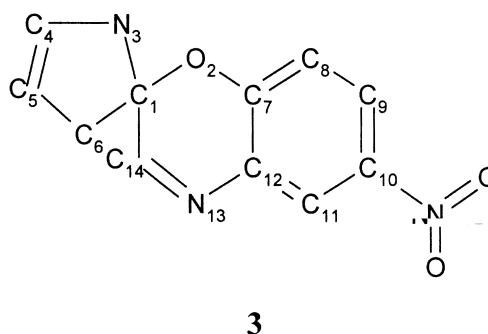
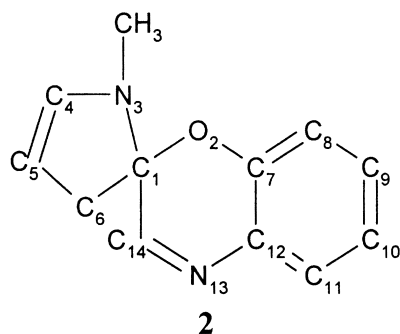
\* Expected photochemically active excited singlet state.

### 3.2. Properties of excited singlet states

Structure of the photochromic compounds has been extensively studied by X-ray diffraction experiments [2]. Less is known about the nature of their excited states.

In this section an influence of  $n_{\text{N}}-\sigma_{\text{CO}}^*$  interaction on the length of  $C_{\text{spiro}}-\text{O}$  bond in the excited state of model spirooxazines **2** and **3** has been considered.

To establish the nature of the lowest excited singlet states and to reproduce their spins correctly CI was imposed. Results of these calculations are shown in Tables 4 and 5. To fit in our limited computer resources we had to use limited CI with 3-21G basis



set. Thus the results presented are assumed to be qualitative.

Two first excited singlet states of **2** and **3** were computed. We assume that limited CI may not correctly reproduce a sequence of the excited states, which does not allow us to discuss a difference between the first and second excited states. So we are focusing on determining a photochemically active excited singlet state (PAES) that leads to the opened merocyanine form. To determine it we relied on assumption that excitation should weaken the C<sub>spiro</sub>–O bond which will be broken later in the way of transforming the molecule into a merocyanine form. The states in Tables 4 and 5, marked by asterisk, confirm this criterion. Nevertheless we list both excited singlet states of **2** and **3** in the Tables 4 and 5, respectively, to let a reader make his own choice.

From the total 1764 considered CSFs only limited number of the configuration states have large weighting factors. Tables 4 and 5 list only first three CSFs with the greatest coefficients. It is well known from

spectroscopic experiments [14] that in spiropyrans electronic density transfers from an oxygen atom onto vacant molecular orbitals under photoexcitation and formation of PAES. Assuming close similarity in behaviour of spiropyrans and spirooxazines we should examine those MOs of ground states of **2** and **3** where the oxygen atom has significant atomic orbital coefficients. From our calculations, HOMO does not have considerable coefficients on the oxygen atom, all such orbitals lie lower, they are HOMO-1, HOMO-3, for example, and so on. This explains why HOMO does not play a significant role in the formation of the PAES and testifies that there is a multiconfigurational nature of the PAES, because excitation proceeds from deep MOs of **2** and **3**. Population of those MOs included in CI are given in the Tables 4 and 5; they show that HOMO-1 (CSF 5) plays the most important role in formation of the both  $S_2$  of **2** and  $S_1$  of **3**.

Generally, a single configuration excited singlet state is constructed only from HOMO-LUMO excitations, but as follows from our calculations, the studied

Table 6  
Optimized geometry of **2** and **3**

Bond	<b>2</b>			<b>3</b>		
	$S_0$	$S_1$	$S_2$	$S_0$	$S_1$	$S_2$
C1–O2	1.4530	1.4463	1.4603	1.4629	1.4660	1.4628
C1–N3	1.4519	1.4514	1.4556	1.4435	1.4413	1.4432
C1–C14	1.5075	1.4960	1.4894	1.5075	1.5070	1.5000
O2–C7	1.3746	1.3979	1.3604	1.3595	1.3565	1.3544
N3–C4	1.4131	1.4197	1.4167	1.4152	1.4180	1.4176
C4=C5	1.3228	1.3249	1.3241	1.3231	1.3241	1.3242
C5–C6	1.5217	1.5214	1.5196	1.5226	1.5240	1.5240
C7–C12	1.3834	1.3995	1.4192	1.3870	1.4186	1.4001
C9–C10	1.3886	1.4047	1.4244	1.3832	1.4148	1.3964
C12–N13	1.4189	1.4007	1.3800	1.4153	1.3914	1.3962
N13=C14	1.2608	1.2814	1.2889	1.2607	1.2795	1.2743

Table 7  
Atomic electronic densities on **2** and **3**

Atom	<b>2</b>			<b>3</b>		
	$S_0$	$S_1$	$S_2$	$S_0$	$S_1$	$S_2$
O2	-0.75	-0.69	-0.65	-0.75	-0.68	-0.66
N13	-0.65	-0.52	-0.76	-0.65	-0.58	-0.66
C14	0.18	-0.14	-0.01	0.18	0.20	0.09
C1	0.42	0.48	0.42	0.40	0.40	0.41
N3	-0.79	-0.71	-0.78	-0.81	-0.80	-0.80
C5	-0.34	-0.30	-0.34	-0.32	-0.31	-0.31
N(NO <sub>2</sub> )	—	—	—	0.17	-0.02	0.09
O(NO <sub>2</sub> )	—	—	—	-0.39	-0.50	-0.43
C7	0.42	0.35	0.51	0.46	0.41	0.44
C8	-0.25	-0.23	-0.24	-0.25	-0.23	-0.16
C9	-0.24	-0.30	-0.34	-0.18	-0.13	-0.31
C10	-0.26	-0.23	-0.07	0.26	0.36	0.41
C11	-0.21	-0.26	-0.28	-0.16	-0.22	-0.13
C12	0.19	0.22	0.24	0.19	0.33	0.18
<i>Charge transfer by fragment from ground state to excited one</i>						
O2	0	0.06	0.10	0	0.07	0.08
N13=C14	0	-0.19	-0.29	0	0.09	-0.09
C1,N3,C5	0	0.19	0.01	0	0.02	0.03
NO <sub>2</sub>	—	—	—	0	-0.42	-0.16
Ph	0	-0.10	0.17	0	0.21	0.12

systems (**2** and **3**) and probably spirooxazines are exclusions from this very simple rule. In other words one can state an important role of electronic correlation for correct prediction of electronic properties and geometries of spirooxazines.

Optimized geometries of **2** and **3** are given in Table 6. Excitation results in significant geometry changes. As will be shown later, this is due to essential polarisation of the total wave function and charge redistribution. The most important geometry changes are related to the C1, O2, N13, C14 atoms and phenyl fragment.

The C1–O2 bond is shortened in  $S_1$  and elongated in  $S_2$  state of **2** (Table 6). We suppose the  $S_2$  state is the PAES for **2** where cleavage of the C1–O2 bond takes place. We assume that the more precise CI can reorder the states and bring this  $S_2$  to be the first excited singlet state for **2**.

It is interesting to note that excitation lengthens the N13=C14 bond both in **2** and **3**, populating its vacant antibonding orbital. Later we will show that electronic density is transferring on this bond in the excited state. Elongation of the C1–O2 and N13=C14 bonds and

shortening of the C1–N3 one take place in  $S_1$  state of **3** and here this effect is more evident than that of  $S_2$ .

Significant elongation of the C7–C12 and C9–C10 bonds in  $S_1$  of **3** and  $S_2$  of **2** shows an important role of the phenyl fragment in polarisation of total wave function under excitation. The maximum elongation of these bonds takes place in  $S_1$  of **3** and  $S_2$  of **2** again, that confirms the special nature of these states.

Electronic densities and charge redistribution in  $S_0$ ,  $S_1$  and  $S_2$  of **2** and **3** are shown in Table 7. They demonstrate that electronic density leaves the O2 atom in  $S_2$  (**2**) and  $S_1$  (**3**). The N13=C14 bond is a single acceptor of electronic density in  $S_2$  (**2**). All the density transfers onto NO<sub>2</sub> group in  $S_1$  (**3**), since this group is a very strong acceptor. The N3 atom does not change its electronic population significantly in both molecules. As a non-trivial result, we have found that the phenyl group loses density under excitation to a greater extent than the O2 atom in  $S_2$  (**2**) and  $S_1$  (**3**). It is possible because the phenyl fragment has six carbon atoms versus one oxygen atom.

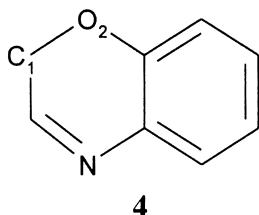
Table 8  
Results of CI calculation of **4**

$S_0$			$S_1$			$S_2$		
CSF	Coeff.	Population	CSF	Coeff.	Population	CSF	Coeff.	Population
15	0.966	22220000	9	0.863	21221000	5	-0.362	22121000
140	0.073	12211010	137	0.395	21220010	14	0.784	22211000
1284	-0.085	22020200	522	0.122	21220100	530	-0.270	22210100
<i>Total energy (hartree)</i>								
-433.91098660			-433.69110068			-433.68942629		
<i>Dipole moment, D</i>								
X	-0.451		-0.807			1.842		
Y	0.875		0.477			1.917		
Z	0.000		0.000			0.000		
Total	0.984		0.938			2.659		
<i>Bond length</i>								
C1–O2	1.4469		1.4412			1.4461		
C=N	1.2619		1.2810			1.2883		
<i>Charge transfer by fragment from ground state to excited one</i>								
O2	0		0.084			0.029		
C=N	0		-0.075			-0.230		
Ph	0		-0.061			0.087		

From the standpoint of polarization, it is interesting to consider the value of dipole moments in excited states (Tables 1 and 2). As one can see, excitation increases a value of total dipole moment of the molecules. The maximum dipole moment is for  $S_2$  (**2**) and  $S_1$  (**3**) which we assume to be the PAES. The value of dipole moment of  $S_1$  (**3**) is probably overestimated, although it should be greater than that of  $S_2$  (**2**).

### 3.3. Chromene

As mentioned above, the length of the C–O bond in spiroopyrans and spirooxazines is elongated in their ground state owing to anomeric interaction. A model chromene **4** does not have such an interaction.



In this context, it would be interesting to compare the length of the C–O bond in the excited state of **2**, **3** and **4**. Results of CI calculations of **4** are summarized in Table 8. Two first excited states of **4** were computed.

The length of the C1–O2 bond in ground state of **2**, **3** and **4** is 1.4530, 1.4629 and 1.4469, respectively (Tables 6, and 8). Thus the role of anomeric interaction in elongation of the C–O bond in the ground state of **2** and **3** is undoubted. In the excited states  $S_2$  (**2**) and  $S_1$  (**3**) this bond is elongated, compared to the ground state. Shortening of the C–O bond have been found in both excited states  $S_1$  and  $S_2$  of **4** in contrast to spirooxazines, which confirms an assumption about important role of  $n_N-\sigma^*_{CO}$  interaction for the value of the C–O bond in an excited state.

## 4. Conclusions

Model spirooxazines were studied via *ab initio* quantum-chemical calculations. These results demonstrate that anomeric interaction between the nitrogen

lone pair and the antibonding orbital of C<sub>spiro</sub>–O bond plays important role in elongation of the C–O bond both in the ground state and the excited one. It is very important to use CI for correct reproduction of an excited singlet state of spirooxazines because of its multiconfigurational nature. Excitation results in increasing of a total dipole moment of the system. Upon excitation electronic density transfers from the O7 atom and phenyl fragment onto N13=C14 bond in the case of spirooxazine **2** and onto the NO<sub>2</sub> group in the case of nitro-spirooxazine **3**.

### Acknowledgements

The authors are grateful to the Russian Foundation for Basic Research, grant number 96-03-32046, and to the International Science Foundation, grant number IFN000 for support of these investigations.

### References

- [1] R.C. Bertelson, in: G.H. Brown (Ed.), *Techniques of Chemistry*, vol. 3, Photochromism, Wiley-Interscience, New York, 1971.
- [2] S.M. Aldoshin, *Russian Chemical Reviews*, 59 (1990) 663.
- [3] U.W. Grummt, M. Reichenbacher, R. Paetzold, *Tetrahedron Letters* 22 (1981) 3945.
- [4] S.A. Krysanov, M.V. Alfimov, *Chemical Physics Letters* 91 (1982) 77.
- [5] Y. Kalisky, T.E. Orłowski, D.J. Williams, *Journal of Physical Chemistry* 87 (1983) 5333.
- [6] N. Tamai, H. Masuhara, *Chemical Physics Letters* 191 (1992) 189.
- [7] M. Fan, Y. Ming, Y. Liang, X. Zhang, S. Jin, S. Yao, N. Lin, *Journal of the Chemical Society Perkin Transactions 2* (1994) 1387.
- [8] V. Malatesta, G. Raghino, U. Romano, P. Allegrini, *International Journal of Quantum Chemistry* 42 (1992) 879.
- [9] S. Nakamura, K. Uchida, A. Murakami, M. Irie, *Journal of Organic Chemistry* 58 (1993) 5543.
- [10] S.M. Aldoshin, *Molecular Crystals and Liquid Crystals* 246 (1994) 207.
- [11] S. Aldoshin, I. Chuev, A. Utenishev et al., *Acta Crystallographica C* 51 (1995) 141.
- [12] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, *Journal of Computational Chemistry* 14 (1993) 1347.
- [13] J.J.P. Stewart, MOPAC 93, Fujitsu Limited, Tokyo, Japan (1993).
- [14] A.S. Kholmanskij, A.V. Zubkov, K.M. Djumaev, *Uspekhi Khimii* 50 (1981) 569.