SPECTROSCOPIC STUDY OF THE STRUCTURE OF N-(2-BENZIMIDAZOLYL)-O-METHYLCARBAMATE

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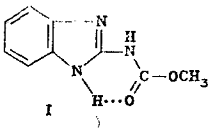
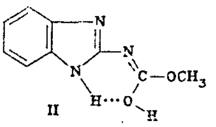
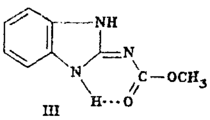
X-ray electronic, IR, and electronic spectroscopy were used to determine that N-(2-benzimidazolyl)-O-carbamate in the crystalline state and in organic solvents exists predominantly in the benzimidazole carbamate form. The acid–base characteristics of N-(2-benzimidazolyl)-O-methylcarbamate were evaluated. The spectra of this compound were interpreted using quantum chemical calculations and experimental data.

Benzimidazole derivatives have a set of biological properties which permit their use as pesticides and drugs. N-(2-Benzimidazolyl)-O-methylcarbamate (BMC) occupies a special position among these compounes [1, 2]. However, the structure and properties of this compound have not been studied. In the present work, we carried out a detailed study of the structure and physicochemical properties of BMC in the polycrystalline state and in various media.

The structure of BMC may be represented as tautomers I-III


I


II


III

Since monocrystals of BMC could not be grown, x-ray electronic spectra (XES), IR and UV spectra as well as quantum chemical calculations were used to establish the predominant tautomer.

The x-ray electronic spectra were taken on a Kratos ES-100 spectrometer by pressing the compound into a copper lattice. The C1s line at 285.0 eV obtained from the vapor of diffusion oil condensed on the sample was used as the standard. Since the bond energy of the internal electrons in atoms within molecules depends on the electron density of their outer shells, the XES method permits the qualitative differentiation of the valence states of atoms in molecules. Thus, one of the oxygen atoms is in a C═O double bond and the other is in an OCH$_3$ group. Of the three nitrogen atoms, one is a C═N double bond, and the other two have three σ-bonds and supply p$_z$ electrons of the unshared pair to the π-bond system. In structure II, both oxygen atoms are of the same bridging type while the three nitrogen atoms are divided among two nitrogen atoms in double bonds and one atom supplying p$_z$ electrons to the π-system. In accord with the valence state types for the oxygen and nitrogen atoms in the XES of tautomers I and III, we should expect the appearance of two O1s lines with 1:1 intensity ratio and two N1s lines with 1:2 intensity ratio. In the XES of tautomer II, there should be one O1s line and two N1s lines with inverse intensity relative to the intensity of the N1s lines in tautomers I and III.

The XES of BMC shows two O1s lines with energies 531.4 and 533.2 eV and 1:1 intensity ratio (Table 1). The assignments of these values to oxygen atom types were carried out using literature data for the XES of compounds containing oxygen atoms of a determined type. Table 1 shows that the O1s bond energy of the oxygen atom within a double bond is 1.5-2 eV lower than the O1s line for the oxygen atom in the bridging bond. Thus, the BMC molecule has carbonyl and bridging oxygen atoms, which correspond to structures I and III and excludes structure II. The O1s values in the XES of BMC hydrochloride are higher by 0.3-0.5 eV (Fig. 1). The XES of BMC shows two N1s lines. The intensity of the line with higher energy is twice

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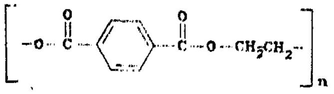
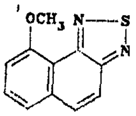
TABLE 1. Bond Energies of Internal Electrons

Compound	E_b, eV			
	O1s		N1s	
	>C=O	—OCH_3	N=C	
 [3]	531,0	532,7	—	—
 [4]	—	533,5	399,4	—
	531,4	533,2	398,5	400,2
BMC·HCl	531,9	533,5	398,9	400,6
Benomil (V)	531,6	533,4	398,7	400,4

that of the low-energy line. According to XES data, the N1s bond energy in α,α'-dipyridine is 399.1 eV [4], while for the N1s values for pyridines in the solid state lie in the range from 388 to 399 eV [5]. In five-membered aromatic rings such as imidazole, the N1s line atom of a double bond nitrogen atom is 399.1 eV and the corresponding value for a hydrogen atom in p, π-conjugation is 1.5 eV higher [6]. Finally, two N1s energies of 400.5 and 399.1 eV are observed in phthalocyanine for the eight nitrogen atoms with signal halfwidth $\delta_{1/2}$ = 1.7 eV and 1:3 intensity ratio. The N1s value of 400.5 eV is related to the six "pyrrolic" nitrogen atoms  while the value of 399.1 eV is related to two "pyridinic" nitrogen atoms (N=C) [7]. Hence, the N1s energy of 400.2 eV in the XES of BMC was assigned to two NH group nitrogen atoms and the line at 398.5 eV was assigned to the C=N bond nitrogen atom. The N1s values in BMC•HCl are higher by 0.4 eV due to the induction effect of the proton. The XES of benomil shows two N1s lines close to the N1s values in BMC (Table 1) but with 1:3 intensity ratio.

Thus, the examination of the XES indicates that BMC in the crystalline state exists predominantly as tautomer I or III.

Pariser—Parr—Pople quantum chemical calculations [8, 9] were carried out using a variable β [10] according to the program of Kosobutskii [11]. The energy characteristics of tautomers I-III were calculated in order to determine the existence of tautomers in the gas phase, the effect of the electrostatic interaction with the medium and evaluation of the contribution of the π- and σ-energies to the total energy of BMC (Table 2). According to the heats of atomization of tautomers I-III, these compounds have similar stability with some preference for tautomer I in the gas phase due to the gain in π-bond energy in the tautomer series I-III. The similarity in the atomization energies of tautomers I and III and the enhanced solvation coefficient in tautomer III relative to I indicate that, the facile tautomeric transition between these forms is possible depending on the solvent.

The electronic absorption spectra were taken on Specord UV-VIS spectrometer in ethanol and $CHCl_3$. The electronic spectrum of BMC tautomer I has three absorption regions (Fig. 2). According to the calculation, the first absorption region is related to the complex electronic transition from the highest occupied molecular orbital (HOMO) Ψ_n to the lowest unoccupied molecular orbital (LUMO) Ψ_m (41%), from Ψ_{n-1} to Ψ_m (33%) and from Ψ_n to Ψ_{m+1} (10%). The transition is polarized at an angle of −13° relative to the long molecular axis (x-axis). The redistribution of π-charge in the molecule upon going from the ground state to the first excited state indicates that the electron-donor fragment in this transition is the carbamate group, while the electron-withdrawing fragment is the benzimidazole ring (Fig. 3). The observed fine structure of the long-wavelength band with difference in frequency between the components $\Delta\nu$ = 800 cm^{-1} is a consequence of electronic-vibrational transitions (Fig. 2).

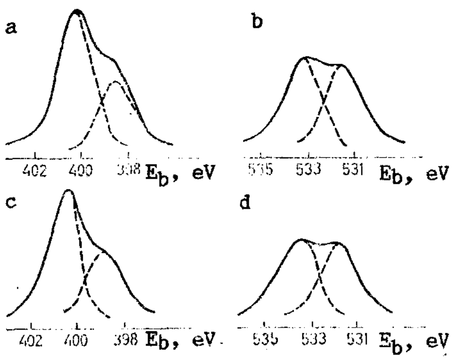


Fig. 1

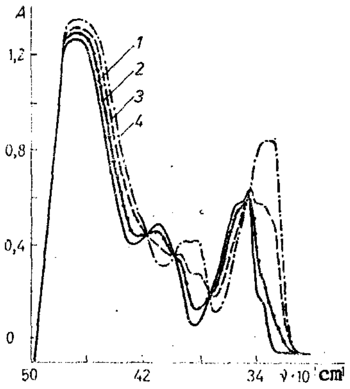
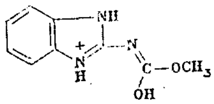


Fig. 2

Fig. 1. X ray electronic spectra: a) N1s for BMC, b) O1s for BMC, c) N1s for BMC•HCl and d) O1s for BMC•HCl.

Fig. 2. Electronic absorption spectra of BMC in ethanol (1) and of BMC in alkaline ethanolic solutions (2-4).

TABLE 2. Energy Characteristics of Tautomers and Ionic Forms of BMC

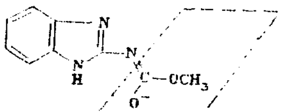
Compound	π-Bond energy, E_π, eV	σ-Bond energy E_σ, eV	Heat of atomization, ΔH, eV	Solvation coefficient, M
I	23,92	49,26	103,78	4,10
III	23,73	49,30	103,62	4,70
II	23,50	49,27	103,60	3,24
	24,44	49,30	108,67	4,38
IA	24,78	49,29	108,77	5,17

The second π-electron transition is also complex: $\Psi_n \to \Psi_m$ (48%), $\Psi_n \to \Psi_{m+1}$ (19%), and $\Psi_{n-1} \to \Psi_m$ (17%) This transition is polarized by −32° relative to the x-axis and is localized predominantly in the benzimidazole system ($C_{(1)}$, $C_{(4)}$, $C_{(5)}$ and $N_{(9)}$ are electron-withdrawing while $C_{(2)}$, $C_{(3)}$, $C_{(6)}$ and $N_{(7)}$ are electron donating). The band with two resolved vibrational components ($\Delta\nu$ = 950 cm^{-1}) corresponds to this transition in the observed spectrum.

The third complex electronic transition appears in the experimental spectrum as a shoulder (Table 3) and is localized in the benzene ring ($C_{(2)}$ and $C_{(3)}$ are electron-withdrawing and $C_{(1)}$ and $C_{(6)}$ are electron-donating) and in the carbamatoimidazole fragment (the imidazole ring is electron-donating and the carbamate group is electron-withdrawing).

The fourth transition is given in Table 3.

A bathochromic shift is observed in the spectra for BMC in alkaline ethanolic solutions relative to the spectra in ethanol for all bands. The existence of isobestic points indicates the existence of an ionized form of the molecule in solution (Fig. 2). According to the calculation, the anionic form IIA of tautomer II is formed in alkaline solution (Table 3):



IIA

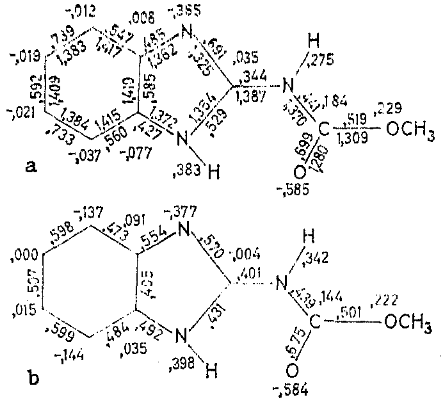


Fig. 3

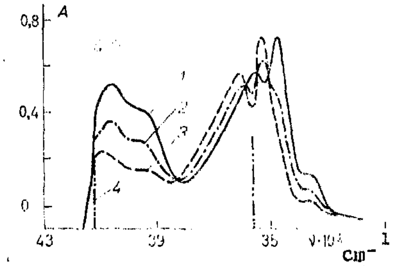


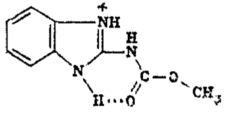
Fig. 4

Fig. 3. Molecular diagrams of tautomer I: a) in the ground state, and b) in the first excited state.

Fig. 4. Electronic absorption spectra for 1) BMC in $CHCl_3$; 2, 3) BMC in $CHCl_3$ after the passage of gaseous HCl; and 4) calculated spectrum for protonated tautomer IA.

The long-wavelength band is attributed to the extent of 87% to the transition Ψ_n(HOMO) → Ψ_m(LUMO) and the intensity (f = 0.621) is 2.6 times greater than for the neutral form (f = 0.238). The calculated $f_{neutr}/f_{anion} = 0.4$ and experimental $\varepsilon_{neutr}/\varepsilon_{anion} = 0.3$ ratios for the long-wavelength transitions are in satisfactory accord (Table 3). This transition is polarized along the long molecular axis. The oxide anion is electron-donating while the benzimidazole system is electron-withdrawing. The doublet nature of the band is due to the appearance of vibrational structure in the electronic transition.

The spectra of the solutions of BMC in acidic ethanol media and in $CHCl_3$ through which gaseous HCl was introduced show that the BMC molecules are protonated as indicated by the observation of isosbestic points (Fig. 4). This protonation leads to a significant change in the absorption spectrum (Table 3). The intensities of the bands at 212 and 228 nm undergo inversion and a hypsochromic shift of 4 nm. The intensity of the 250/245 nm band is very reduced. According to the calculation, this band is shifted hypsochromically, which prevents its observation due to overlap with the adjacent strong band. The long-wavelength band retains its fine structure and undergoes hypsochromic shift by 4 nm. The calculated spectrum of protonated tautomer IA is in satisfactory accord with the experimental spectrum (Fig. 4).

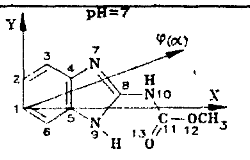
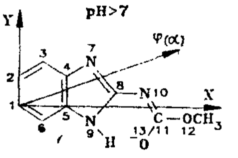
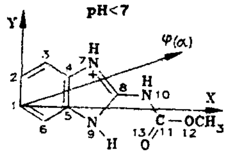


IA

The acidity and basicity constants of BMC in 50% ethanol were determined spectrophotometrically using $Na_2B_4O_7 \cdot 10H_2O$ (pH 9.18) and KH_2PO_4 (pH 6.86) buffer solutions, respectively. The pK_a value of 11.64 and pk_b value of 5.60 fall withing the pK ranges for reported benzimidazole derivatives: pK_a 13.2 and pK_b 5.53 for benzimidazole and pK_a 12.0 for 2-phenylbenzimidazole [12].

The IR absorption spectra were taken on a Specord IR-75 spectrometer. The IR spectrum of BMC in vaseline oil at 3700-2100 cm^{-1} shows a diffuse band with a set of maxima at 2555, 2675, 2755, and 2810 cm^{-1} which we assigned to the stretching vibrations of the NH group bound by a strong intramolecular bond to the carbonyl group. This assignment is in accord with the lack of this band in the IR spectra of polycrystalline benomil (Fig. 5) and in dilute solutions of BMC in $CHCl_3$. The band at 3330 cm^{-1} is assigned to vibrations of the exocyclic NH bond forming strong intermolecular hydrogen bonds. The bands at 1640-1655 cm^{-1} were assigned to the C=O bonds since the $\nu_{C=N}$ band of benzimidazole is observed at 1620 cm^{-1} while the $\nu_{C=N}$ band of iminoesters are observed at 1615-1575 cm^{-1} [13, 14]. The strong shift

TABLE 3. Experimental and Calculated Absorption Spectra for BMC Tautomer I in Ethanol (7 ≤ pH ≤ 7)

Form of tautomer I	λ_{max}, nm		Intensity		Transition polarization direction (α), deg	MKV eigen vectors
	exp.	calc.	Exp., λ_{max} liter/mole·cm	calc.		
	294 287 281 276	278	5333,7 14142,3 13360,9 11159,7	0,238	−13	−0,64 (8—9); 0,57 (7—9); 0,32 (8—10)
	250 245	249	9273,3 12520,7	0,397	−32	0,69 (8—9); 0,43 (8—10); 0,41 (7—9)
	228	227	14318,8	0,308	10	0,59 (8—10); −0,54 (7—9); 0,42 (7—11)
	212	197	23483,5	0,287	60	0,79 (8—11); −0,39 (7—9); −0,27 (7—10)
	304 296	301	18446,6 18203,9	0,621	−12	0,93 (8—9)
	261 253	266	11650,5 11407,8	0,140	−19	0,69 (8—10); 0,46 (7—9); 0,35 (7—11)
	226	237	66504,9	0,239	−64	0,59 (7—9); 0,54 (8—11); −0,35 (8—10); −0,32 (7—10)
		208*		0,429	−41	0,76 (8—11); −0,52 (7—9)
		204*		0,224	71	−0,60 (8—10); 0,51 (6—9); 0,46 (7—11)
	283 277 266	280	14508,9 14508,9 8816,9	0,339	−13	0,81 (8—9); −0,35 (7—11); −0,34 (7—9)
		242 †		0,256	−35	0,57 (7—9); 0,50 (8—9); 0,41 (8—10); 0,38 (8—11)
	225	231	21316,9	0,276	10	−0,61 (7—9); 0,50 (8—10); 0,47 (7—11)
	208	199	12276,8	0,083	−84	−0,62 (8—11); 0,57 (7—10); 0,32 (7—9)

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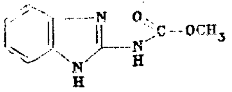
*Experimentally not distinguished since the solvent has strong absorption in this region.

†Overlapped by a broad band in the region 210-250 nm in the experimental spectrum.

of the $\nu_{C=O}$ band is a result of strong hydrogen bonding. The existence of a C=O bond in BMC in the polycrystalline state is also indicated by the sharp bands at 1276 and 1292 (doublet) and 1198 cm^{-1} characteristic for vibrations of ester C—O— bonds [15, 16]. The low-intensity band at 1712 cm^{-1} in the IR spectrum of BMC is related to rotational isomer I':



I'

This hypothesis is supported by the finding of a very strong band at 1712 cm^{-1} in the spectrum of benomil. The replacement of a hydrogen atom at the ring nitrogen atom by an amide group destroys the intramolecular hydrogen bond with the carbamate group in isomer I and leads to the formation of a new bond:

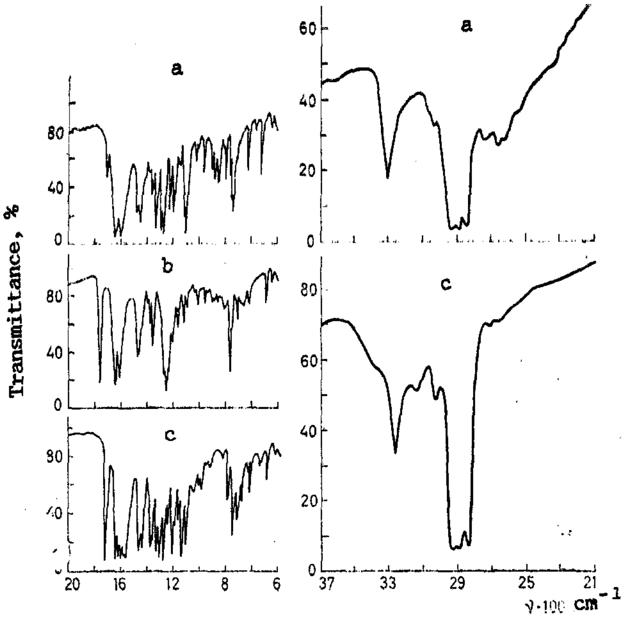
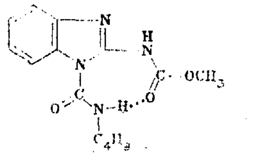
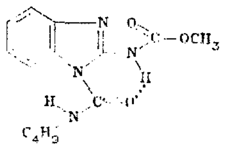


Fig. 5. IR spectra in the crystalline state and in vaseline oil for BMC (a), BMC•HCl (b), and benomil (c).


IV


V

Since an eight-membered ring is formed in isomer IV, while a six-membered ring is formed in V, the latter is favored energetically. This is in accord with the assignment of the band at 1712 cm^{-1} to the vibration for the free carbamate group of V since the vibrational frequency of the free amide group does not exceed 1680 cm^{-1} [15]. The $\nu_{NC=O}$ frequency of the amide group is strongly shifted toward lower values due to intramolecular hydrogen bonding and is 1635 cm^{-1}.

The carbamate and amide group C=O bands in the spectra of dilute solutions of benomil in CCl_4 are higher by 19 cm^{-1}. The form and number of bands in the NH stretching band region in the spectra of benomil in vaseline oil and in CCl_4 solution are the same but are shifted toward higher frequencies in solution by 20 cm^{-1}. This behavior indicates that the structures of the benzimidazole ring and the carbamate group in BMC and benomil are the same.

The IR spectra of BMC•HCl in the crystalline state shows a strong band at 1753 cm^{-1}, which was assigned to C=O group vibrations. The increase in $\nu_{C=O}$ relative to the frequency of this band in BMC is attributed to a strong inductive effect. This is in accord with the XES data which indicate that the energy of the C=O group increases upon protonation of BMC.

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REACTIVITY OF METHYL DERIVATIVES OF NITROGENOUS HETEROCYCLES IN VAPOR-PHASE CATALYTIC OXIDATION

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A study has been made of the reactivity of methylpyridines, methylpyrazines, and methylquinolines in oxidation in the vapor phase in the presence of β-VO $(PO_3)_2$. Relationships have been found between the overall reaction rates of heterocyclic compounds and the charge on the ring nitrogen, and between the partial oxidation rate and the charge on the ring carbon atom adjacent to the methyl group. The partial oxidation rate of methylpyridines is given to a first approximation by the Hammet-type expression $\ln W_a = -3.5 + 4.6\ \Sigma\sigma$, with a correlation coefficient of 0.93.

The vapor phase oxidation of methylheterocycles with atmospheric oxygen over vanadium catalysts forms the basis of the industrial production of heteryl aldehydes, which are intermediates in the synthesis of biologically active compounds. In order to establish the most important structural features governing the reactivity of heterocyclic compounds in oxidation, and to obtain further information on the reaction mechanisms under comparable conditions, the oxidation of representatives of three classes of nitrogen heterocycles has been studied, namely pyridines, diazines, and quinolines. In the pulsed vapor-phase oxidation of these compounds (Table 1) in the presence of vanadyl β-polyphosphate at 400°C, the principal reaction products are the monoaldehyde and oxides of carbon. Under these conditions, 4-MP, 2,3-DMP, 2,5-DMP, 3,4-DMP, 2-MQ, and 4-MQ give predominantly the partial oxidation products, whereas oxidation of 3-MP, 3,5-DMP, and DMPZ results in extensive oxidation. The rates of total and partial oxidation W_a of the remaining compounds are similar. Comparison of the total oxidation rates (W_{tot}) of the pyridine bases shows that introduction of methyl substituents into the pyridine ring increases the overall reaction rate, but there is not clear relationship between the reactivity of the pyridines and the number of methyl groups present.

Under impulse conditions, the total conversion rate of monomethylpyridines and the amounts of aldehydes formed on oxidation over β-VO$(PO_3)_2$ decreases in the isomer sequence 4- > 2- > 3-, just as when vanadium oxide catalysts are used [1].

It is noteworthy that the sequence of reactivities of 2-, 3-, and 4-MP obtained under conditions which restrict the occurrence of subsequent reactions is similar to the rate of deuteration of the methyl groups in these compounds [2], and also to their reactivity in prototropic reactions, for example with sodamide [3]. In the quinoline series, 4-MQ also undergoes vapor phase oxidation more readily than 2-MQ both in total and partial oxidation (Table 1). These facts lead to the conclusion that the limiting step in the heterogeneous catalytic

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