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CRYSTAL AND MOLECULAR STRUCTURE OF N-(2-BENZIMIDAZOLYL)-O-ALKYL CARBAMATES

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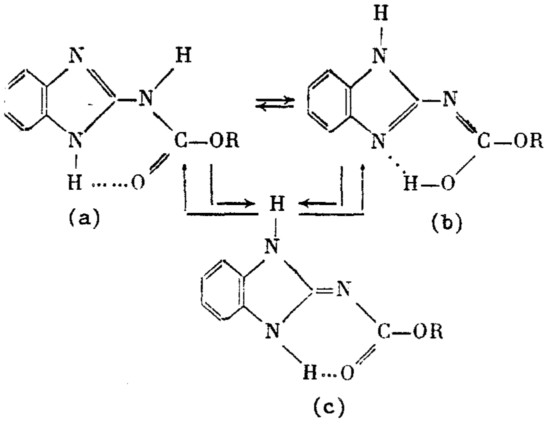
N-(2-Benzimidazolyl)-O-methyl carbamate (I) and N-(2-benzimidazolyl)-O-ethyl carbamate (II) possess valuable pesticidal properties and are widely used in agriculture [1, 2]. Nevertheless, unresolved issues remain concerning the form of existence of these compounds in the crystalline state and in solution and concerning the nature of hydrogen bonds (HB) which they form. It was recently proposed [3, 4], based on analysis of spectroscopic (x-ray electronic, IR, and electronic spectra) and quantum mechanical (PPP approximation) data, that in the crystalline state and in solutions the most probable forms for compound (I) are tautomers of the type (Ia) and (Ic).



R = Me(I), Et(II).

A hypothesis was also advanced concerning the presence of strong intermolecular HB (IHB) for (I) in the crystalline state.

In the present paper we report our results of x-ray structural analyses of (I) and (II), and have also discussed their spectral characteristics in light of this new data.

EXPERIMENTAL

Synthesis of Single Crystals. a) A solution was prepared from $2.5 \cdot 10^{-3}$ moles (I) in 30 ml DMF at ∿20°C. The solvent was gradually evaporated over a period of several weeks to

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0568-5230/88/3706-1148$12.50

TABLE 1. Atomic Coordinates of Molecules of (I)

Atom	X	Y	Z
O^1	0,2008(1)	0,4702(4)	0,2433(1)
O^2	0,1162(1)	0,2214(4)	0,2259(1)
N^1	0,0849(1)	0,4927(5)	0,1128(2)
N^2	0,1546(1)	0,8176(5)	0,1045(2)
N^3	0,0444(1)	0,7723(5)	−0,0132(2)
C^1	0,0958(1)	0,6807(6)	0,0725(2)
C^2	0,1404(1)	0,9979(6)	0,0380(2)
C^3	0,1815(2)	1,1817(6)	0,0374(2)
C^4	0,1500(2)	1,3399(6)	−0,0401(2)
C^5	0,0796(2)	1,3121(6)	−0,1152(2)
C^6	0,0385(2)	1,1250(6)	−0,1150(2)
C^7	0,0699(1)	0,9686(6)	−0,0374(2)
C^8	0,1396(1)	0,4049(6)	0,1967(2)
C^9	0,1682(2)	0,098(1)	0.3131(3)
H^1	0,193(2)	0,797(6)	0,160(2)
H^2	0,001(2)	0,693(8)	−0,047(3)
H^3	0,229(2)	1,199(6)	0,042(2)
H^4	0,175(1)	1,480(6)	−0,044(2)
H^5	0,061(2)	1,433(6)	−0,170(2)
H^6	−0,012(2)	1,108(6)	−0,166(2)
H^7	0,203(2)	0,011(9)	0.304(3)
H^8	0,187(4)	0,19(1)	0,365(5)
H^9	0,141(3)	−0,03(1)	0,323(3)

TABLE 2. Atomic Coordinates for Independent Molecules of (II)

Atom	X	Y	Z
O^1	0,342(2)	0,1695(5)	−0,165(2)
O^2	0,590(2)	0,0962(5)	−0,224(2)
O^3	0,156(2)	−0,2421(5)	−0,089(2)
O^4	0,919(3)	−0,1702(5)	−0,025(2)
N^1	−0,007(3)	0,1161(5)	0,921(2)
N^2	1,006(3)	0,0024(7)	0,929(2)
N^3	0,297(3)	0,0539(6)	0,849(2)
N^4	0,511(3)	−0,1847(6)	−0,175(2)
N^5	0,499(3)	−0,0775(6)	−0,173(2)
N^6	0,205(3)	−0,1271(6)	−0,099(2)
C^1	0,640(8)	0,128(2)	0,012
C^2	0,471(4)	0,0954(9)	0,056(2)
C^3	0,490(4)	0,024(1)	0,061(2)
C^4	0.661(4)	−0,015(1)	0.020(2)
C^5	0.818(3)	0,0220(7)	0,975(2)
C^6	0,808(4)	0,0924(8)	0,972(2)
C^7	0.117(4)	0,0588(8)	0,898(2)
C^8	0.406(4)	0,1113(8)	0,822(2)
C^9	0,711(4)	0.1528(9)	−0.258(2)
C^{10}	0,868(6)	0,128(1)	−0,317(2)
C^{11}	0,873(4)	−0,2005(9)	0,740(2)
C^{12}	−0,040(4)	0,1632(9)	0,198(2)
C^{13}	−0,036(4)	0,0931(8)	0,196(2)
C^{14}	0,857(4)	−0,0610(8)	0,739(2)
C^{15}	0,689(4)	−0,0947(7)	0.799(2)
C^{16}	0.702(4)	−0,1672(7)	0,781(2)
C^{17}	0,387(4)	−0,1316(7)	0,859(2)
C^{18}	0,099(3)	−0,1846(8)	0,926(2)
C^{19}	0,207(4)	0,2285(9)	0,508(2)
C^{20}	0,390(5)	0,299(1)	0,061(3)

give single crystals of (I). Found: C 55.68; H 4.67; N 22.30%. $C_9H_9N_3O_2$. Calculated: C 56.49; H 4.71; N 21.97%.

b) To a solution of 0.05 mole $MnCl_2 \cdot 4H_2O$ in 200 ml EtOH was added 0.01 mole of powdered (I). The mixture was heated with stirring to the boiling point and refluxed for 7 h. Under these conditions (I) dissolved in solution and underwent transetherification. The reaction mixture was cooled to ~20°C and maintained at this temperature for 12 h. Crystals of (II) were isolated in the form of slightly tinted nodes; they were filtered, washed with EtOH, and dried over P_2O_5. Found: C 58.81; H 5.18; N 20.51%. $C_{10}H_{11}N_3O_2$. Calculated: C 58.48; H 5.36; N 20.47%.

X-ray Structural Analysis. Single crystals of (I) are monoclinic, a = 23.082(4), b = 5.425(1), c = 16.957(3) Å, β = 124.2(1)°, Z = 8, d_{calc} = 1.44 g/cm³, V = 1756.2(1) Å³, C2/c space group. The cell parameters and intensities of 972 independent reflections with I ≥ 2σ

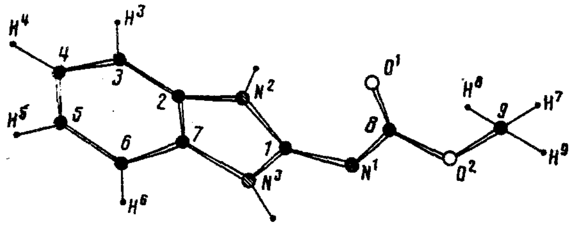

Fig. 1

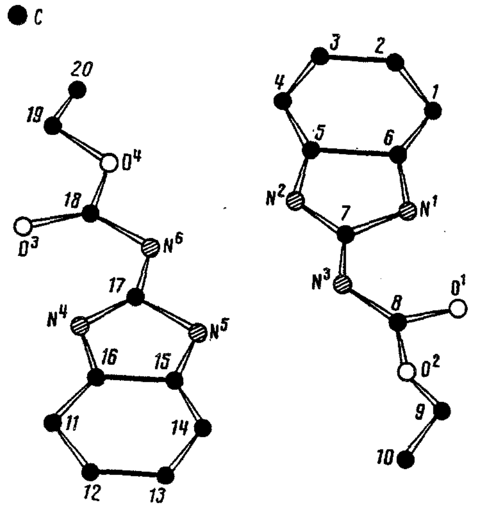

Fig. 2

Fig. 1. Molecular configuration of (I) in the crystal state (projected onto the XY plane).

Fig. 2. Orientation of independent molecules of (II) in a unit cell (projected onto the XY plane).

were measured on a Syntex $P2_1$ four-circle automatic diffractometer (λCu K_α, graphite monochromator, Ni-filter, $\theta/2\theta$ scanning). The structure was solved by direct methods using the SHELX system of programs on an ÉS-1060 computer. The structure was refined to isotropic full-matrix approximations (R = 0.035). All of the H atoms were located by analysis of difference Fourier synthesis in the final stage of the investigation. Atomic coordinates are summarized in Table 1; the orientation configuration of (I) in the unit cell is shown in Fig. 1.

Crystals of (II) are rhombohedral, a = 5.525(3), b = 19.922(9), c = 17.448(9) Å, Z = 8, d_{calc} = 1.42 g/cm³, V = 1920.5(1) Å³, $Pbc2_1$ space group. The methods used in data measurement and treatment were the same as described above for (I). The intensities of 990 independent reflections with $I \geqq 2\sigma$ were used in data treatment. The structure was refined by full-matrix least squares with anisotropic approximations, to give a final R-factor of 0.074.

Due to an inadequate number of measured reflections for (II) it was not possible to localize the H atoms after anisotropic refinement. However, the electron density distributions obtained after isotropic full-matrix least squares (at R = 0.12) showed significant electron density peaks, which could be interpreted as H atoms, between the N^3, N^5 and N^2, N^6 atoms (Fig. 2). The refined coordinates for the nonhydrogen atoms in (II) are summarized in Table 2.

The methodology for spectroscopic analysis and quantum mechanical calculations has been reported previously [3, 4].

RESULTS AND DISCUSSION

Of the three possible tautomeric forms a-c for (I) and (II) in the crystalline state only form c is, in fact, realized (Figs. 1 and 2). This is indicated by the following data. In the case of (I), H atoms were detected for both of the N atoms in the imidazole ring, which precludes form (Ia). Of the exocyclic C–N distances, the shortest is assigned to the first bond from the heterocycle [in (I), C^1–N^1 1.327(3) Å, in (II) C^7–N^3 and C^{17}–N^6 average value 1.28 Å]; the second exocyclic bond is longer than the first by 8σ [in (I) N^1–C^8 is 1.352(3) Å, in (II) N^3–C^8 and N^6–C^{18} have an average value of 1.37 Å].

The observed bond lengths for the endocyclic C–N bonds reveal only small, insubstantial differences from those in the heterocycle [in (I) C^1–N^2 1.364(3) Å and C^1–N^3 1.352(3) Å, in (II) the average value for C^7–N^1 and C^{17}–N^4 is 1.37 Å, the average for C^7–N^2 and C^{17}–N^5 is 1.38 Å].

Molecules of the indicated compounds (I) and (II) were practically planar. The CO bond lengths in (I) and (II) [for (I), C^8–O^1 1.222(4) Å, C^8–O^2 1.352(3) Å; for (II), C^8–O^1 and

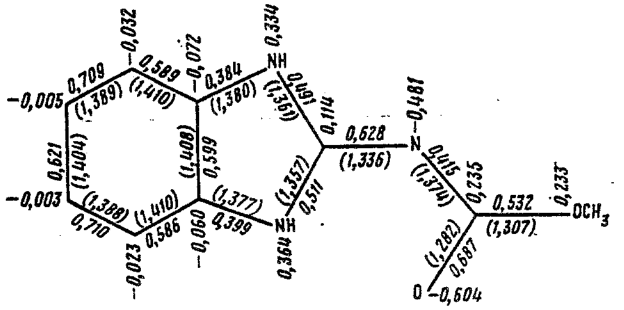

Fig. 3. Molecular diagram of (I) in its ground state [tautomer (Ic)]: π-charges on atoms, π-bond orders, and in parentheses, calculated interatomic distances in Å.

$C^{18}-O^{3}$ average value 1.23 Å; $C^{8}-O^{2}$ and $C^{18}-O^{4}$ average value 1.34 Å] correspond to conventional C–O distances for esters: 1.22 and 1.36 Å [5].

The five-membered diazole ring in these compounds is weakly distorted, in contrast to the symmetrical diazole ring which has been observed in the crystal structure of the thione form of 2-mercaptobenzimidazole [6]. An analogous distortion of the heterocycle has been noted previously in the case of 2-hydroxybenzimidazole [7]. The difference in the $C^{1}-N^{2}$ and $C^{1}-N^{3}$ bond lengths [1.364(3) and 1.352(3) Å, respectively] and deviation of the $N^{2}C^{1}N^{1}$ and $N^{3}C^{1}N^{1}$ bond angles [130.3(2)° and 122.0(2)°, respectively] can be explained in terms of the formation of a quasiaromatic six-member ring as a consequence of intramolecular HB between the carbonyl and imino groups, of the type C=O...N–H. The hydrogen bonded $O^{1}...H^{1}$ length in (I) is 2.21 Å (the distance between the O^{1} and N^{2} atoms is equal to 2.72 Å).

The benzene ring in compounds (I) and (II) is slightly distorted. The bond length and bond angle values correlate satisfactorily with the correponding values for benzimidazole and its 2-mercapto- and 2-hydroxy derivatives [6-8].

Two molecules of (I), which are related to one another by an inversion center (in the crystalline state), form very strong IHB of the type $H^{2}...N^{1}$ (1.93 Å) with one another, between the $N^{3}H^{2}$ group of the molecule and the exocyclic N^{1} atom of the other molecule (the distance between these two nitrogen atoms is 2.87 Å). Two symmetrically unrelated molecules of (II) are also bound together pairwise by an analogous type of HB (Fig. 2).

The molecular structure of (I) and (II) are very similar. The presence of an ethyl substituent in (II) does not have a large influence on the molecular geometry or on the crystal packing arrangements, despite differences in the symmetry and size of the unit cells. Thus, as in (I), molecules of (II) are stretched or extended along the axis corresponding to the smallest cell parameter (5.425 and 5.525 Å, respectively). In both structures pairwise associated complexes exist due to IHB between the azole and exocyclic N atoms in two different molecules, although in the case of (II) this association is between two crystallographically independent molecules, while in (I) the association is between two molecules related by an inversion center.

For the compounds under investigation, which exist in the crystalline state in the form of tautomer (Ic), the π-electron system of the benzimidazole ring is stabilized via a shift of excess π-electron density to the exocyclic system of CN– and CO– bonds. According to quantum mechanical calculations, in fact, the amount of excess charge on the exocyclic bond system is equal to $-0.617\bar{e}$, while in 11 of the π-electron benzimidazole ring, the deficiency is $+0.617\bar{e}$ (Fig. 3). The observed shift of π-electron density can be explained in terms of the tendency of the benzimidazole system to achieve the formation of a stable number (10) of π-electrons, in accordance with the Hückel rule [9].

By knowing the crystal structure of (I) it should be possible to obtain more accurate information concerning its spectral characteristics, which is important from the point of view of studying the structures of salts of (I) with acids and metal complexes.

In a previous paper [3], the broad diffuse band at 3700-2100 cm^{-1} in the IR spectrum of (I) was assigned to νNH of an imino group, which was bound via strong intramolecular HB with a carbonyl group, and the band at 3330 cm^{-1} was assigned to νNH of the exocyclic NH-group, which was involved in IHB. However, the N–H...N distance corresponding to the intermolecular HB is ~0.3 Å smaller than the N–H...O=C intramolecular HB, i.e., the intermolecular HB

TABLE 3. Experimental and Calculated EAS of (I) [Tautomer (Ic)]

λ, nm (log ε) (in EtOH)	Calculate	
	λ, nm (oscillator strength)	MO transitions (contribution, %)*
294(3,72), 287(4,15), 281(4,13), 276(4,05) †	297(0,485)	$\psi_n \rightarrow \psi_m$ (83)
250(3,97)	254(0,447)	$\psi_n \rightarrow \psi_{m+2}$ (38), $\psi_{n-2} \rightarrow \psi_{m+1}$ (25)
245(4,10)	249(0,056)	$\psi_n \rightarrow \psi_{m+1}$ (61)
228(4,16)	214(0,079)	$\psi_{n-1} \rightarrow \psi_m$ (49)
212(4,37)	210(0,437)	$\psi_{n-2} \rightarrow \psi_m$ (56),
	207(0,399)	$\psi_n \rightarrow \psi_{m+2}$ **(33)** $\psi_{n-2} \rightarrow \psi_{m+1}$ (25)

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*ψ_n is the higher occupied molecular orbital (MO); ψ_m is the lowest unoccupied MO. Only the transitions which contribute more than 20% to the indicated bands are cited here.

†Vibrational structure.

(IHB) is considerably stronger than the intramolecular HB in this case. It follows, therefore, that the band at 3700-2100 cm^{-1} must be assigned to νNH of an imino group engaged in IHB formation, while the 3330 cm^{-1} band is due to νNH for an imino group involved in intramolecular HB. This is also consistent with the observation that in the IR spectra of solutions of (I) the band at 3700-2100 cm^{-1} disappears, whereas the band at 3330 cm^{-1} is retained in solution [3, 4]. The band at 1712-1718 cm^{-1} has been assigned to νC=O of a rotational isomer of (I) with a free C=O group [3, 4]. This assignment is inconsistent with the observed x-ray structural results. Instead, the weakly intense band is probably due to an overtone band of the 850-860 cm^{-1} vibrational band. The x-ray structural results also make it possible to assign more rigorously the signals in the x-ray electronic spectrum (XES) of (I). The highly energetic, most intense signal at 400.2 eV should be assigned to N1s of the imino group N atoms, while the less intense low energy signal (398.5 eV) should be assigned to N1s of the exocyclic N atom.

Based on these x-ray structural results for (I), we have carried out appropriate calculations to assign the bands in its electronic absorption spectrum (EAS) (Table 3). The highly intense absorption band in the short wavelength region, with maxima at 212 and 228 nm is attributed to three transitions, and not two, as in the case of tautomer (Ia) [3]. Based on these calculations, furthermore, the absorption in the 250-245 nm region is assigned to two transitions, and not one, as was calculated based on tautomer (Ia) [3]. The calculated EAS for tautomer (Ic) is superimposable to a greater extent on the experimental spectrum of (I) in EtOH solution than is the calculated spectrum of tautomer (Ia). This observation may be regarded as evidence that in ethanol solution compound (I) exists in the form of tautomer (Ic).

CONCLUSIONS

1. The crystal and molecular structures of N-(2-benzimidazolyl)-O-methyl carbamate and N-(2-benzimidazolyl)-O-ethyl carbamate have been determined. It was found that these compounds exist in the form of their tautomers (Ic) and (IIc). The spectroscopic characteristics (IR, EAS, and x-ray electronic spectrum) of N-(2-benzimidazolyl)-O-methyl carbamate were refined; these should prove beneficial in establishing the structures of metal complexes and salts of the indicated compounds.

2. It was also established that upon heating a solution of N-(2-benzimidazolyl)-O-methyl carbamate in ethanol in the presence of $MnCl_2 \cdot 4H_2O$ transesterification takes place to form N-(2-benzimidazolyl)-O-ethyl carbamate.

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ROLE OF WATER IN STABILIZATION OF THE CRYSTAL STRUCTURE AND PHOTOCHEMICAL CONVERSION OF p-DIFLUOROMETHYLSULFO[N'-(5-NITROFURFULIDENE)]BENZHYDRAZIDE

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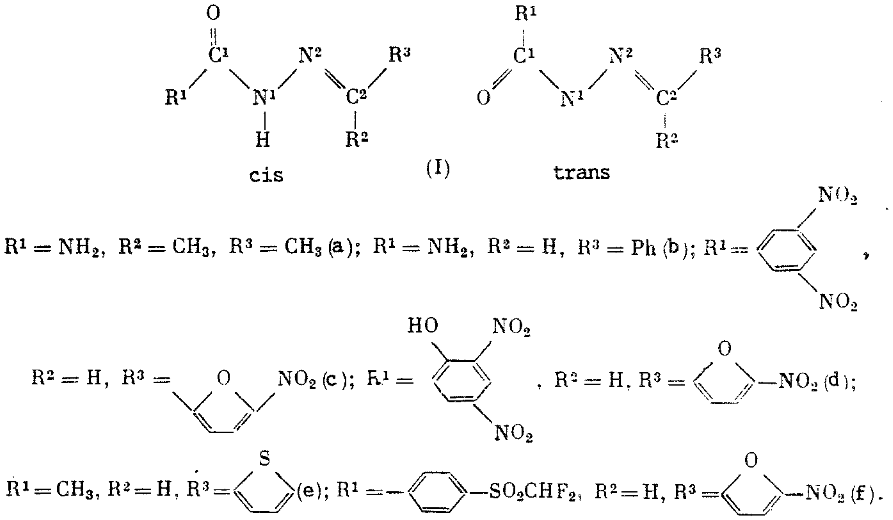
UDC 548.737:543.422.4:
541.14:547.582.6

X-ray diffraction study of semicarbazones (Ia, b) [1] has established that in crystals, these compounds are realized in two conformations: with cis and with trans arrangement of the carbonyl and hydrazone groups relative to the C^1-N^1 amide bond



It has been suggested [2] that in contrast to thiosemicarbazones, which form only the trans structure, in semicarbazones these two conformations are approximately energetically equivalent; and realization of one or the other of them in the crystals depends on the characteristic intermolecular interaction, particularly formation of intermolecular hydrogen bonds. In fact, in solutions the ketohydrazone (Ie) exists as a mixture of cis and trans conformers, which are separated in the crystal state; their structure has been proven by x-ray diffraction analysis [3]. In crystals, the highly polar cis conformations of the ketohydrazons form solvates with the solvent molecules, for example with acetic acid (Ic) and acetonitrile (Id) [2].

The formation of different conformers and solvates of these compounds should also be apparent in their properties. We have observed that one of the polymorphic modifications of ketohydrazone (If), p-difluoromethylsulfo[N'-(5-nitrofurfulidene)]benzhydrazide, is photochemically active in the crystalline state. UV irradiation of films of this compound leads

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