SPECTROPHOTOMETRIC AND X-RAY CRYSTALLOGRAPHIC STUDIES OF 1-CARBAMOYLBENZ-[c,d]INDOL-2-ONES

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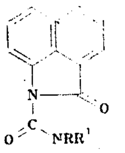
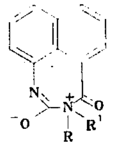
On the basis of a measurement of the frequencies and intensities of the stretching vibrations of the amino, amido, and ester groups in the IR spectra, it was established that products of the reaction of N-benzenesulfonylhydroxynaphthalimides with ammonia in alcohol solutions have a structure of the type of 1-carbamoylbenz[c,d]-indol-2-ones and are not molecules with a seven-membered heterocycle, by analogy with 3-oxido-2-alkylnaphtho[1,8-d,e][1,3]oxoniazepin-1-ones. A determination of the molecular and crystal structure of one of these compounds ($C_{13}H_{10}N_2O_2$) confirmed this conclusion: The molecule is 1-(N-methylcarbamoyl)benz[c,d]indol-2-one. In the naphthalene ring of the molecule the bond angles at the central bond are deformed analogously to that found in acenaphthene. The intramolecular hydrogen bond O•••HN closes a six-membered ring in the molecule. The crystal is constructed from dimers formed by intermolecular hydrogen bonds O•••HN.

In the interaction of N-benzosulfonylhydroxynaphthalimides with amines and ammonia in alcohol solutions, compounds are formed, the structure of which is depicted in the form of greatly differing structures I and II on the basis of the chemical properties [1]:



I



II

NRR'=NH₂,NHAlk,NAlk₂

Since an establishment of the structure of the products of the above-mentioned reactions is of fundamental importance for explaining their chemical properties, in this work this problem was solved by the methods of IR spectroscopy and x-ray crystallographic analysis.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in tablets of KBr in liquid petrolatum, as well as in solutions in carbon tetrachloride and chloroform. The integral intensities were measured according to the Burgen method [2]. The accuracy of the measurement of the frequencies in the region of absorption 1600-1800 cm^{-1} is ±2 cm^{-1}, in the region of 3200-3600 cm^{-1} it is ±3 cm^{-1}, and for the integral intensity it is ±5%

Single crystals of $C_{13}H_{10}N_2O_2$ were grown from chlorobenzene. The x-ray experiment for this crystal was conducted on a Hilger-Watts four-circle diffractometer (λCuK_α, graphite monochromator, ω-scan). The intensities of 980 reflections with $F^2 \geq 1\ \delta$ were measured. The crystals were monoclinic, a = 19.6852 (19), b = 9.8450 (18), c = 5.3289 (6) Å, β = 96.71 (1)°, V = 1025.7 (4) Å³, z = 4, d_{calc} = 1.47 g/cm³, space group $P2_1/a$. The structure was determined by a direct statistical method of determining the signs of the structural amplitudes. From E-

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synthesis (170 E-norms) all the atoms of the molecule were detected, R = 0.195; the structure was refined by the method of least squares in an anisotropic approximation (Roentgen-3 program [3]). In refinement in the usual variant without finding supplementary conditions R = 0.176; in this case a significant dispersion in the chemically equivalent bonds of the naphthalene ring (1.37 and 1.46 Å) was observed. Further refinement was performed according to the EXTL program (R = 0.085). In the refinement of the structures the positions of the hydrogen atoms, localized from a differential synthesis with B = 6 $Å^2$, were considered. The hydrogen atoms of the methyl group could not be localized

RESULTS AND DISCUSSION

IR Spectra. For a selection between structures I and II we analyzed the parameters of the bands of the stretching vibrations of the amino and carbonyl groups in the spectra of compounds that are products of the above-mentioned reaction (Table 1, compounds Ib-e). Compound Ia is a model known to contain a lactam group.

In the spectra of compound Ib two bands are observed at 3506 and 3344 cm^{-1}, and in the spectrum of Ic one band at 3434 cm^{-1}. The positions of these bands do not correspond to the vibrations of NH_2 and NHR in the ammonium cations, which absorb in the region of 2800-2300 cm^{-1} [4]. At the same time, the positions of the observed bands correspond to the vibrations of the amino groups bonded by a weak intramolecular hydrogen bond. Its existence follows from the following facts: In the first place, in the case of successive dilution of solutions of compounds Ib and Ic, the position and intensity of the bands are unchanged; in the second place, for compound Ib the frequency ratio for primary anions is not fulfilled [5]: $\nu^s = 345.53 + 0.876\ \nu^{as}$; in the third place, the high-frequency band ν^{as} of compound Ib is more intense than the low-frequency band, which is characteristic of the vibrations of the NH_2 group bonded by an intramolecular hydrogen bond [6].

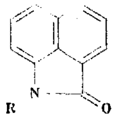
The measured integral intensities of the bands of the NH and NH_2 groups in the spectra of compounds Ib and If are 4-6 times as high as for saturated amines, which is evidence of conjugation of the amino groups with multiple or aromatic bonds. Consequently, on the basis of a study of the positions of the bands of the amino groups in the IR spectra of compounds Ib and Ic we arrived at the conclusion that the structure of the products of cleavage of derivatives of N-benzenesulfonylhydroxynaphthalimide under the action of amines is depicted by structure I.

An analysis of the bands of the stretching vibrations of the C=O groups in the IR spectra (Table 1) leads to an analogous conclusion. As can be seen from the table, the maxima of the bands of the vibrations of the C=O groups of compounds Ib and Ic have freuqencies of 1732 and 1734/1703 cm^{-1}, respectively. The values of these frequencies can also be brought into agreement with structure II, as was done in [1], and with structure I. To select among these structures we measured the integral intensities of these bands. In the spectrum of the model compound Ia, containing a lactam group, in the region of the vibrations of the C=O group intense bands 1726 and 1705 cm^{-1} are observed, the summary intensity of which is equal to 7.9 units, which is significantly less than the intensity of the bands 1732 and 1734/1703 cm^{-1} in the spectra of compounds Ib and Ic. The high value of the intensity in the spectra of the latter compounds can be explained by the presence of lactam and amide groups in the molecules, the bands of which overlap, and this corresponds to structure I. From the data of [6] it follows that the intensity of the bands of the lactam group is 5.5 units, of the amide C=O, 4.5 units. For compounds Ib and Ic, on the assumption of additivity of A(C=O), the summary intensity is made up of the intensity of the lactam group (7.9 units) and of the amide group (4.5-5 units) and is 12-13 units, which agrees with the values of the intensities found experimentally.

In [7] it was established that when both hydrogen atoms at the nitrogen atom are replaced, νC=O in the spectra of the amides is lowered by 30-40 units, while the intensity changes little. In the spectra of compounds Id and Ie (Table 1), the value of νC=O is 1738 cm^{-1}, while the intensity is close to the intensity for compound Ib, which confirms the overlapping of the lactam and lactime groups in this compound and leads to the conclusion that the products of the above-mentioned reactions have the structure I.

X-Ray Crystallographic Data. A determination of the molecular and crystal structures was performed for the compound $C_{13}H_{10}N_2O_2$ (Ic, Table 1). The bond lengths and bond angles of the molecule, together with their standard deviations, are cited in Fig. 1 and in Table 2.

TABLE 1. Frequencies and Intensities of the Bands of the Stretching Vibrations of the Carbonyl and Amino Groups of Compounds I (solutions in CCl_4)



Compound	R	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	Intensity $A \cdot 10^{-4}$ liters/mole · cm^2
I	H	1705 1726 3467	12,4 19,4 32,4	2,1 } ν C=O 5,8 } 0,94 ν NH
Ib	$CONH_2$	1732 3506 3344	22,0 17,3 35,5	13,0 ν C=O 2,0 ν^{as} NH 1,3 ν^{s} NH
Ic	$CONHCH_3$	1703 1734 3434	20,2 13,5 32	2,7 } ν C=O 8,0 } 2,5 ν NH
Id	$CON(CH_2)_5$	1690 1737	22,1 20,7	6,6 } ν C=O 7,9 }
Ie	$CON(CH_3)_2$	1695 1739	18,9 15,6	5,2 } ν C=O 5,6 }

TABLE 2. Bond Length d and Bond Angles ω

Bond	*d*, Å	Angles	ω, deg
$O_{(1)}-C_{(1)}$	1,204 (10)	$H_{(N2)}O_{(1)}C_{(1)}$	101,68 (53)
$O_{(1)}-H_{(N2)}$	1,760 (5)	$C_{(10)}N_{(1)}C_{(1)}$	109,65 (62)
$O_{(2)}-C_{(12)}$	1,201 (11)	$C_{(12)}N_{(1)}C_{(1)}$	125,94 (66)
$N_{(1)}-C_{(1)}$	1,431 (11)	$C_{(12)}N_{(1)}C_{(10)}$	124,29 (65)
$N_{(1)}-C_{(10)}$	1,436 (10)	$C_{(13)}N_{(2)}C_{(12)}$	120,32 (65)
$N_{(1)}-C_{(12)}$	1,413 (10)	$H_{(N2)}N_{(2)}C_{(12)}$	116,96 (62)
$N_{(2)}-C_{(12)}$	1,337 (11)	$H_{(N2)}N_{(2)}C_{(13)}$	121,15 (57)
$N_{(2)}-C_{(13)}$	1,519 (10)	$N_{(1)}C_{(1)}O_{(1)}$	126,58 (76)
$N_{(2)}-H_{(N2)}$	1,185 (6)	$C_{(2)}C_{(1)}O_{(1)}$	129,26 (77)
$C_{(1)}-C_{(2)}$	1,506 (11)	$C_{(2)}C_{(1)}N_{(1)}$	104,15 (65)
$C_{(2)}-C_{(3)}$	1,394 (11)	$C_{(3)}C_{(2)}C_{(1)}$	131,93 (72)
$C_{(2)}-C_{(11)}$	1,405 (11)	$C_{(11)}C_{(2)}C_{(1)}$	107,47 (66)
$C_{(3)}-C_{(4)}$	1,402 (12)	$C_{(11)}C_{(2)}C_{(3)}$	120,59 (70)
$C_{(3)}-H_{(3)}$	1,083 (8)	$C_{(4)}C_{(3)}C_{(2)}$	117,15 (73)
$C_{(4)}-C_{(5)}$	1,398 (12)	$H_{(3)}C_{(3)}C_{(2)}$	120,97 (72)
$C_{(4)}-H_{(4)}$	1,081 (8)	$H_{(3)}C_{(3)}C_{(4)}$	121,87 (74)
$C_{(5)}-C_{(6)}$	1,421 (11)	$C_{(5)}C_{(4)}C_{(3)}$	121,54 (78)
$C_{(5)}-H_{(5)}$	1,082 (8)	$H_{(4)}C_{(4)}C_{(3)}$	119,13 (78)
$C_{(6)}-C_{(7)}$	1,420 (7)	$H_{(4)}C_{(4)}C_{(5)}$	119,33 (79)
$C_{(6)}-C_{(11)}$	1,371 (11)	$C_{(6)}C_{(5)}C_{(4)}$	121,31 (74)
$C_{(7)}-C_{(8)}$	1,362 (12)	$H_{(5)}C_{(5)}C_{(4)}$	119,75 (75)
$C_{(7)}-H_{(7)}$	1,083 (9)	$H_{(5)}C_{(5)}C_{(6)}$	118,94 (72)
$C_{(8)}-C_{(9)}$	1,425 (12)	$C_{(7)}C_{(6)}C_{(5)}$	129,44 (74)
$C_{(8)}-H_{(8)}$	1,076 (8)	$C_{(11)}C_{(6)}C_{(5)}$	115,98 (71)
$C_{(9)}-C_{(10)}$	1,373 (12)	$C_{(11)}C_{(6)}C_{(7)}$	114,57 (72)
$C_{(9)}-H_{(9)}$	1,087 (8)	$C_{(8)}C_{(7)}C_{(6)}$	121,00 (77)
$C_{(10)}-C_{(11)}$	1,376 (11)	$H_{(7)}C_{(7)}C_{(6)}$	119,71 (76)
		$H_{(7)}C_{(7)}C_{(8)}$	119,29 (78)
		$C_{(9)}C_{(8)}C_{(7)}$	122,11 (78)
		$H_{(8)}C_{(8)}C_{(7)}$	118,74 (78)
		$H_{(8)}C_{(8)}C_{(9)}$	119,13 (75)
		$C_{(10)}C_{(9)}C_{(8)}$	117,14 (75)
		$H_{(9)}C_{(9)}C_{(8)}$	121,16 (75)
		$H_{(9)}C_{(9)}C_{(10)}$	121,69 (76)
		$C_{(9)}C_{(10)}N_{(1)}$	132,73 (74)
		$C_{(11)}C_{(10)}N_{(1)}$	108,17 (66)
		$C_{(11)}C_{(10)}C_{(9)}$	119,09 (74)
		$C_{(6)}C_{(11)}C_{(2)}$	123,42 (71)
		$C_{(10)}C_{(11)}C_{(2)}$	110,54 (68)
		$C_{(10)}C_{(11)}C_{(6)}$	126,02 (73)
		$N_{(1)}C_{(12)}O_{(2)}$	119,61 (75)
		$N_{(2)}C_{(12)}O_{(2)}$	125,32 (79)
		$N_{(2)}C_{(12)}N_{(1)}$	115,07 (71)
		$N_{(2)}H_{(N2)}O_{(1)}$	131,24 (36)

TABLE 3. Equations of the Planes AX + BY + CZ − D = 0 of Fragments of Molecules, Projection of Atoms from the Plane (thousandths of an Å), and Angles between Planes (deg)*

Planes	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{(11)}$	$C_{(12)}$	$C_{(13)}$	$N_{(1)}$	$N_{(2)}O_{(1)}O_{(2)}H$ $N_{(2)}$	A	B	C	D
I	11	5	2	4	6	3	23			43	3				6	−0,28	−0,71	−0,65	3,22
II		−18			−50	−11	4	9	16	9	5	−38		15		−0,31	−0,69	−0,66	3,27
III	0	−4								−5	6	−65		3	−93 13 −237	−0,30	−0,69	−0,66	3,26
IV	18	18	−13	−24	0	15	12	−4	−36	7	25	−59		14	−87 31 −227	−0,29	−0,70	−0,66	3,27
V	−21											3		−16	61 61 −89	−0,36	−0,70	−0,61	3,17
VI												0	0		99 0	−0,35	−0,73	−0,59	3,16
VII	0									0		0		28		−0,32	−0,68	−0,65	3,27

*Angles between planes: I-II 1.96, II-V 4.11, I-III 1.24, III-IV 6.25, I-IV 0.99 III-V 4.24, I-V 4.93, IV-V 4.38, II-III 0.72, VI-VII 5.02, II-IV 0.97. The following planes were constructed: $C_{(2)}-C_{(6)}$, $C_{(11)}$ (I), $C_{(6)}-C_{(11)}$ (II), $C_{(1,2,5,6,12)}N(1:2)$ (III), $C_{(2)}-C_{(11)}$ (IV), $C_{(1,12)}N_{(1)}$, $N_{(2)}$, $O_{(1)}$, $HN_{(2)}$ (V), $C_{(12-13)}$, $HN_{(2)}$ (VI), $C_{(1,10,12)}$ (VII).

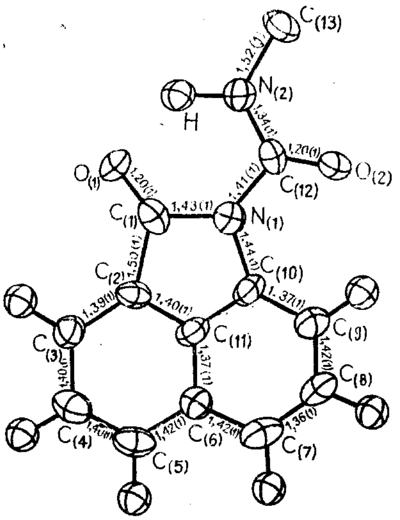


Fig. 1. Bond lengths in the molecule.

From Fig. 1 it is evident that the structure of the molecule corresponds to the structural formula I. The central bond $C_{(6)}-C_{(11)}$ is shorter than the corresponding bond in naphthalene (1.418 Å) [8]. The remaining bonds of the naphthalene fragment of the molecule under investigation are close to the corresponding values in naphthalene and in N-benzenesulfonylhydroxynaphthalimide [9]. The external bond angle $C_{(5)}C_{(6)}C_{(7)}$ is increased to 129.44 (74)°, which can be explained by the contracting effect of the added five-membered heterocycle on the geometry of the naphthalene ring, similar to that found in acenaphthene and its derivatives [10-12]. In the heterocycle the bonds $C_{(2)}-C_{(1)}$ and $C_{(10)}-N_{(1)}$, $C_{(1)}-N_{(1)}$ were localized. The bond lengths of the carbonyl groups $C_{(1)}-O_{(1)}$ and $C_{(12)}-O_{(2)}$ were the usual for aromatic compounds. The outer valence angles at the carbon atom of the carbonyl group of the heterocycle were increased in comparison with 120° [129.26 (77) and 126.58 (76)°]. The bond $C_{(12)}-N_{(1)}$ [1.413 (10) Å] was localized, while $C_{(12)}-N_{(2)}$ [1.377 (11) Å] was substantially shorter than the standard values for the bond $C_{sp^2}-N$ (1.44 Å [13, 14]), which was due to delocalization of the unshared pair of electrons of nitrogen on the $N_{(2)}-C_{(12)}$ bond.

The bond angle $O_{(2)}C_{(12)}N_{(2)}$ is 5° greater than 120° the angle next to it $N_{(1)}C_{(12)}O_{(2)}$ is the same amount less than 120°, while the angle $N_{(1)}C_{(12)}O_{(2)}$ has a normal structure. The bonds at the nitrogen atom $N_{(2)}$ deviate somewhat from a single plane (sum of the angles 358.37°, projection of the $N_{(2)}$ atom from the plane VI equal to 0.099 Å), in contrast to the bonds at the $N_{(1)}$ atom (sum of the angles 359.88°, projection of $N_{(1)}$ out of the plane VII 0.028 Å).

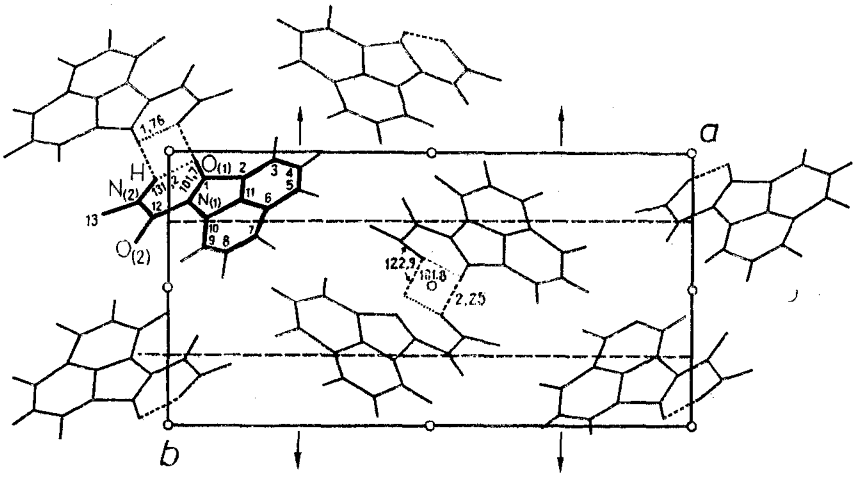


Fig. 2. Arrangement of molecules in the crystal.

The length of the bond $N_{(2)}$–$C_{(13)}$ [1.519 (10) Å] corresponds within 3δ to a single bond C_{sp^3}–N (1.48 Å). The hydrogen atoms are not ordered in the methyl group. The hydrogen atom of the methylamino group and the oxygen $O_{(1)}$ of the carbonyl group close the six-membered ring with an intramolecular hydrogen bond with a length of 1.760 Å, with the sum of the van der Waals radii 2.46 Å [15], 2.72 Å [16]. From the packing of the molecules in the crystal presented in Fig. 2, it is evident that the hydrogen atom of the methylamino group also participates in the formation of an intermolecular hydrogen bond NH•••O with a length 2.245 Å (N...O 3.059 Å). The hydrogen bond found lies within the limits of acceptable values of N•••O 2.6-3.2 Å [17] and is classed as a weak hydrogen bond. Thus, the hydrogen atom at $N_{(2)}$ participates in the formation of two hydrogen bonds and ultimately gives a forked hydrogen bond (angles $O_{(1)}HN_{(2)}$ 131.24° and $O_{(1)}HO_{(1)}$ 122.90°). The crystal is constructed from dimers formed by intermolecular bonds NH•••O, situated around the center of symmetry. To determine the real conformation of the molecule we constructed a series of planes through individual fragments of it (Table 3). The naphthalene ring of the molecule is flat within 0.04 Å (plane IV). The maximum projection from this plane (in the same direction) is observed for the atoms $C_{(12)}$ and $N_{(2)}$ (0.059 and 0.087 Å). The six-membered ring formed by the hydrogen bond (plane V) is flat within 0.06 Å; the torsional angle between the planes IV-V is equal to 4.38 Å.

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