X-RAY DIFFRACTION STUDY OF 1-BENZOYL-2-(N-ACETYL-N-PHENYLAMINO)ETHYLENE

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An x-ray diffraction study has been carried out of the photochemically inactive 1benzoy1-2-(N-acety1-N-phenylamino)ethylene  $C_{17}H_{15}NO_2$  (diffractometer,  $\lambda CuK_{\alpha}$  radiation, 1110 independent reflections, direct method, full-matrix least-squares method, R = 0.037). The crystals are monoclinic, a = 8.268(8), b = 9.703(4), c = 17.473(6)Å,  $\gamma = 83^{\circ}20'(3')$ , space group P2<sub>1</sub>/b, Z = 4. The possible reasons for the photostability of the compound related to the absence of steric strains in the molecule are discussed.

The decrease in the photochemical activity of 2-(N-acety1-N-phenylaminomethylene)-3(2H)-benzo[b]furanone Ia (X = 0) compared with <math>2-(N-acety1-N-3'-nitrophenylaminomethylene)-3(2H)-benzo[b]thiophenone Ib (X = S) was assumed [1] to be due to the decrease in the steric strains in the molecule of Ia as the result of decrease in the size of the heteroatom X.



To study the influence of steric factors on the photochemical properties of compounds in this series, we carried out the synthesis, and the photochemical and x-ray diffraction study of 1-benzoy1-2-(N-acety1-N-phenylamino)ethylene (II), i.e., an analog of I with an opened 5-membered ring and without the heteroatom X.

## EXPERIMENTAL

To obtain II, we start from 1-benzoy1-2-(N-phenylamino)ethylene (III), synthesized from benzoylacetaldehyde [2] and aniline by 10 min boiling in ether. mp 130°C. Found: C 80.5, H 6.0, N 6.2%. C15H13NO. Calculated: C 80.7, H 5.8, N 6.3%.

A 0.02 M portion of III is dissolved in a minimal amount of isopropanol and an equivalent amount of sodium isopropylate solution in isopropanol is added. The sodium salt precipitate is filtered, washed with hot hexane, and suspended in 30 ml of dry benzene, and the corresponding amount of acetyl chloride is added. After 3 h, NaCl is filtered, the solution is evaporated, and II is crystallized from a benzene—heptane mixture. Pale yellow needles. Yield 63%. mp 147°C. Found: C 76.9, N 5.2, H 5.7%.  $C_{17}H_{15}NO_2$ . Calculated: C 77.0, H 5.7, N 5.3%.

The transparent edged crystals of II are monoclinic,  $\alpha = 8.268(8)$ , b = 9.703(4), c = 17.473(6) Å,  $\gamma = 83^{\circ}20'(3')$ , space group P2<sub>1</sub>/b, V = 1392(3) Å<sup>3</sup>, M = 265.31, d<sub>calc</sub> = 1.278 g/ cm<sup>3</sup>, Z = 4. The intensities of 1110 independent reflections with I > 2 $\sigma$  type hkO-hk17 with 5.2° <  $\theta < 57.9^{\circ}$  were measured on an automatic diffractometer DAR-UM on CuK<sub> $\alpha$ </sub> radiation. The structure was solved by the direct method according to the "Roentgen-75" programs [3], and

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TABLE 1. Coordinates and Anisotropic Temperature Factors in Molecule of (II)  $\cdot 10^4$  T = exp[-(b<sub>11</sub>h<sup>2</sup> + b<sub>22</sub>k<sup>2</sup> + b<sub>33</sub>l<sup>2</sup> + b<sub>12</sub>hk + b<sub>13</sub>hl + b<sub>23</sub>kl)]

x	у	z	b11	b22	b33	$b_{12}$	b <sub>13</sub>	$b_{23}$
4063(2)	2370(2)	72(1)	288	123	35	130	16	33
1329(2)	6253(1)	1112(1)	277	119	28	-17	10	9
1751(2)	6315(2)		183	80	26	27	5	9
3330(2)	4281(2)	-732(1)	170	83	31	50	8	2
4127(2)	2872(2)	-571(1)	147	85	34	20	-26	10
5827(3)	745(2)	-1003(1)	185	89	43	34		3
6627(3)	-72(2)		213	118	49	55	3	-10
6602(3)	348(2)	-2307(2)	199	115	51	-7	40	-40
5757(3)	1604(3)	-2506(1)	240	135	38	2	19	8
4955(3)	2439(2)	-1951(1)	188	101	38	30	9	6
2602(3)	4991(2)		160	83	-33	20	-12	15
1529(2)	7058(2)	-887(1)	151	78	24	42	14	12
2426(2)	8149(2)	-1032(1)	165	96	31	31	1	13
2140(3)	8887(2)	-1702(1)	215	101	37	40	23	19
1017(3)	8541(2)	-2233(1)	195	118	30	17	$^{2}$	26
168(3)	7432(2)	-2084(1)	172	129	32	22	-30	3
389(2)	6694(2)		169	93	30	-10	6	-5
1082(2)	6868(2)	508(1)	173	97	29	-27	7	2
24(3)	8226(2)	464(1)	235	110	40	54	43	-10
	x 4063(2) 1329(2) 1751(2) 3330(2) 4127(2) 5827(3) 6602(3) 5757(3) 4955(3) 2602(3) 1529(2) 2426(2) 2140(3) 1017(3) 168(3) 389(2) 1082(2) 24(3)	x y   4063(2) 2370(2)   1329(2) 6253(1)   1751(2) 6315(2)   3330(2) 4281(2)   4127(2) 2872(2)   5827(3) 745(2)   6602(3) 348(2)   5757(3) 1604(3)   4955(3) 2439(2)   2602(3) 4991(2)   1529(2) 7058(2)   2426(2) 8149(2)   2140(3) 8887(2)   1017(3) 8541(2)   168(3) 7432(2)   389(2) 6694(2)   1082(2) 6868(2)   24(3) 8226(2)	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

TABLE 2. Coordinates  $(\times 10^{\,3})$  and Isotropic Temperature Factors of Hydrogen Atoms

Atom	x	y	z	$B_{iso}, \mathring{A}^2$
H(4)	580(3)	44(2)		4,7
H(5)	729(3)	-98(2)		4,4
H(6)	715(2)	-24(2)	-269(1)	2,2
H(7)	566(2)	190(2)	-302(1)	3,4
H(8)	444(3)	338(2)	-212(1)	4,5
H(1)	337(3)	469(2)	-127(1)	3,8
H(9)	259(2)	459(2)	37(1)	3,1
H(11)	329(2)	832(2)	63(1)	3,1
H(12)	272(3)	971(2)	-180(1)	5,5
H(13)	80(2)	905(2)	-275(1)	3,5
H(14)	-61(2)	718(2)	-246(1)	2,0
H(15)	-19(2)	585(2)	-129(1)	2,4
H(17.1)	54(3)	843(2)	92(1)	3,4
H(17.2)	-76(3)	826(3)	7(7)	4,7
H(17.3)	66(4)	898(3)	34(2)	7,7

was refined by the method of least squares in the anisotropic (nonhydrogen atoms) and isotropic (hydrogen atoms) approximation, up to R = 0.037. The general view of the molecule is shown in Fig. 1, which was prepared by the program ELLIDS [4]. The coordinates and the temperature factors of the atoms are given in Tables 1 and 2, and the bond lengths and valence angles, in Table 3.

The conformational energy of molecules of Ia, Ib, and II was calculated according to the program MOLBILD [5].\* In these calculations, a search was made for the local energy minimum, assuming that the conformation obtained from the data of x-ray diffraction analysis is a zero approximation, and taking into account the energy of bond stretching, the deformation of valence angles, torsional rotations around the bonds, and nonvalence interactions.

<sup>\*</sup>The program was submitted by Yu. T. Struchkov, and T. V. Timofeeva (Institute of Heteroorganic Compounds, Academy of Sciences of the USSR) helped in the preparation of the program, to whom the authors express their gratitude.

1	2	3	4
O(1) - C(2)	1,227(2)	C(13)-C(14)	1,376(3)
O(2) - C(16)	1,218(2)	C(14)-C(15)	1,370(3)
N-C(9)	1,391(2)	C(16) - C(17)	1,497(2)
NC(10)	1,444(2)	H(4) - C(4)	1,00(2)
N-C(16)	1,392(2)	H(5) - C(5)	1,02(2)
C(1)-C(2)	1,475(2)	H(6) - C(6)	0,95(2)
C(1) - C(9)	1,328(2)	H(7) - C(7)	0,94(2)
C(2)—C(3)	1,482(2)	II(8)C(8)	1,01(2)
C(3) - C(4)	1,400(2)	H(1)-C(1)	1,02(2)
C(3) - C(8)	1,385(3)	H(9) - C(9)	1,00(2)
C(4) - C(5)	1,372(3)	H(11) - C(11)	1,02(2)
C(5) - C(6)	1,370(3)	H(12)-C(12)	0,99(3)
C(6) - C(7)	1,378(3)	H(13) - C(13)	1,03(2)
C(7) - C(8)	1,382(3)	H(14) - C(14)	0,97(2)
C(10) - C(11)	1,384(2)	H(15) - C(15)	1,02(2)
C(10) - C(15)	1,394(2)	H(17.1) - C(17)	0,95(2)
C(11) - C(12)	1,377(2)	$\Pi(17.2) - U(17)$	0,94(2)
C(12) - C(13)	1,382(3)	H(17.3) - C(17)	0,98(3)
C(9)NC(10)	120,2(2)	H(5)C(5)C(4)	119(1)
C(9)NC(16)	118,1(2)	H(5)C(5)C(6)	120(1)
C(10)NC(16)	121,7(2)	H(6)C(6)C(5)	120(1)
C(2)C(1)C(9)	117,5(2)	H(6)C(6)C(7)	121(1)
O(1)C(2)C(1)	120,5(2)	H(7)C(7)C(6)	122(1)
O(1)C(2)C(3)	119,4(2)	H(7)C(7)C(8)	118(1)
C(1)C(2)C(3)	120,1(2)	H(8)U(8)U(3)	122(1)
C(2)C(3)C(4)	118,4(2)	$\Pi(0)\cup(0)\cup(1)$	420(4)
U(2)U(3)U(8)	123,7(2)	H(1)C(1)C(2)	120(1) 122(1)
C(4)C(3)C(8)	117,9(2)	H(1)C(1)C(3) H(0)C(0)N	110(1)
O(3)O(4)O(3) O(4)O(5)O(6)	120,0(2) 420,0(2)	H(9)C(9)C(1)	122(1)
C(4)C(3)C(0) C(5)C(6)C(7)	120,9(2)	H(14)C(14)C(10)	116(1)
C(6)C(7)C(8)	119, 5(2) 120, 1(2)	H(11)C(11)C(12)	125(1)
C(3)C(8)C(7)	120,1(2) 121,1(2)	H(12)C(12)C(11)	120(1)
C(1)C(9)N	127,7(2)	H(12)C(12)C(13)	119(1)
NC(10)C(11)	119,4(2)	H(12)C(12)C(13) H(13)C(13)C(12)	123(1)
NC(10)C(15)	119,8(2)	H(13)C(13)C(14)	118(1)
C(11)C(10)C(15)	120,7(2)	H(14)C(14)C(13)	119(1)
C(10)C(11)C(12)	118,6(2)	H(14)C(14)C(15)	120(1)
C(11)C(12)C(13)	121,6(2)	H(15)C(15)C(10)	117(1)
C(12)C(13)C(14)	118,8(2)	H(15)C(15)C(14)	124(1)
C(13)C(14)C(15)	121,4(2)	H(17.1)C(17)C(16)	111(1)
C(10)C(15)C(14)	119,0(2)	H(17.1)C(17)H(14)	107(2)
O(2)C(16)N	121,0(2)	H(17.1)C(17)H(15)	109(2)
O(2)C(16)C(17)	121,6(2)	H(17.2)C(17)C(16)	113(1)
NC(16)C(17)	117,4(2)	H(17.2)C(17)H(15)	104(2)
H(4)C(4)C(3)	118(1)	H(17.3)C(17)C(16)	111(2)
H(4)C(4)C(5)	122(2)		
		l	1

TABLE 3. Bond Lengths and Valence Angles in Molecule of (II)

## DISCUSSION OF RESULTS

The molecules of II in the crystal are bound in pairs through a center of inversion by H-bonds  $O_2 \dots H_{15}$  '- $C_{15}$ ' and  $O_2' \dots H_{15}$ - $C_{15}$  (0...H 2.17 Å).

The molecule has a ketoamine structure with a Z-configuration with respect to the  $C_1=C_9$ bond, similar to the structure of Ia and Ib. The molecule is planar because of the stabilization of this configuration by an intramolecular H-bond  $O_2...H_9-C_9$  (O...H 2.23 Å), and the Nphenyl substituent is inclined away from the plane by 76°, and is located in the s-cis-position with respect to the  $C_1=C_9$  bond. The Ac group occupies the trans-position in the plane of the



Fig. 1. General view of molecule of II with thermal ellipsoids of nonhydrogen atoms corresponding to 50% probability. The hydrogen atoms are represented by circumferences with a radius of 0.15 Å.

molecule. The rotation of the Ph ring away from the plane of the molecule by even  $76.0^{\circ}$  increases the intramolecular nonvalence distances of  $C_{10}...H_1$ ,  $C_{15}...H_1$ , and  $C_{11}...H_1$  to normal values for C...H contacts of 2.68, 2.97, and 3.38 Å, respectively; the molecule of II, in contrast to Ia and Ib, is sterically unstrained. Its calculated conformational energy is not more than 2.2 kcal/mole, while for Ia it is equal to 4.7 and for Ib to 9.0 kcal/mole. The increase in the conformational strains in Ia and Ib is due mainly to increase in nonvalence interactions between the heteroatom X and the Ph substituent. The decrease in steric strains in the molecule of compound II is accompanied by a sharp decrease in its photochemical activity, which confirms our supposition [1] on the influence of steric factors on the photochemical properties of compounds of this class.

Within the experimental error, the bond lengths in the molecule of II coincide with similar values in Ia and Ib. However, the N-Ac bond shows a tendency to shorten on transition from Ib to Ia and II: 1.425(5), 1.415(4), and 1.392(2) Å, respectively. At the same time, the length of this bond remains more typical of the length of an amide bond (1.325 Å [6]), which in fact, it formally is. This elongation of the amide bonds in Ia, Ib, and II, indicates a weakening in the conjugation of the unshared electron pair with the  $\pi$ -system of the C<sub>16</sub>=O<sub>2</sub> carbonyl group, probably because of the competing interaction of this pair with the  $\pi$ -system of the neighboring C<sub>1</sub>=C<sub>9</sub> bond. The elongation of the amide bonds was also detected in 2benzoyl-2-phenylazoindane-1,3-diones that exhibit a thermal acetyl rearrangement [7].

Thus, our study has shown that the possible photoinitiated N  $\rightarrow$  0 acylotropic rearrangement in compounds of type I and II is largely explained by the presence of a weakened N-Ac amide bond in the molecules, which on photoexcitation of these molecules can be cleaved.

As already noted in [1, 8], compounds I and II are structurally unsuitable for  $N \rightarrow 0$ phototransfer of the acyl group. However, the steric strains in the molecule of Ia and Ib appreciably increase their conformational energy and increase the tendency towards a conformation withmore closely located N- and O-nucleophilic centers. In the ground state, these molecules are stabilized by the strong delocalization of the electron density in the plane of the molecule. The photoexcitation of the molecules breaks down the conjugated system, as shown by the data of quantum-chemical calculations [9], indicating a decrease in the order of the  $C_1=C_9$  bond in the singlet excited state. Therefore, in the excited state, the determining factors are the conformational ones, which cause a rearrangement of the molecules, decreasing their conformational energy and the distance between the N- and O-nucleophilic centers. In the molecule of compound II, there are no steric strains, and the N-Ac bond is the strongest bond, which also causes its photostability. Increase in the steric strains and weakening of the N-Ac bond in the series II < Ia < Ib lead to an increase in the photochemical activity of compound Ia and especially Ib, which is the most effective photochrome [8]. Further increase in the steric strains in the molecule should lead to further increase in the photochemical activity.

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BIPOLAR STRUCTURE OF 2-(N-4-METHOXYPHENYLAMINOMETHYLENE)-1,3-INDANEDIONE

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An x-ray study has been carried out of 2-(N-4-methoxyphenylaminomethylene)-1,3indanedione  $C_{17}H_{13}NO_3$  (diffractometer,  $CuK_{\alpha}$ -radiation, 1016 independent nonzero reflections, direct method, anisotropic least-squares method up to R = 0.038). The crystals are monoclinic,  $\alpha = 25.725(9)$ , b = 27.890(6), c = 3.856(2) Å,  $\gamma = 73.48'(3')$ , space group B2/b, Z = 8,  $d_{calc} = 1.404 \text{ g/cm}^3$ . It was shown that the compound has a planar structure, stabilized by intramolecular hydrogen bonds, which is correctly described by a bipolar structure.

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The absence of photochromic properties in 2-(N-phenylaminomethylene)-3(2H)benzo[b]furanone (I) may be due to the fact that its molecules are structurally unsuitable for N  $\rightarrow$  0 prototropic rearrangements [1].



Replacement of the oxygen atom in the 5-membered heterocyclic ring by carbonyl groups produces more favorable structural conditions for this rearrangement. In accordance with the program of further studies of the tautomeric properties [2], we carried out photochemical and x-ray diffraction studies of one of these compounds, 2-(N-4-methoxyphenylaminomethylene)-1,3-indanedione II.

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