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The Influence of Molecular and Crystal Structure on the Character of Photoconversions in the Crystals of C-(2-naphthyl-1-vinyl)-N-n-methylphenyl Nitrone and C-(2-naphthyl-1-vinyl)-N-phenyl Nitrone

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The Influence of Molecular and Crystal Structure on the Character of Photoconversions in the Crystals of C-(2-naphthyl-1-vinyl)-*N*-*n*-methylphenyl Nitrone and C-(2-naphthyl-1-vinyl)-*N*-phenyl Nitrone

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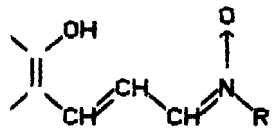
An X-ray study of the crystals of C-(2-naphthyl-1-vinyl)-*N*-*n*-methylphenyl nitrone (I) and C-(2-naphthyl-1-vinyl)-*N*-phenyl nitrone (II) has been performed. The main crystal data of I: $C_{20}H_{17}NO_2$. a = 15.937(7) Å, b = 13.240(9) Å, c = 8.000(7) Å, γ = 74.3(2)°, M = 303.84, V = 1688(1) Å^3, d_{calc} = 1.195(3) g/cm^3, Space gr. $P2_1/b$, Z = 4. The main crystal data of II: $C_{19}H_{15}NO_2 \times 1/2H_2O$, a = 26.428(11) Å, b = 17.504(6) Å, c = 6.657(2) Å, γ = 97.3(2)°, M = 298.02, V = 3053(1) Å^3, d_{calc} = 1.296(2) g/cm^3, Space gr. B2/b, Z = 8.

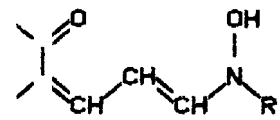
Compound II forms a crystallohydrate of the 1:1 composition. The crystal structure of I and II has centrosymmetric dimeric association formed due to strong intermolecular hydrogen bonds (IMHB). The presence of strong IMHB accounts for the possibility of photochemical intermolecular proton transfer and formation of the coloured quinoid form as distinct from formation of the oxaziridine type known for nitrone derivatives from literature.

INTRODUCTION

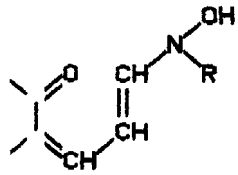
The photochemical reaction of the molecules of aldonitrone vinylogs in solutions are known[1–3] to be connected with non-barrier irreversible diabatic formation of oxaziridine in the singlet state typical for nitrones and an *E*-, *Z*-photoisomerization in the triplet state relative to the C=N bond.[3,4] It has been established[1,3] that an introduction of an *o*-OH-group in the α-aryl nucleus in the molecules of aldonitrones vinylogs (A) leads to thermally reversible photoinduced processes to give short-lived isomeric quinoid structure (B1, B2) and a chromene structure (C).



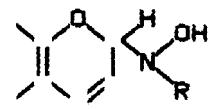
A



B1

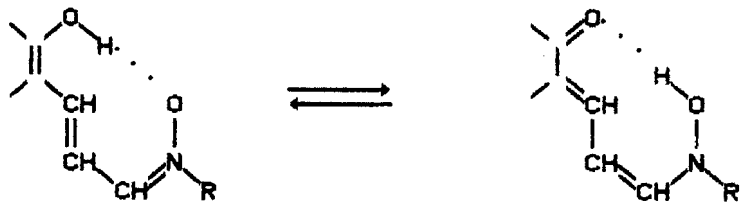


B2

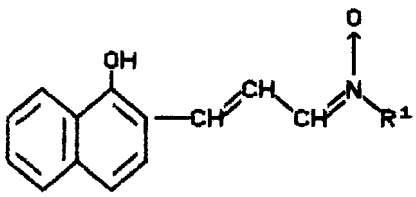


C

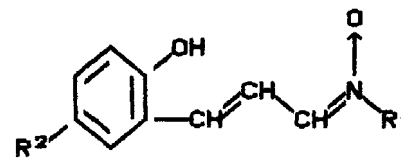
In Reference 3 the processes of proton transfer are presented in a scheme:



To study in detail the structure and photochemical conversions in the crystals of aldonitrones vinylogs we have performed a detailed spectral, luminescent and photochemical study of I–IX nitrones in solid state and an X-ray study of I and II.



I - I V



V - I X

I R^1=PhMe—p; II R^1=Ph; III R^1=$CHMe_2$; IV R^1=Me; V R^1=PhBr—p, R^2=H; VI R^1=PhMe—p, R^2=Br; VII R^1=PhMe—p, R^2=H; VIII R^1=Ph, R^2=H; IX R^1=Me, R^2=H.

EXPERIMENTAL

Compound I crystallizes as light-yellow plates of monoclinic syngony. The main crystal data of I: $C_{20}H_{17}NO_2$, a = 15.937(7) A^0, b = 13.240(9) A^0, c = 8.000(7)

A^0, γ = 74.3(2)^0, M = 303.84, V = 1688(1) A^{03}, d_{calc} = 1.195(3) g/cm^3, space gr. $P2_1/b$, Z = 4.

Compound II crystallizes as red plates of irregular form of monoclinic syngony. The main crystal data of II: $C_{19}H_{15}NO_2 \times 1/2H_2O$, a = 26.428(11) A^0, b = 17.504(6) A^0, c = 6.657(2) A^0, γ = 97.3(2)^0, M = 298.02, V = 3053(1) A^{03}, d_{calc} = 1.296(2) g/cm^3, space gr. B2/b, Z = 8.

The integral intensities of 735 independent reflections from crystal I ($I > 2\sigma(I)$) of the hk0-hk7 type in the range of $1.6° < \theta < 46.3°$ were obtained on an automatic three-circle diffractometer DAR-UM (CuK_α-radiation) with graphite monochromator by $\omega - \omega/2\omega$ layer registration.

The integral intensities of 1627 independent reflections of crystal II ($I > 2\sigma(I)$) were obtained on an automatic four-circle diffractometer KM-4 (MoK_α-radiation). X-ray absorption in crystals was not taken into consideration. Structures I and II were solved by a direct method by a complex of programs "SHELL-76"[5] and "SHELL-86"[5] and refined by a full-matrix least-squares technique in anisotropic approximation (nonhydrogen atoms). Hydrogen atoms for I and II were defined in a difference Fourier synthesis. The final values of R-factor for I and II are 0.055 and 0.055. Atomic coordinates for I and II are given in Tables I and II, respectively.

Calculation of the energy of intermolecular interactions was made in the frame work of atom-atom approximations using "6-exp" potentials with parameters given in Reference 6.

Reflectance spectra of crystalline powder samples were obtained on a "Specord M40" spectrophotometer with an attached instrument to measure geometry 8°/d. Impulse photolysis spectra were obtained with a flash-photolysis lamp.[7] To carry out photochemical investigations a radiation source on the basis of a DRShch-250 lamp was used supplied with a set of light filters.

DISCUSSION

The photochemical reactions of nitrones I–IX in the solid state are irreversible and detected by a visually observed coloured form. To determine the mechanism of these photoinitiated conversions we have studied the reflectance spectra of crystalline powder samples in the visible region before and after irradiation by photoactive light.

When the crystals of nitrone I are irradiated, the reflectance spectra show decreased intensities in the range of 520–600 nm, which is evidently connected with appearance of the form which absorbs in this region of the spectrum (Figure 1). In solutions of hydroxyaldonitrones, this absorption leads to an appearance of a short-lived trans-isomer (B2).[1,3] In particular, an impulse photolysis of a nitrone I solution in toluene leads to an absorption band at 560 nm and a life time ca.10^{-1} s (Figure 1). As distinct from solutions, in the solid state the colouring is irreversible.

A general view of molecules I and II is given in Figures 2 and 3, respectively. Both molecules are non-planar. The nonplanarity of I and II is explained by a turn of a naphthalene fragment about the C^3—C^4 bond by 13.5(2)^0, 18.1(2)^0 and a turn of a phenyl fragment about the N^1—C^{14} bond by 39.3(3)^0, 22.9(2)^0 in opposite directions.

TABLE I

Coordinates of nonhydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) in molecule $C_{19}H_{17}NO_2$

Atom	X	Y	Z
O^1	3949(4)	6643(3)	92(7)
O^2	6298(4)	4978(3)	719(7)
N^1	4505(5)	7241(4)	1094(8)
C^1	5424(6)	7229(4)	1698(10)
C^2	5942(6)	6579(5)	1350(10)
C^3	6872(6)	6640(5)	2127(11)
C^4	7577(6)	6105(5)	2072(9)
C^5	7283(7)	5277(5)	1383(11)
C^6	7945(6)	4693(5)	1490(12)
C^7	8899(7)	4992(6)	2179(11)
C^8	9249(7)	5826(6)	2867(11)
C^9	10255(8)	6134(8)	3596(15)
C^{10}	10586(9)	6939(9)	4249(14)
C^{11}	9936(9)	7499(6)	4124(12)
C^{12}	9005(7)	7226(6)	3435(12)
C^{13}	8571(6)	6383(5)	2790(11)
C^{14}	4039(7)	7959(5)	1365(9)
C^{15}	4654(7)	8799(6)	1475(10)
C^{16}	4178(8)	9474(5)	1650(10)
C^{17}	3140(9)	9303(7)	1737(10)
C^{18}	2584(10)	10001(7)	1879(14)
C^{19}	2528(6)	8468(7)	1816(10)
C^{20}	2968(7)	7781(6)	1635(9)
H^1	552(4)	780(3)	196(6)
H^2	552(4)	695(3)	248(6)
H^3	707(4)	714(3)	238(6)
H^6	737(4)	416(3)	75(6)
H^7	945(4)	472(3)	234(6)
H^9	1055(4)	572(4)	377(4)
H^{10}	1124(4)	712(3)	465(6)
H^{11}	1031(4)	816(3)	463(6)
H^{12}	845(4)	762(4)	315(4)
H^{15}	550(4)	897(3)	138(6)
H^{16}	469(4)	1015(3)	159(6)
$H^{18.1}$	295(4)	1048(3)	283(6)
$H^{18.2}$	269(4)	1037(3)	118(6)
$H^{18.3}$	197(4)	981(3)	163(6)
H^{19}	180(4)	815(3)	185(6)
H^{20}	281(4)	710(3)	122(6)

TABLE II

Coordinates of nonhydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) in molecule $C_{19}H_{17}NO_2 \times 1/2H_2O$

Atom	X	Y	Z
O^1	708(0)	1687(1)	- 147(3)
O^2	- 520(0)	- 333(1)	-1676(3)
O^W	0(0)	2500(0)	2072(4)
N^1	769(0)	1877(1)	-2071(3)
C^1	436(1)	1614(1)	-3445(4)
C^2	1(1)	1070(1)	-3082(4)
C^3	- 302(1)	829(1)	-4648(4)
C^4	- 748(1)	258(1)	-4713(4)
C^5	- 850(1)	- 298(1)	-3234(4)
C^6	-1292(1)	- 852(2)	-3313(4)
C^7	-1629(1)	- 847(2)	-4876(5)
C^8	-1536(1)	- 306(1)	-6439(4)
C^9	-1887(1)	- 313(2)	-8046(5)
C^{10}	-1797(1)	191(2)	-9605(5)
C^{11}	-1353(1)	718(2)	-9600(4)
C^{12}	-1007(1)	745(1)	-8046(4)
C^{13}	-1090(1)	241(1)	-6403(3)
C^{14}	1235(1)	2379(1)	-2549(4)
C^{15}	1639(1)	2393(2)	-1227(5)
C^{16}	2098(1)	2849(2)	-1693(6)
C^{17}	2150(1)	3287(1)	-3387(6)
C^{18}	1740(1)	3274(1)	-4654(5)
C^{19}	1282(1)	2820(1)	-4284(4)
H^1	52(1)	180(2)	- 488(4)
H^2	- 4(1)	82(2)	- 179(5)
H^3	- 20(1)	109(2)	- 592(4)
H^6	- 131(1)	- 133(2)	- 197(5)
H^7	- 195(1)	- 126(2)	- 495(5)
H^8	- 220(1)	- 69(2)	- 796(5)
H^{10}	- 206(1)	17(2)	-1078(6)
H^{11}	- 129(1)	106(2)	-1055(5)
H^{12}	- 69(1)	113(1)	- 803(4)
H^{15}	160(1)	212(2)	29(4)
H^{16}	243(1)	286(2)	- 84(5)
H^{17}	248(1)	366(2)	- 370(4)
H^{18}	178(1)	355(2)	- 575(5)
H^{19}	96(1)	283(2)	- 524(5)
H_{O2}	- 54(1)	- 85(1)	- 60(3)
H_W	23(1)	228(2)	126(5)

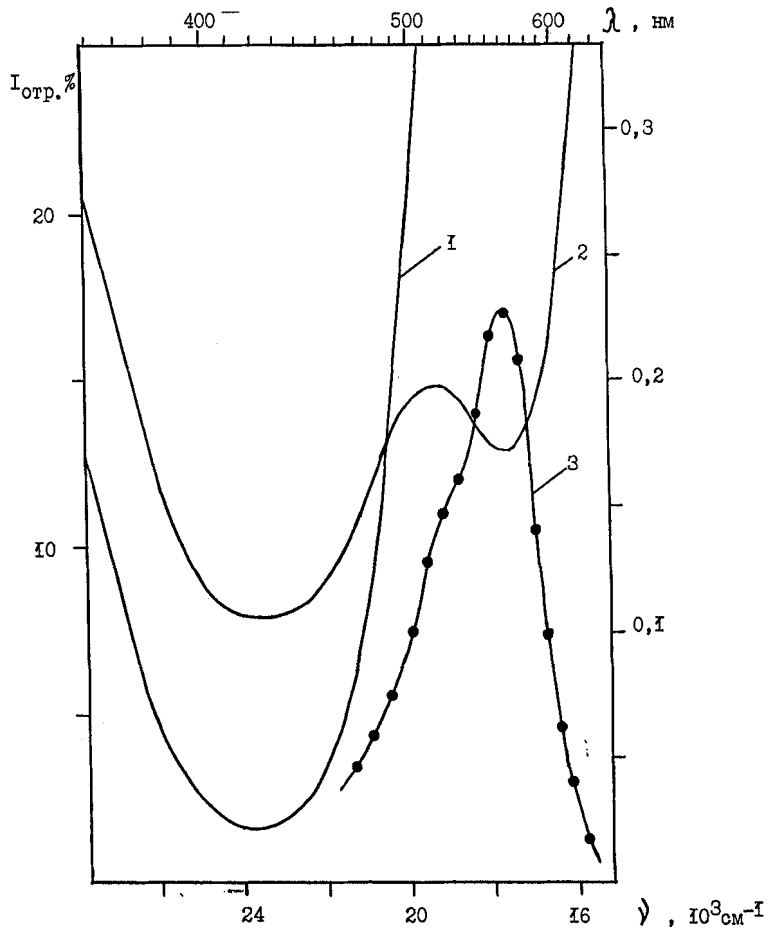


FIGURE 1 Reflectance spectrain nitrone I in the solid state, 1, 2 before and after irradiation (λ_{irr} = 365 nm), respectively; the photoinduced absorption spectrum of nitrone I registered 10^{-5} s after the photolytic lamp impulse ($c = 1.5 \times 10^{-6}$ mol/l, toluene) – 3.

The central vinyl nitrone fragment II, as distinct from I, is non-planar. Its non-planarity is explained by a turn about the C^1—C^2 bond by 7.6(3)^0.

The bond lengths and angles characteristic of the nitrone group are given in Table III. The obtained values coincide with the literature data.[8,9]

The projections of crystal packings of molecules I and II on the XYO plane are shown in Figures 4 and 5, respectively. The characteristic feature of the crystal structures under study is formation of centrosymmetric dimer associates owing to stable intermolecular hydrogen bonds between a hydrogen hydroxyl atom and an oxygen nitrone atom of another molecule. The main geometric parameters of intermolecular hydrogen bonds for I and II are given in Table IV.

As distinct from I, compound II forms a crystalline hydrate of the 1:1/2 composition. The water molecule is in a particular position on the C_2 axis and participates in formation of additional IMHB with oxygen nitrone atoms of the neigh-

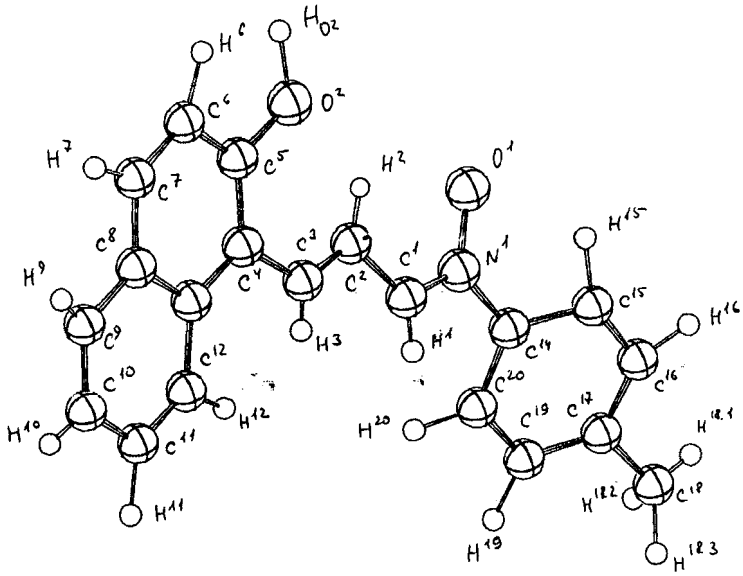


FIGURE 2 A general view of molecule I.

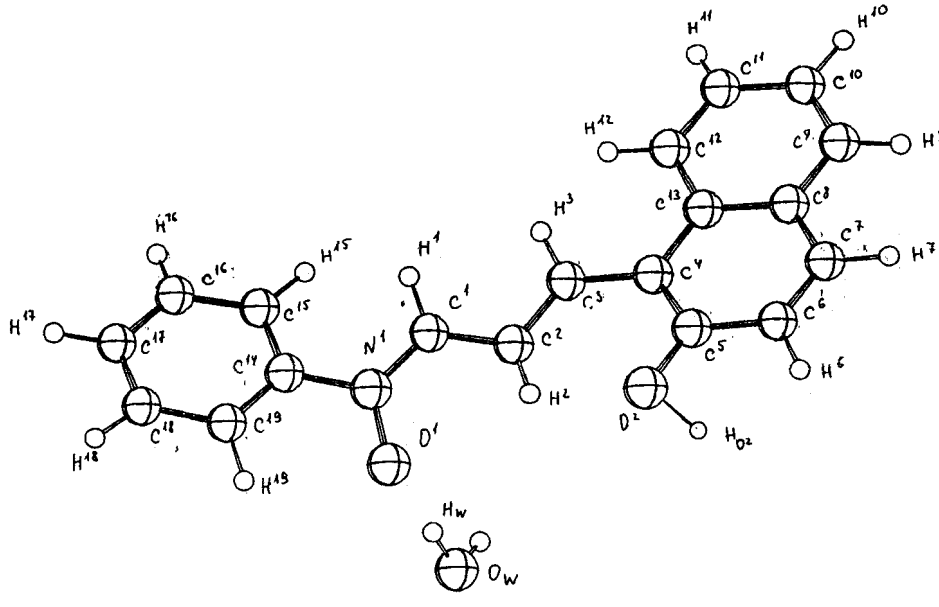


FIGURE 3 A general view of molecule II.

TABLE III

	N^1-O^1	$>C^1=N^1$	N^1-C^{14}	$C^1N^1O^1$	$O^1N^1C^{14}$	$C^1N^1C^{14}$
I	1.313(7)	1.313(10)	1.451(11)	124.0(7)	112.9(6)	122.9(6)
II	1.308(3)	1.312(3)	1.454(4)	121.7(4)	115.5(5)	122.8(3)
[8-9]	1.266÷ ÷1.308	1.270÷ ÷1.357	1.438÷ ÷1.511	120.3÷ ÷126.3	113.4÷ ÷116.0	118.0÷ ÷123.0

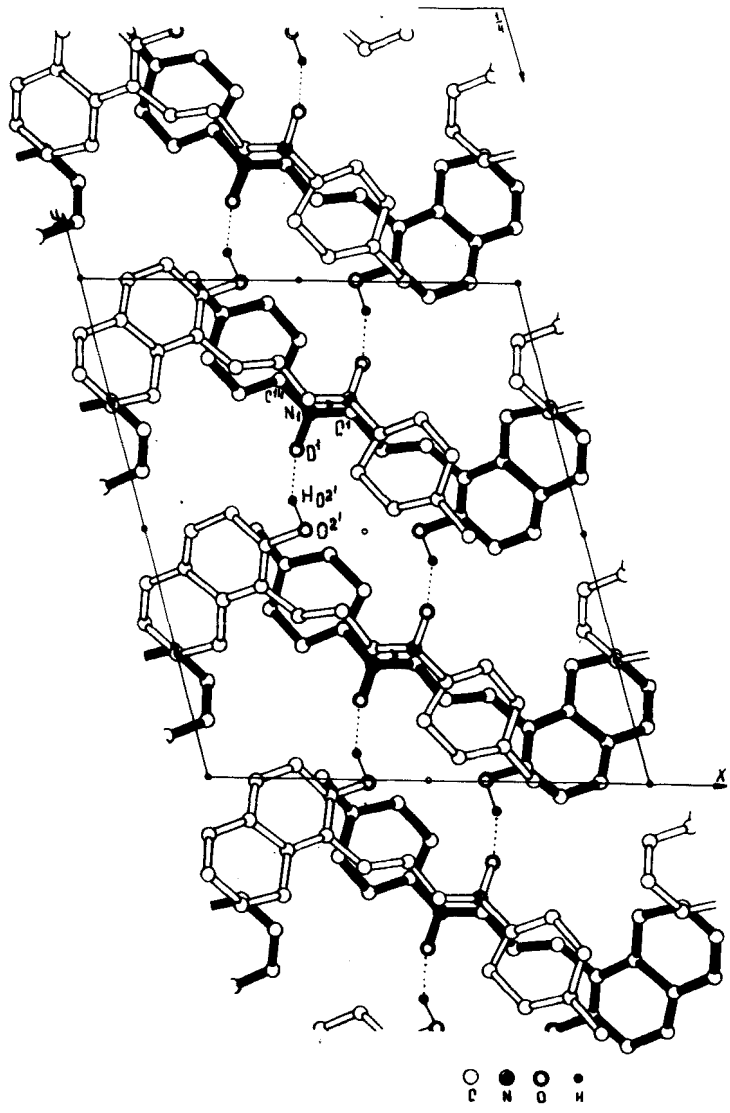


FIGURE 4 Projection of a crystal packing of molecules I on the XYO plane.

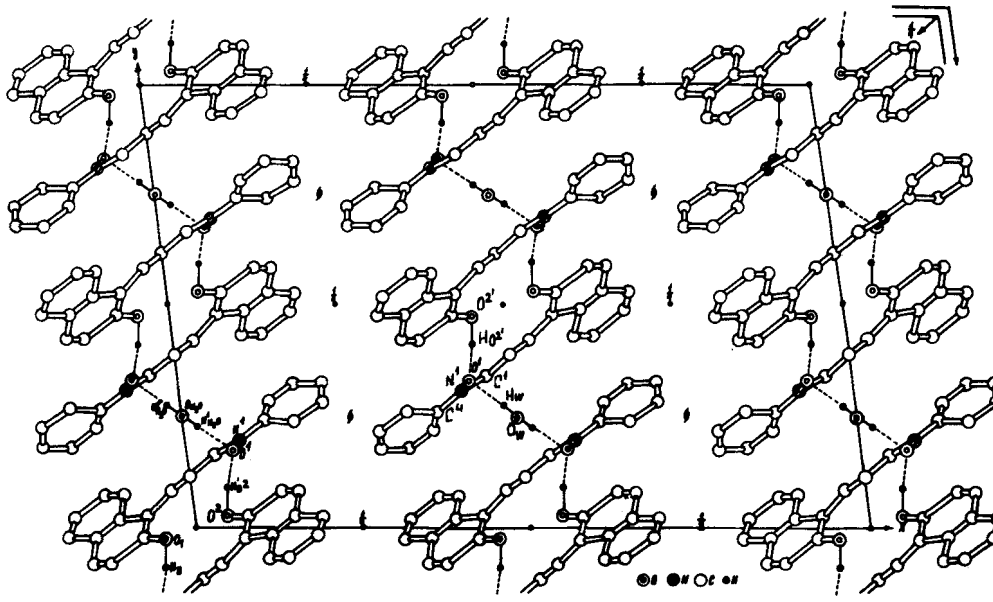


FIGURE 5 Projection of a crystal packing of molecules II on the XYO plane.

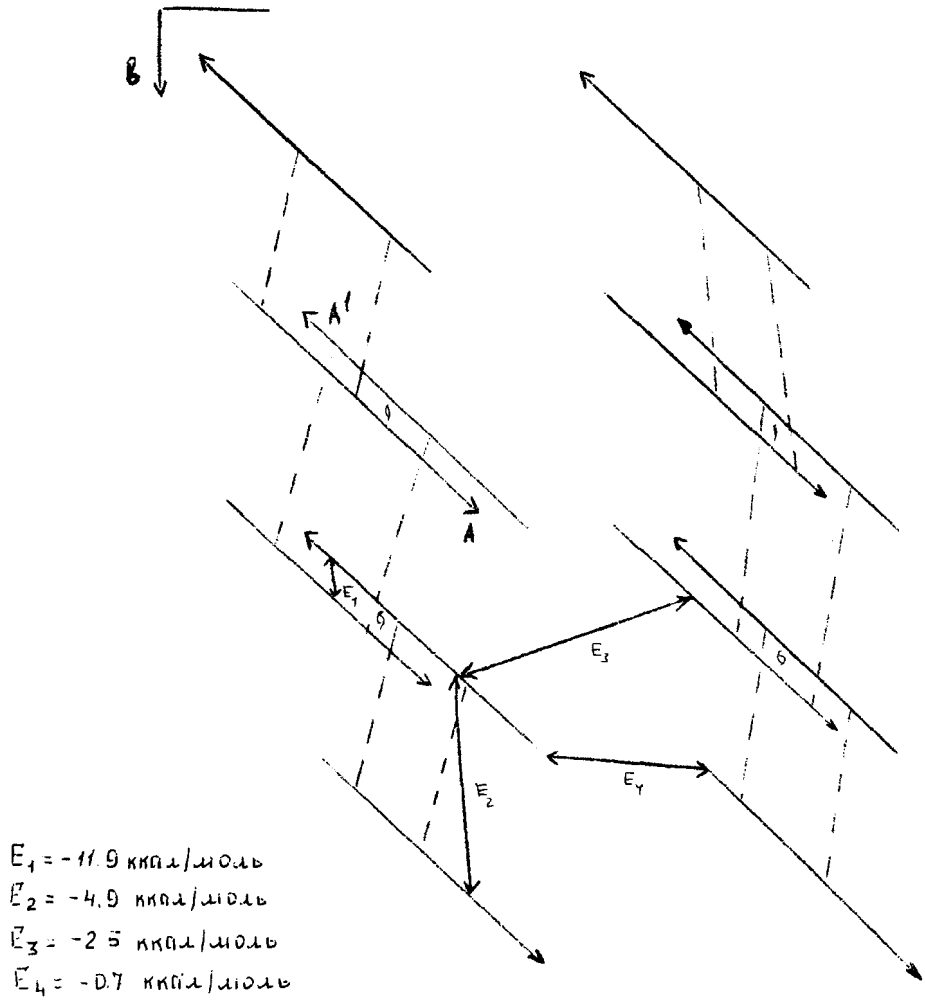
TABLE IV

	$O^1 \ldots O^{2'}$	$O^1 \ldots H_{O^2}$	$O^1H_{O^2}O^{2'}$	$N^1O^1H_{O^2}$
I	2.580(3)	1.44(3)	180(1)	140(1)
II	2.651(3)	1.53(3)	156.0(3)	123.7(3)

boring dimer associates: $O^1 \ldots H_W$ = 1.93(4) Å, $O^1 \ldots O_W$ = 2.894(2) Å, $O^1H_WO_W$ = 169(5)^0, $H_WO^1N^1$ = 113(3)^0, atoms H_W and O_W are a 2.54 Å and 1.94 Å out of the plane drawn through atoms O^1, C^1, C^{14}, the angle between the $O_W - H_W$ direction and the above lane is 63(3)^0 (Figure 5). The presence of crystallohydrate water molecules results in a considerable change in the IMHB geometric parameters in II, as compared with I. Atom H_{O^2} is 0.34 Å out of the plane O^1, C^1, C^{14} for I and 0.93 Å for compound II (Figures 4 and 5). The angle between the $O^1 \ldots H_{O^2}$ direction and the above mentioned plane is 14.3° for I and 36.8° for II. The hydrogen hydroxyl atom in compound I is in the nitrone group plane, while in compound II it is off this plane: the torsion angle $C^6C^5O^2H_{O^2}$ in I is 1.6°, while in II it is 12.0°. The values of angle $H_{O2}O^1N^1$ (123.7(4))^0 and $O^1H_{O^2}O^2$ (156(1)^0) in II and the $O^1 \ldots H_{O^2}$ contact (1.53(3) Å) testify for a less favorable IMHB, as compared with I, where these values are 140.0(7)^0, 180(1)^0 and 1.44(3) Å, respectively (Table IV).

Formation of crystallohydrate in II leads to a considerable difference in the way of mutual packing of the dimer associates. In crystals I, the dimer associates are

stacked by the "head-to-head" principle. The stacks here are formed by molecules A and A^1 connected by a screw axis and belonging to different dimer associates that are connected by a sliding plane along the *b* axis (Scheme I). Therefore, the molecular stacks in crystals I appear to be connected by strong IMHB in blocks along the *b* axis. The energy of intermolecular interactions in stacks (I) is the same and equal to -11.9 kcal/mol (Scheme I). In crystals II, the dimer associates are also packed in stacks A, A^1 by the "head-to-tail" type, the stacks being connected by stable IMHB in blocks. Besides, these blocks are connected with each other by water molecules that form stable IMHB with the molecules of the neighboring blocks. As a result, stable three-dimensional IMHB frameworks are formed in crystals II. The pair IMHB in stacks A, A^1 account for -14.5 kcal/mol. The conjugated IMHB E_2, E_3 in the block and E_4 between the molecules of the neigh-



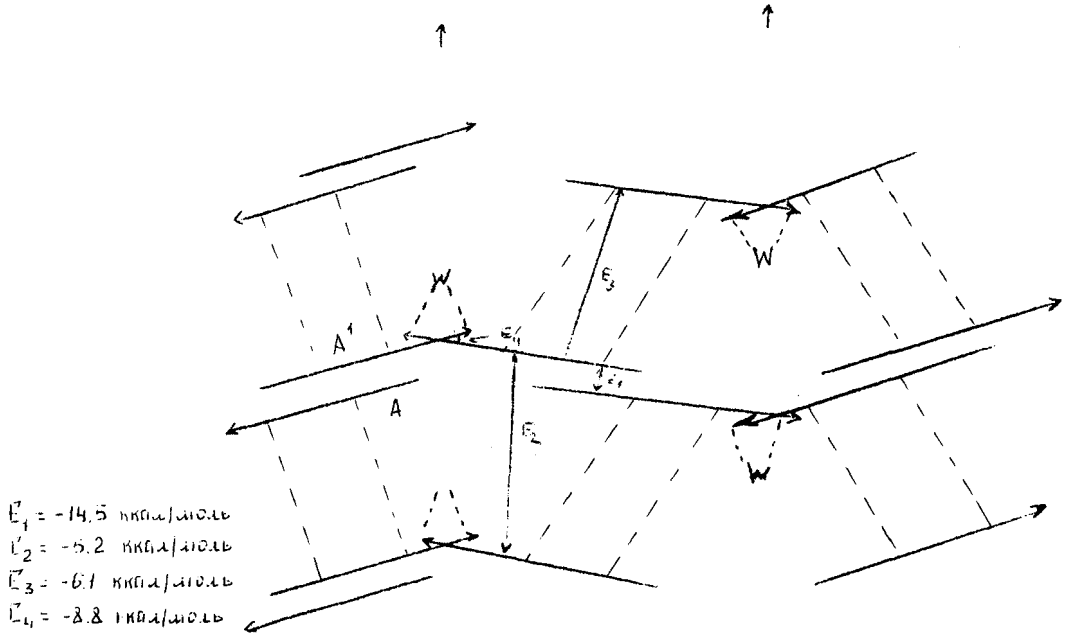
SCHEME I

boring blocks are −5.2, −6.1, and −8.8 kcal/mol in compound II and −4.9, −2.5, −0.7 kcal/mol in compound I. (Schemes I and II).

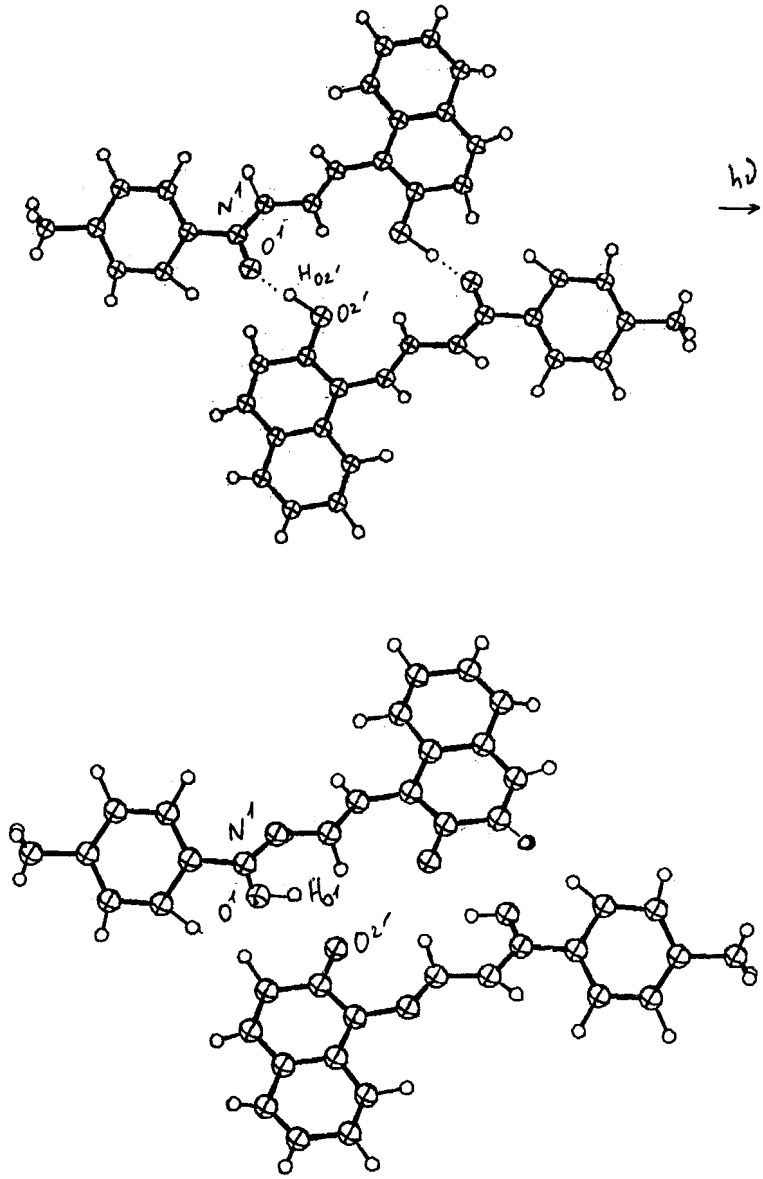
The found peculiarities of the crystal structures I and II allow us to believe that the photochemical conversions in their crystals are due to a synchronous intermolecular proton transfer in the dimer associates. Stable IMHB in the dimer associates ensure a low O→O barrier of proton transfer to give coloured quinoid forms. Geometric modelling of proton transfer in the dimer associates shows significantly weakened IMHB in the quinoid associates formed after proton transfer which is due to an increase of $H_{O^1} \ldots O^2$ up to 1.90 Å in I and 2.14 Å in II and a strong distortion of the $O^1H_{O^1}O^2$ angle approximately to 125° in I and 111° in II (Scheme III). All of this would evidently hinder the back proton transfer. In view of this fact the photoconversions in crystals I and II will have an irreversible character.

Photoconversions of nitrones I and II in solution proceed, as was mentioned,[3] not through the oxaziridine cycle closure common for all of the other compounds of this class, but through formation of structures B1 and B2. The formation of B1 and B2 was assumed to proceed due to an intermolecular proton transfer through the $O^1 \ldots O^2$ line. However, the structure of the initial molecules with a strong intramolecular hydrogen bond for I and II is hardly possible and can take place only in a non-planar molecule with orthogonal π-bonds for the values of torsional angles shown in Figure 6. In the planar molecule, the intramolecular distances are $O^1 \ldots O^2 = 3.617$ Å, $O^1 \ldots H_{O^2} = 2.505$ Å (Figure 7).

Solutions I and II may also have dimer associates, and the photoprocess in solutions, as well as in crystals, is intermolecular.



SCHEME II



SCHEME III

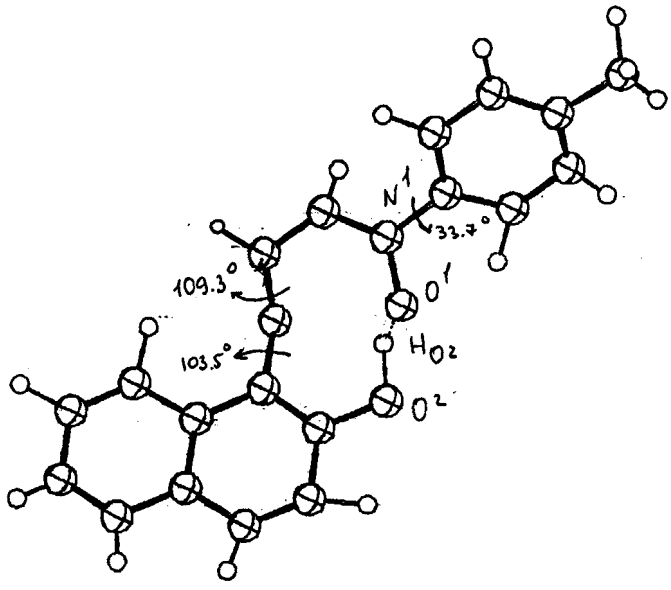


FIGURE 6 A model of intramolecular hydrogen bond in a nonplanar molecule I.

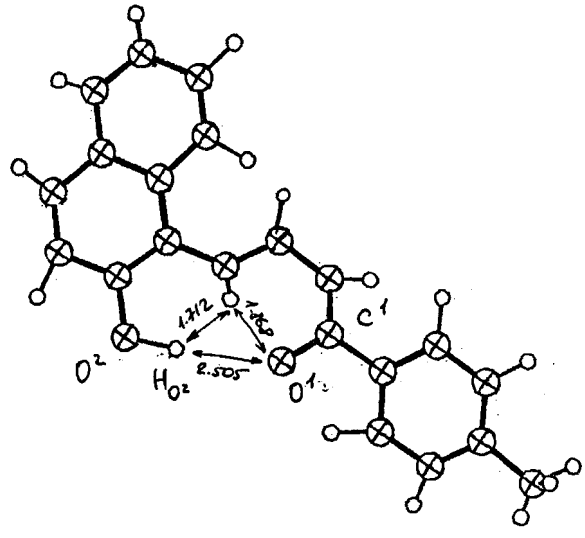


FIGURE 7 A model of intramolecular hydrogen bond in a planar molecule I.

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