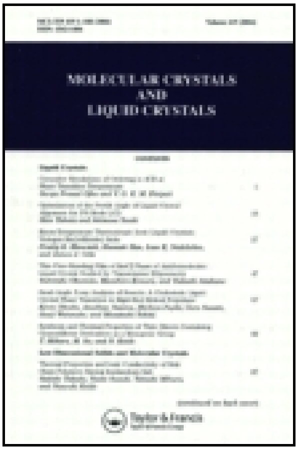

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Some Specific Features of the Formation of Hydrogen Bonds in Photosensitive Crystals

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Version of record first published: 04 Oct 2006.

To cite this article: A. N. Utenyshev & S. M. Aldoshin (1996): Some Specific Features of the Formation of Hydrogen Bonds in Photosensitive Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 281:1, 251-265

To link to this article: http://dx.doi.org/10.1080/10587259608042249

Mol. Cryst. Liq. Cryst., 1996, Vol. 281, pp. 251–265
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Some Specific Features of the Formation of Hydrogen Bonds in Photosensitive Crystals

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(Received October 12, 1994; in final form October 12, 1994)

The crystal structures of new substituted photosensitive azomethine N-oxides (nitrones): C-(2-phenoxy-1-vinyl)-N-*p*-methyl-phenyl nitrone (1), C-(3-bromo-6-phenoxy-1-vinyl)-N-*p*-methyl-phenyl nitrone (2), C-(3-bromo-6-phenoxy-1-vinyl)-*p*-phenyl nitrone (3) and C-(2-phenoxy-1-vinyl)-N-methyl nitrone (4) have been studied.

As distinct from the previously studied [1,2] C-(2-naphthyl-1-vinyl)-N-*p*-methyl-phenyl (5), C-(2-naphtyl-1-vinyl)-N-phenyl (6), C-(2-phenoxy-1-vinyl)-N-*p*-methylphenyl (8), these nitrones have anti, and not *syn*, orientation of the nitrone and hydroxy groups. Because of such structural arrangement of the proton-donor hydroxy and proton-acceptor nitrone groups, the molecules in crystals 1–4 form chains with intermolecular hydrogen bonds (IHB), and not centrosymmetric dimer associates (CDA).

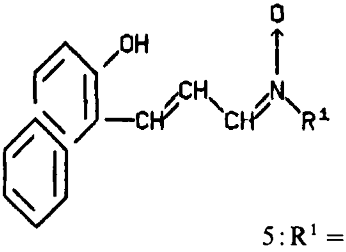
Two types of chain arrangement have been revealed: "head-to-tail" and "tail-to-head" types. The replacement of the aryl substituent at the nitrone group nitrogen atom in 4 by the alkyl one has been shown to result in the IMB geometry alteration in the H-associate.

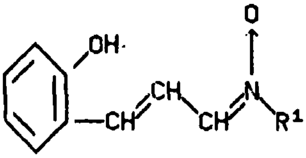
Justified is the structural possibility of an intermolecular O → O hydroxy proton transfer along the chain of hydrogen bonds in crystals 1–4, which may be responsible for photochemical conversions in the crystals.

Keywords: Hydrogen bonds, photosensitive crystals, azomethine N-oxide (nitrones), crystal structure.

INTRODUCTION

It was reported[1,2] that the substituted aldonitrone vinylogs, 5–8,

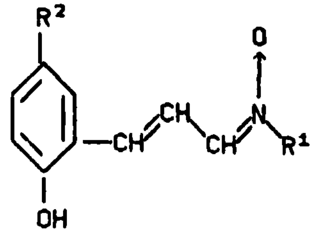




5 : $R^1 = p$-MePh 7 : $R^1 =$ Ph
6 : $R^1 =$ Ph 8 : $R^1 = p$-BrPh

had a *syn*-orientation of the hydroxy and N → O groups and formed centrosymmetric dimer associates due to strong IHB between the hydrogen atom of the hydroxy group and that of the nitrone group. Such a structure is favourable for proton phototransfer along the O → O coordinate in the CDA.

The X-ray study of the substituted nitrones has been carried out in order to investigate the effect of the substituents on the character of crystal packing and molecular structure of new photosensitive aldonitrone vinylogs: C-(2-phenoxy-1-vinyl)-N-*p*-methyl-phenyl nitrone (1), C-(3-bromo-6-phenoxy-1-vinyl)-N-*p*-methyl-phenyl nitrone (2), C-(3-bromo-6-phenoxy-1-vinyl)-N-phenyl nitrone (3) and C-(2-phenoxy-1-vinyl)-N-methyl nitrone (4).



$1: R^1 = p$-MePh, $R^2 = H$
$2: R^1 = p$-MePh, $R^2 = Br$
$3: R^2 = Ph$, $R^2 = Br$
$4: R^1 = Me$, $R^2 = H$

EXPERIMENTAL

Plate-like crystals 1, 2, 4 are monoclinic: crystal 3 is rhombic. Main crystal data:

1) $C_{16}H_{15}NO_2$, $M = 253.28$, $a = 21.521(7)$ Å, $b = 13.205(4)$ Å, $c = 9.339(3)$ Å, $\beta = 87.0(2)°$, $Z = 8$, $d_{calc.} = 1.278$ g/cm³, $V = 2650.1(2)$ Å³, Space group $P\,2_1/c$;
2) $C_{16}H_{14}NO_2Br$, $M = 332.21$, $a = 15.418(5)$ Å, $b = 12.625(6)$ Å, $c = 7.208(4)$ Å, $\gamma = 90.9(2)°$, $Z = 4$, $d_{calc.} = 1.567$ g/cm³, $V = 1416.2(2)$ Å³, Space group $P\,2_1/b$;
3) $C_{15}H_{12}NO_2Br$, $M = 319.02$, $a = 14.607(6)$ Å, $b = 11.287(5)$ Å, $c = 8.224(3)$ Å, $Z = 4$, $d_{calc.} = 1.562$ g/cm³, $V = 1355.9(2)$ Å³, Space group $P2_12_12_1$;
4) $C_{10}H_{12}NO_2$, $M = 117.18$, $a = 17.121(6)$ Å, $b = 13.926(4)$ Å, $c = 7.936(3)$ Å, $\beta = 82.2(2)°$, $Z = 8$, $d_{calc.} = 1.254$ g/cm³, $V = 1877.5(2)$ Å³, Space group $B\,2/b$;

The integral intensity data of 3956(1), 1592(3) and 1467(4) independent reflections ($(I > 2\sigma(I))$) were collected with an automatic four-circle KM-4 diffractometer (MoK_α-radiation), the intensities of 1551(2) ($(I > 2\sigma(I))$) independent reflections were collected with an automatic three-circle DAR-UM diffractometer (CuK_α-radiation). No absorption correction was applied.

Structures of 1–4 were determined by direct methods using the set of "SHELL-76" programs[3] and refined with full-matrix least-squares in an anisotropic approximation (non-hydrogen atoms). The coordinates of the hydrogen atoms for 1, 2, 4 were determined from the difference Fourier synthesis; for compound 3 they were calculated geometrically. The final R values are 0.037(1), 0.059(2), 0.084(3), and 0.066(4), respectively. The atomic coordinates of the compounds are given in Tables 1–4.

The energy calculations of the intermolecular interactions (IMI) for 1–4 were performed in the framework of atom-atomic approximations using "6-exp" potential with the parameters found in.[4]

TABLE 1

Coordinates of non hydrogen atoms ($*10^4$) and hydrogen atoms ($*10^3$) in molecule 1a

	X	Y	Z
N	5172(3)	6402(4)	5257(3)
O(1)	4737(3)	6834(4)	4524(4)
O(2)	4654(4)	6329(4)	11790(4)
C(1)	5082(4)	6212(4)	6634(4)
C(2)	4521(4)	6423(4)	7463(4)
C(3)	4493(4)	6293(3)	8892(4)
C(4)	3975(4)	6494(3)	9904(4)
C(5)	4070(4)	6500(3)	11387(4)
C(6)	3576(3)	6674(4)	12360(4)
C(7)	2988(3)	6836(3)	11906(4)
C(8)	2887(3)	6847(3)	10453(3)
C(9)	3374(4)	6677(3)	9472(3)
C(10)	5759(3)	6171(4)	4514(3)
C(11)	5975(3)	6806(4)	3424(4)
C(12)	6534(4)	6580(4)	2692(4)
C(13)	6880(4)	5745(3)	3006(4)
C(14)	7494(4)	5501(4)	2208(4)
C(15)	6653(4)	5128(4)	4116(3)
C(16)	6091(3)	5333(3)	4848(3)
H(1)	542(4)	590(3)	701(4)
H(2)	418(4)	671(3)	705(4)
H(3)	485(4)	602(4)	922(4)
H(6)	366(4)	672(4)	1337(5)
H(7)	268(4)	700(4)	1264(3)
H(8)	250(3)	696(4)	1017(4)
H(9)	330(4)	666(4)	843(4)
H(11)	579(4)	735(5)	327(4)
H(12)	666(4)	710(4)	222(4)
H(141)	759(4)	495(4)	221(4)
H(142)	756(4)	589(4)	162(4)
H(143)	792(4)	563(4)	276(4)
H(15)	684(4)	453(4)	425(4)
H(16)	592(3)	493(4)	556(4)
H(O2)	467(3)	654(4)	1275(4)
N	0905(3)	4941(3)	5707(4)
O(1)′	1047(4)	5812(3)	5126(4)
O(2)′	2926(4)	1740(3)	4277(4)
C(1)′	1226(4)	4140(3)	5348(4)
C(2)′	1749(4)	4146(4)	4373(4)
C(3)′	2108(4)	3337(4)	4122(4)
C(4)′	2658(4)	3259(4)	3137(3)
C(5)′	3060(4)	2439(4)	3236(3)
C(6)′	3578(3)	2347(4)	2287(3)
C(7)′	3702(3)	3074(4)	1267(3)
C(8)′	3324(3)	3906(4)	1180(4)
C(9)′	2808(4)	3985(3)	2114(4)
C(10)′	0371(4)	4935(4)	6709(3)
C(11)′	0010(3)	5788(4)	6851(3)
C(12)′	−0501(3)	5807(4)	7807(3)
C(13)′	−0666(3)	4987(4)	8632(4)
C(14)′	−1228(4)	5016(4)	9669(4)
C(15)′	−0295(4)	4140(3)	8510(3)
C(16)′	0221(4)	4112(3)	7548(4)
H(1)′	108(5)	354(5)	572(5)

TABLE 1 *(Continued)*

	X	Y	Z
H(2)′	184(4)	475(4)	394(5)
H(3)′	199(5)	271(4)	444(5)
H(6)′	381(4)	179(4)	238(5)
H(7)′	405(4)	301(4)	067(4)
H(8)′	340(4)	447(4)	066(4)
H(9)′	257(4)	453(4)	204(4)
H(11)′	011(5)	625(4)	636(4)
H(12)′	− 075(5)	653(4)	792(5)
H(141)′	− 149(5)	452(4)	937(5)
H(142)′	− 131(4)	568(4)	977(5)
H(143)′	− 117(4)	472(4)	1084(4)
H(15)′	− 039(4)	358(4)	898(4)
H(16)′	049(5)	359(4)	755(4)
H(O2)′	325(5)	140(4)	445(4)

TABLE 2

Coordinates of non hydrogen atoms (* 10^4) and hydrogen atoms (* 10^3) in molecule 2

	X	Y	Z
BR	4427(4)	2872(3)	1536(3)
N	− 385(4)	1436(3)	1649(3)
O(1)	114(4)	667(3)	2159(4)
O(2)	1500(3)	5919(3)	774(4)
C(1)	− 94(3)	2390(3)	1275(4)
C(2)	798(3)	2685(3)	1415(4)
C(3)	1054(3)	3688(4)	1106(5)
C(4)	1953(3)	4103(4)	1187(4)
C(5)	2129(3)	5180(3)	973(4)
C(6)	2981(3)	5583(3)	917(5)
C(7)	3659(4)	4889(4)	1102(4)
C(8)	3498(4)	3816(3)	1335(4)
C(9)	2651(3)	3419(3)	1386(4)
C(10)	− 1293(3)	1148(3)	1464(4)
C(11)	− 1506(3)	99(4)	1143(4)
C(12)	− 2373(3)	− 227(4)	983(4)
C(13)	− 3020(3)	527(3)	1192(4)
C(14)	− 3977(3)	185(3)	1132(4)
C(15)	− 2796(4)	1587(4)	1544(4)
C(16)	− 1922(4)	1913(3)	1645(4)
H(1)	− 47(2)	281(2)	59(2)
H(2)	116(2)	224(1)	253(2)
H(3)	63(1)	427(2)	53(1)
H(6)	304(2)	644(2)	87(2)
H(7)	425(2)	526(2)	111(2)
H(9)	253(2)	249(2)	148(2)
H(11)	− 106(2)	− 38(1)	110(2)
H(12)	− 254(2)	− 105(2)	70(2)
H(141)	− 434(2)	70(2)	230(2)
H(142)	− 424(1)	51(2)	− 28(2)
H(143)	− 396(2)	− 58(2)	79(2)
H(15)	− 330(2)	216(2)	174(2)
H(16)	− 178(2)	269(1)	250(2)
H(O2)	118(1)	578(2)	127(2)

TABLE 3

Coordinates of non hydrogen atoms (* 10^4) and hydrogen atoms (* 10^3) in molecule 3

	X	Y	Z
BR	2239(3)	2027(3)	5076(3)
N	−451(3)	97(3)	−2168(3)
O(1)	−184(3)	1186(3)	−2037(3)
O(2)	456(3)	−2743(3)	4227(3)
C(1)	−253(4)	−686(4)	−1048(3)
C(2)	233(4)	−428(4)	0379(3)
C(3)	346(4)	−1102(3)	1685(3)
C(4)	792(4)	−844(3)	3168(4)
C(5)	842(4)	−1663(4)	4442(4)
C(6)	1252(3)	−1358(4)	5907(4)
C(7)	1658(3)	−248(4)	6125(4)
C(8)	1645(3)	520(4)	4862(4)
C(9)	1240(4)	249(4)	3381(4)
C(10)	−953(3)	−213(3)	−3624(4)
C(11)	−1027(3)	671(3)	−4798(4)
C(12)	−1478(4)	436(4)	−6178(4)
C(13)	−1907(4)	−622(4)	−6430(4)
C(14)	−1792(4)	−1510(4)	−5313(4)
C(15)	−1342(4)	−1307(4)	−3873(4)
H(1)	−45(4)	−146(4)	−120(4)
H(2)	52(5)	32(5)	043(5)
H(3)	9(4)	−187(5)	159(5)
H(6)	125(4)	−192(4)	680(5)
H(7)	194(5)	−4(4)	712(4)
H(9)	128(5)	82(5)	250(4)
H(11)	−75(4)	141(4)	−462(4)
H(12)	−154(5)	105(5)	−699(6)
H(13)	−224(4)	−76(5)	−738(4)
H(14)	−204(5)	−231(4)	−550(4)
H(15)	−125(5)	−193(5)	−309(4)
H(O2)	10(4)	−289(4)	499(4)

RESULTS AND DISCUSSION

A general view of molecules 1–4 (compound 1 crystallized as two independent molecules 1a and 1b) is represented in Figure 1. As distinct from 5–8, the hydroxy group and the nitrone oxygen atom in molecules 1–4 are anti-oriented. In addition, the hydroxy group orientation is different in molecules 1–4. In molecule 2 (Fig. 1) the OH group proton is turned towards the vinylnitrone fragment, while in 1, 3, 4 and[1,2] it is turned in the opposite direction (Fig. 1). This arrangement of the OH group apparently results in a considerable increase of the C(4)C(5)O(2) bond angle in 2 up to 123.3°, due to steric repulsions of the hydrogen atoms H(O2) and H(3). In molecules 1a, 1b, 3, and 4 the analogous angles are 117.1, 117.8, 118.3, and 115.7°, respectively. The geometric modeling, with the C(4)C(5)O(2) angle being equal to the mean value of angles in molecules 1, 3, and 4, shows that in molecule 2 the interatomic distances H(O2)···H(3) and H(O2)···C(3) are shortened to 1.97Å and 2.48Å, respectively, as compared to the same contacts, 2.16Å and 2.65Å, in the starting molecule.

TABLE 4

Coordinates of non hydrogen atoms (* 10^4) and hydrogen atoms (* 10^3) in molecule 4

	X	Y	Z
N	649(3)	4657(3)	1624(3)
O(1)	3778(3)	5460(3)	−1612(3)
O(2)	236(3)	5417(3)	2252(3)
C(1)	2925(3)	6391(3)	308(3)
C(2)	2729(3)	7232(3)	1182(3)
C(3)	3155(3)	8012(3)	1100(3)
C(4)	3825(3)	7936(3)	14(3)
C(5)	4021(4)	7121(4)	−895(4)
C(6)	3601(4)	6327(4)	−765(4)
C(7)	2467(4)	5545(4)	371(4)
C(8)	1327(4)	4690(4)	1041(4)
C(9)	272(4)	3757(4)	1561(4)
C(10)	1729(4)	5571(4)	1069(4)
H(1)	219(4)	731(4)	197(4)
H(2)	297(4)	868(4)	182(4)
H(3)	416(4)	854(4)	−9(4)
H(6)	453(4)	706(4)	−170(4)
H(7)	271(4)	480(4)	−17(4)
H(8)	165(4)	419(4)	69(4)
H(9)	−13(4)	375(4)	172(4)
H(101)	57(5)	318(5)	247(5)
H(102)	39(5)	336(5)	32(5)
H(103)	143(5)	628(5)	160(5)
H(O2)	447(4)	530(4)	−215(4)

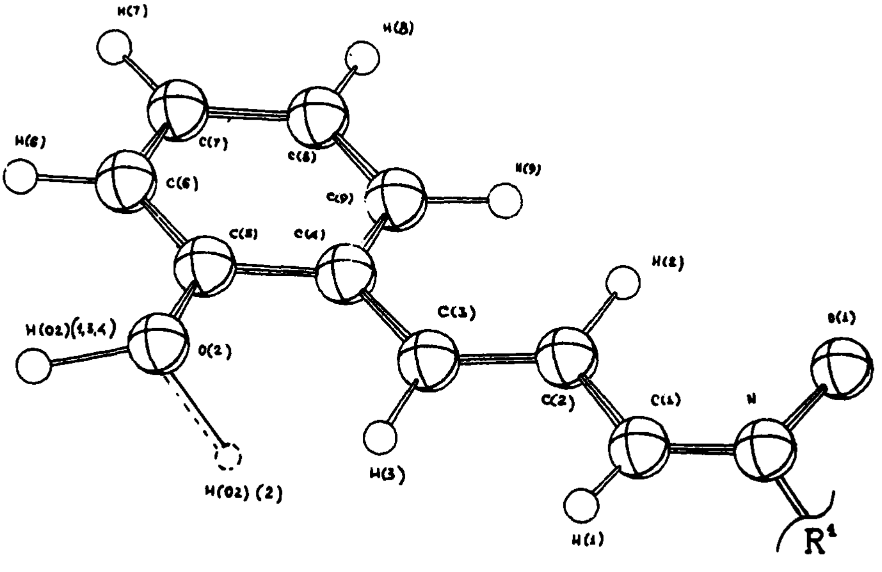


FIGURE 1 A general view of molecules 1–4.

Molecules 1–4 are nonplanar. The nonplanarity of 1a, 1b, 2, and 3 is caused by turnings of the arylic substituents at the nitrone group nitrogen atom by 35.5(2), 10.6(2), 27.1 (2), 6.9(2)°, and turning of the arylic fragments along the C(3)–C(4) bond by 13.2(2), 13.8(2), 7.4(2), 2.6(2)°, respectively. In molecule 4, the latter value is 13.3(2)°. The nitrone fragment in all the investigated compounds is planar. The main structural characteristics of molecules 1–4 are given in Table 5 and coincide, within the experimental error, with the structural parameters of nitrones 5–8.

The bond lengths in the nitrone group of molecules 1–3 and 4 differ significantly, because of different electron nature of substituents at the nitrogen atom. The presence of the arylic substituent (1–3) leads to a conjugation of the phenyl ring π-electron system with the π-bond of the N=C group and consequently to shortening of the single N–C(10) bond in 1–3 down to 1.442(3) Å (1a), 1.44(4) Å (1b), 1.47(3) Å (2), 1.446(5) Å (3), as compared with 1.257(4)Å in molecule 4.

The molecular packing in crystals 1, 3 and 4 is isotropic. This is confirmed by the distribution of the pair energies of intermolecular interactions from −5.5 to 6.0 kcal/mol on the first coordinate sphere. The total energy of the crystal packing in 1, 3, and 4 is −22.0, −27.1 and −26.3 kcal/mol, respectively, not taking into account the IHB energy.

In compound 2, in contrast to compounds 1, 3, 4 molecules, connected by the two-fold screw axis along direction "*Z*", form molecular stacks according to the "head-to-tail" principle. The energy of interaction between molecules in the stacks is −14.2 kcal/mol. The total energy of the crystal packing in 2 is −32.2 kcal/mol, not taking into account the IHB energy.

The crystal structure of 1–4 is characterized by forming the chains of intermolecular hydrogen bonds of the N → O ··· H–O type between the hydroxy group proton and the nitrone group oxygen atom of the neighboring molecules because of their anti-orientation. Figures 2–6 show chain fragments of the molecules linked by IHB. In

TABLE 5

Bond lengths, bond angles of the substituents in molecules (1–4)

	N–O(1)	N=C(1)	N–C(10)	C(1)NO(1) deg.	O(1)NC(10) deg.	C(1)NC(10) deg.
1a	1.318(3)	1.315(3)	1.442(3)	121.0(2)	118.0(2)	120.7(2)
1b	1.301(4)	1.298(3)	1.444(4)	122.2(2)	115.9(2)	122.2(2)
2	1.303(4)	1.306(3)	1.447(3)	123.2(2)	114.8(2)	122.1(2)
3	1.295(7)	1.308(5)	1.446(5)	121.0(2)	116.8(2)	122.2(2)
4	1.298(4)	1.257(4)	1.481(4)	121.7(3)	116.9(2)	121.4(2)

N	Turnings along the bonds (deg.)				
	C(1)–C(2)	C(2)–C(3)	N–C(1)	N–C(10)	C(3)–C(4)
1a	6.1(2)	1.9(2)	0.9(3)	35.5(2)	13.2(2)
1b	6.6(2)	0.0	0.0	10.6(2)	13.8(2)
2	3.5(2)	0.0	1.2(2)	27.1(2)	7.4(2)
3	11.3(2)	3.5(2)	0.0	6.9(2)	2.6(2)
4	1.1(3)	0.0	2.4(2)	–	13.3(2)

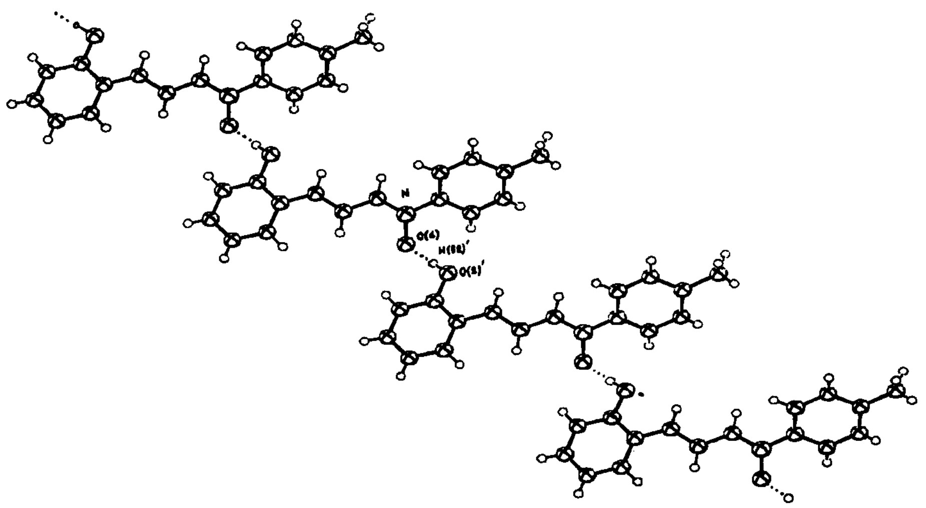


FIGURE 2 A fragment of the chain of molecules 1a linked by translation.

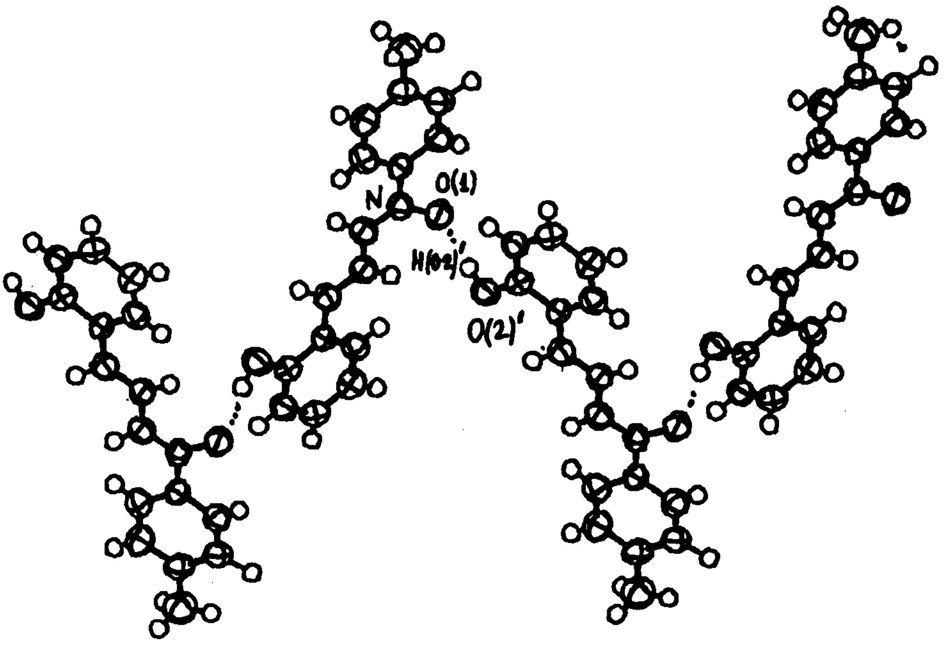


FIGURE 3 A fragment of the chain of molecules 1b linked by 2_1 axis.

Figure 2, the molecules are linked by translation, $O(1)\cdots O(2) = 2.655(3)$, $H(O2)'\cdots O(1) = 1.77(4)$ Å, $O(1)H(O2)O(2) = 176.4(3)°$, $H(O2)'O(1)N = 119.6(3)°$. Molecules 1b (Fig. 3) are connected by the 2_1 screw axis along the "*b*" axis, $O(1)\cdots O(2) = 2.615(3)$, $H(O2)'\cdots O(1) = 1.76(4)$ Å, $O(1)H(O2)'O(2) = 174.5(3)°$, $H(O2)'O(1)N = 110.7(3)°$.

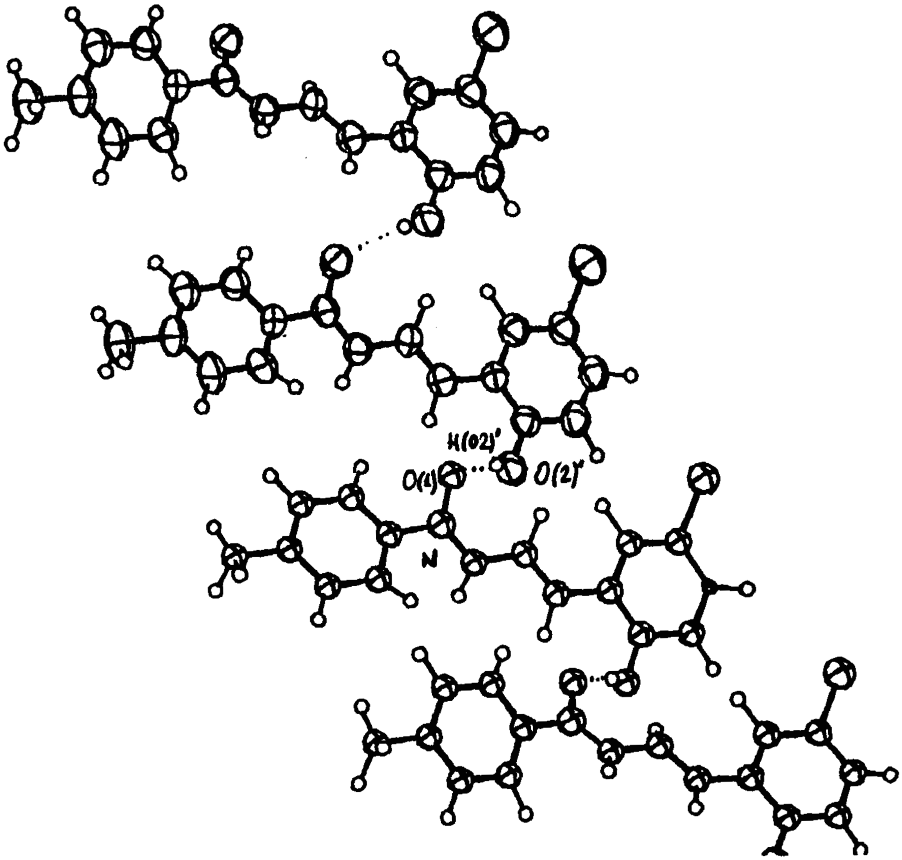


FIGURE 4 A fragment of the chain of molecules 2 linked by "*b*" symmetry plane.

Molecules 2 (Fig. 4) are linked by the "*b*" symmetry plane, $O(1)\cdots O(2)' = 2.629(3)$ Å, $H(O2)'\cdots O(1) = 2.01(4)$ Å, $O(1)H(O2)'O(2)' = 168.0(3)°$, $H(O2)'O(1)N = 127.1(3)°$. Molecules 3 are connected (Fig. 5) by the two-fold screw axis along the "*b*" axis $O(1)\cdots O(2)' = 2.639(4)$ Å, $H(O2)'\cdots O(1) = 2.19(4)$ Å, $O(1)H(O2)'O(2)' = 116.3(3)$ Å, $H(O2)'O(1)N = 125.5(3)°$. Molecules 4 (Fig. 6) are connected by the "*b*" gliding reflection plane $O(1)\cdots O(2)' = 2.650(4)$ Å, $H(O2)'\cdots O(1) = 1.410(8)$ Å, $O(1)H(O2)'O(2)' = 164.0(3)$ Å, $H(O2)'O(1)N = 117.0(3)°$. The H-bond parameters for molecular associates 1–4 are given in Table 6. Judging by these parameters, the IHB in nitrones may be considered as strong.[5] According to geometric characteristics, the IHB in chains 1–4 have no fundamental differences from the IHB in nitrones 5–8 forming CDA (Table 6).

The character of mutual arrangement of the molecules in the chains themselves is not uniform. Thus, the molecules connected by translation (1a) or the gliding reflection plane (2, 4) form chains of the "head-to-tail" type (ht) (Fig. 7.1), while the molecules connected by the 2_1 screw axis (1b, 3) form "head-to-tail", "tail-to-head" chains (ht, th) (Fig. 7.2) with different values of displacement Δ of the molecules in the chains relative to each other. In the ht chains, the molecules are practically coplanar. The angles

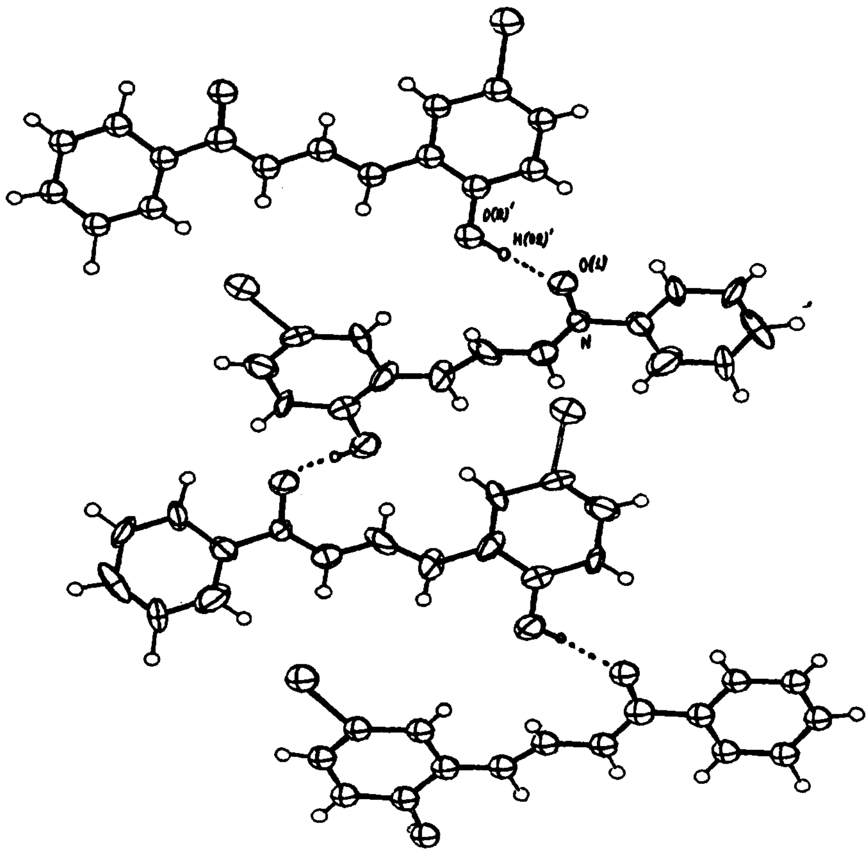


FIGURE 5 A fragment of the chain of molecules 3 linked by 2_1 axis.

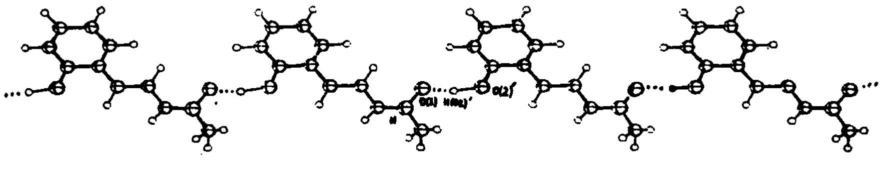


FIGURE 6 A fragment of the chain of molecules 4 linked by symmetry plane.

between the mean molecular planes Ω are 0.6(2)° in la, 11.4(2)° in 2, 1.3(2)° in 4, while in the second type chains molecules are essentially noncoplanar. Angles Ω in the chains of 1b molecules are 45.7(2)°, while in 3 they are 35.8(2)°. Besides, displacement of the molecules relative to each other, Δ_t, is not uniform in the ht chains (Δ_t is the distance between the intersection point of a perpendicular dropped from the carbon atom of the molecule "head" to the principal axis of another molecule and the carbon atom of this molecule "head"). In the chains of molecules la and 4 where OH-group is turned in opposite direction from the vinyl chain, this displacement Δ_t is 7.05 Å and 6.61 Å, respectively. In the chains of molecule 2 where the OH-group is turned in the direction

TABLE 6

Main IHB parameters in H-associates 1–4

Compound	$O^1 \cdots O^{2'}$	$H_{O2'} \cdots O^1$	$O^2H_{O2'}O^{1'}$ deg.	$H_{O2'}O^1N$ deg.
1a	2.655(3)	1.77(4)	176.4(3)	119.6(3)
1b	2.615(3)	1.76(3)	174.5(2)	110.7(2)
2	2.629(3)	2.01(5)	168.0(2)	127.1(2)
3	2.639(4)	2.19(6)	116.3(3)	125.5(3)
4	2.650(4)	1.41(8)*	164.0(3)	117.0(3)
5	2.580(3)	1.44(3)	180.0(1)	140.0(1)
6	2.651(3)	1.53(3)	156.0(2)	123.7(3)
7	2.662(3)	1.96(4)	165.0(3)	133.2(3)
8	2.567(4)	1.57(4)	165.0(0)	137.8(3)

*The short H(O2')···O(2)' contact is due to poor localization of the hydroxy group proton (bond length O(2)'–H(O2) = 1.26(9) Å.

of the vinyl chain, the value of Δ is decreased to 2.77 Å and coincides with the values of $\Delta_{1b} = 2.33$ Å and $\Delta_3 = 3.24$ Å in the ht-th chains.

The specific features of interarrangement of the molecules in chains are revealed in the values of the angles between the nitrone fragment plane and O(1)···O(2)' direction and N···C(4) direction. In 4, the IHB lies along the long molecular axis and the angle between the O(1)···O(2)' and N···C(4) directions is 158.7(2)°, while in 1a it is 138.3(3)°, and in 2 it is 58.8(3). In the ht–th chains, the angles between the O(1)···O(2)' and O···C(4) directions and between O(1)···O(2)' and N···C(4)' directions have different values: in 1b, 37.4(3) and 142.6(3)° and in 3, 50.4(3) and 129.6(3)°, respectively. In the ht chains with coplanar molecular arrangement, the angle between the O(1)···O(2)' and the nitrone fragment plane is 1.7° (Ω = 1.3°) in 4, 10.6° (Ω = 0.6°) in 1a, and 27.1° (Ω = 11.4°) in 2, while in the ht-th chains with noncoplanar molecular arrangement, this angle is 39.5° (Ω = 35.8°) in 3 and 52.7° (Ω = 45.7°) in 1b.

The coplanar and colinear arrangement of the molecules in the chains of 4 results in a number of specific structural features. The hydroxy group proton of one molecule taking part in the IHB formation appears to lie immediately above (below) the nitrone group nitrogen atom of the molecule from another corresponding chain. This results in shortening the intermolecular contact between these atoms to 2.31 Å. The colinear arrangement of the molecules is favorable for arising shortened contacts N···H (O2)' = 2.315 Å (N···O(2)' = 3.550 Å, O(2)'H(O2)'N = 165.1(2)°, H(O2)'NC(1) = 154.0 (2)°).

Molecules 2, because of unusual OH-group orientation, also form additional shortened non-bond contacts: between the OH-group oxygen atom O(2)' and the vinyl hydrogen atom H(2), 2.148 Å, (O(2)'···H(2) = 3.225 Å, O(2)'H(2)C(2) = 157.0°, H(2)O(2)'C(5) = 131.1°) (Fig. 4), and between the nitrone oxygen atom, O(1), and the vinyl hydrogen atom H(3)' (O(1)···H(3)' = 2.570 Å). The intermolecular interaction energies in the chains vary and have the following values: − 1.5 in 1a; − 2.1 in 1b; − 2.9 in 2; − 3.9 in 3; − 0.2 kcal/mol in 4.

To elucidate the reason why, in one case, o-OH aldonitrone vinylogs form CDA, and, in other cases, molecular chains with different orientation of the hydroxy group, we

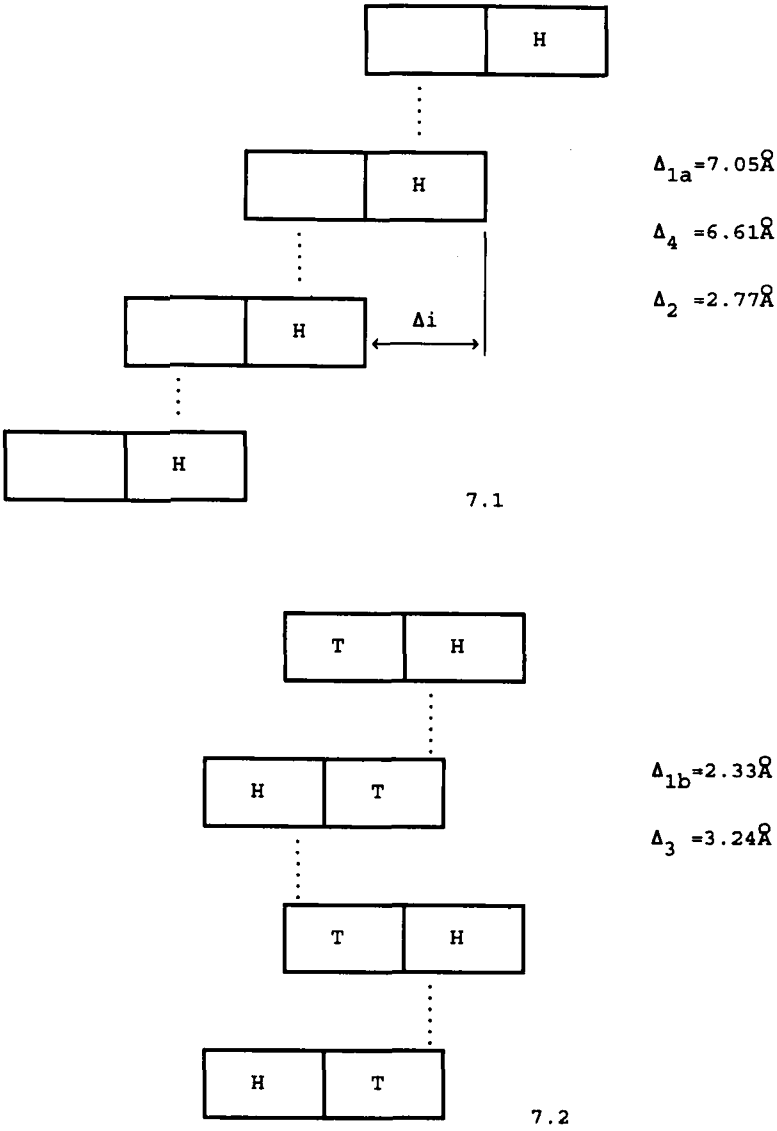


FIGURE 7 A character of interarrangement of molecules 1–4 in the chains.

carried out energy calculations for the conformers with the *syn*-oriented nitrone oxygen atom and OH group and the *cis*-oriented OH group and vinyl fragment (*syn*-*cis*-conformer, − 38.0 kcal/mol), with anti-*trans*-arrangement of these groups (anti-*trans*-conformer, − 40.3 kcal/mol) and with anti-*cis*-arrangement of these groups as in molecule 2 (anti-*cis*-conformer, − 37.6 kcal/mol) (Fig. 8) using the PM3 method with full optimization of the molecular geometry. The barrier of the anti-*syn* transfer was calculated. Its value appeared to be − 0.5 kcal/mol. Besides, CDA and three types of chains arranged by translation, two-fold screw axis and gliding reflection plane,

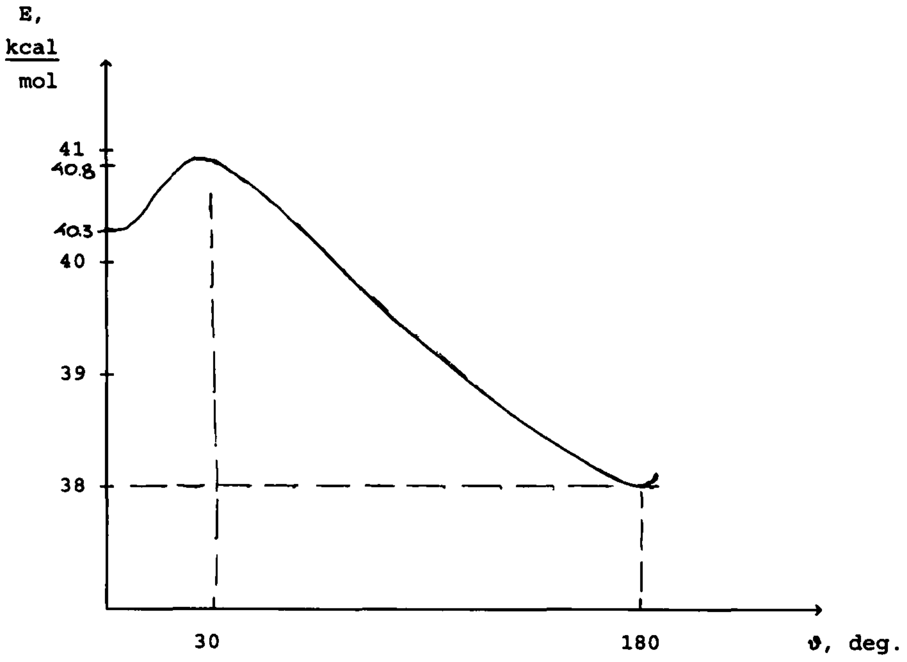
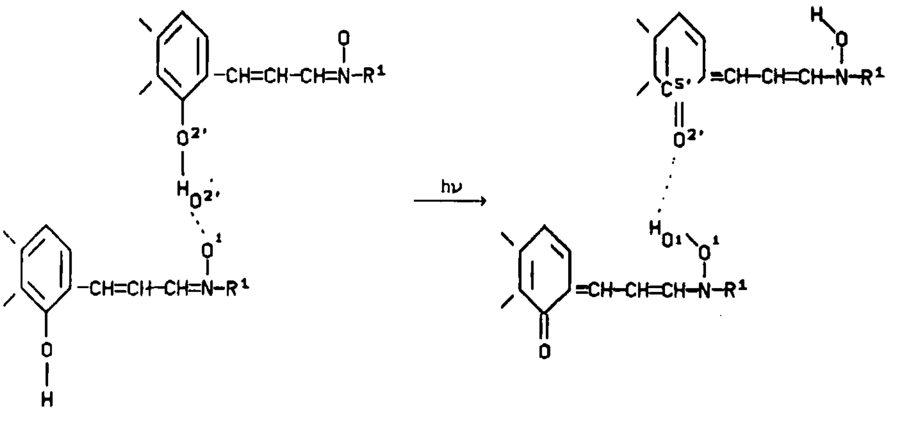


FIGURE 8 A barrier of anti-syn-transfer around C(3)–C(4) bond.

respectively, were modeled based on molecule 1a. Their energies of intermolecular interactions were calculated to be equal to − 1.7, − 1.3, − 1.9, − 1.0 kcal/mol. It can be assumed from these data that different conformers (1–8) in the solutions are in equilibrium, which can be shifted in any direction depending on the solvent nature, while formation of chains or CDA in crystals of o-OH aldonitrone vinylogs is most probably determined by crystallization conditions.

It is known from[1] that compounds 1–4 in the solid state undergo irreversible photochemical conversions similar to 5–8. The discovered specific features of 1–4



SCHEME 1

TABLE 7

Parameters of H-bonds in the model quinoid forms of photoproducts 1–4

Compound	$O^1 \cdots O^{2'}$	$H_{01} \cdots O^{2'}$	$O^1H_{01}O^{2'}$	$H_{01}O^{2'}C^{5'}$
1a	2.645	2.40	130.9°	132.3°
1b	2.693	1.97	130.3°	120.8°
2	2.676	1.95	130.9°	116.1°
3	2.686	2.14	114.6°	129.1°
4	2.661	1.94	130.1°	115.1°

crystal structure allow one to assume that their photoconversion in the crystals is caused by the intermolecular O→O hydroxy proton transfer along the chain of hydrogen bonds in the crystals, while the photoproduct stabilization occurs because of IHB weakening in the quinoid associates (Scheme 1). The geometric modeling of the proton transfer points to an increase in the O–H···O=C hydrogen bond length and distortion of the O(1)H(O1)O(2)′ angle (Table 7) in the forming photoproducts, which insure irreversibility of the photoprocess and stabilization of the quinoid form.

Quantum-chemical calculations (PM3) of the 1–4 molecules with a full optimization of the geometry of the starting nitrones and the suggested quinoid photoproducts showed that the O→O proton transfer was accompanied by a considerable change in the direction of dipole moments. In the starting molecules the dipole moments were oriented mostly along the N→O bond (the "X" axis was drawn through the N→O bond), while in the quinoid products the dipole moments were determined mainly by the carbonyl bond, with resulting orientation along the principal axis of molecules ("Y" axis) (Table 8).

With such dipole moment orientation in quinoid molecule, the chains with "head-to-tail" structure, the coplanar arrangement of molecules and the largest relative Δ displacement, i.e. chains 4 and 1a are the most favorable ones from the dipole–dipole interactions standpoint, while the least favorable are the chains with the least Δ displacement, i.e. 2. From the dipole–dipole interactions standpoint, the chains of the quinoid molecules with the ht–th arrangement could be stable with the coplanar

TABLE 8

Projection of the dipole moments in the starting and quinoid molecules 1–4

N	M_X	M_Y	M_Z	Total, D
1a	3.689	−1.612	−0.127	4.028
1a (quin)	−1.822	−3.295	0.109	3.767
1b	3.630	−1.736	−0.095	4.025
1b (quin)	−1.812	−3.295	0.180	3.765
2	4.354	−4.231	0.343	6.345
2 (quin)	−0.599	−3.840	0.238	3.893
3	4.572	−1.827	−0.070	4.924
3 (quin)	−0.772	−3.570	−0.057	3.653
4	3.303	−0.408	−0.002	3.328
4 (quin)	−1.875	−2.889	0.090	3.445

arrangement of molecules. Increase of the Ω angle in chains 3 and 1b to 35.8° and 45.7° would decrease their stability. Thus, from the dipole-dipole interactions standpoint, stability of the chains will decrease in the row $4 \cong 1a > 3 \cong 1b > 2$, which is in good correlation with photosensitivity of the investigated crystals.

Acknowledgments

This work has received support of the Russian Foundation of Fundamental Investigations.

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