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Crystal Chemical Analysis of a Possibility of Photochemical Transformations in Crystals of C-(4-Methoxy-1-Vinyl)-N-Phenyl and C-(4-Methoxy-1-Vinyl)-N-Bromphenyl Nitrons

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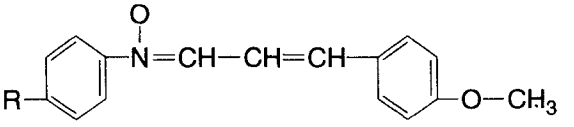
An X-ray single crystal study of C-(4-methoxy-1-vinyl)-N-phenyl nitron (1) and C-(4-methoxy-1-vinyl)-N-bromphenyl nitron (2) was undertaken. The main crystal data: (1): $C_{16}H_{15}NO_2$, $a = 8.402(5)$ Å, $b = 5.408(3)$ Å, $c = 14.554(7)$ Å, $\beta = 93.1(2)°$, $d_{cal.} = 1.273$ g/cm^3, $V_{cal.} = 660.3(2)$ Å^3, $Z = 2$, Sp. gr. Pc. $M = 253.32$: (2): $C_{16}H_{14}NO_2Br$, $a = 17.586(6)$ Å, $b = 14.543(5)$ Å, $c = 5.632(4)$ Å, $\alpha = 89.8(2)°$, $\beta = 90.8(2)°$, $\gamma = 98.9(2)°$, $d_{cal.} = 1.554$ g/cm^3, $V_{cal.} = 1423.0(2)$ Å, $Z = 4$, Sp. gr. $P\bar{1}$, $M = 332.21$

Compound 2, as distinct from 1, crystallizes in the form of two independent molecules. Molecules of 1 and 2 are nonplanar and have similar conformations. The photoconversion connected with the closing of the oxaziridine heterocycle was computer simulated and its possibility proved for crystals of 1 and 2 using the calculation of the unit cell free volume portion and the difference in the volumes of the initial and final molecules.

Keywords: Nitrons, photochemical transformations, crystal structure.

The presence of centrosymmetric dimeric associates[1,2] (CDA) or infinite chains of molecules[3] formed by stable intermolecular hydrogen bonds of the O–H···O type in the crystal structure of earlier investigated *o*-OH vinyl analogs of aldonitrons is their characteristic feature. This packing mode in the molecules of the nitrons is caused by the peculiarities of their molecular structure: the presence of a proton-donor OH and a strong proton-acceptor N-->O group. Using the collected structural data we have proved a possibility of intermolecular proton phototransfer along the hydrogen bond which accounts for the photosensitivity of the crystals.

The proton-donor hydrogen group is absent in molecules of 1 and 2. The present work is devoted to studying the crystal structure of these compounds.



1 : R = H
2 : R = Br

EXPERIMENTAL

Nitron 1 crystallizes as light-yellow plates with monoclinic crystal system. Compound 2 crystallizes as yellow plates with triclinic crystal system. The main crystal data: (1): $C_{16}H_{15}NO_2$, $a = 8.402(5)$ Å, $b = 5.408(3)$ Å, $c = 14.554(7)$ Å, $\beta = 93.1(2)°$, $d_{cal.} = 1.273$ g/cm^3, $V_{cal.} = 660.3(2)$ Å^3, $Z = 2$, Sp. gr. Pc, $M = 253.32$; (2): $C_{16}H_{14}NO_2Br$, $a = 17.586(6)$ Å, $b = 14.543(5)$ Å, $c = 5.632(4)$ Å, $\alpha = 89.8(2)°$, $\beta = 90.8(2)°$, $\gamma = 98.9(2)°$, $d_{cal.} = 1.554$ g/cm^3, $V_{cal.} = 1423.0(2)$ Å, $Z = 4$, Sp. gr $P\bar{1}$, $M = 332.21$.

The intensities of 1090(1) and 1165(2) independent reflections with $I > 2\sigma(I)$ were obtained using an automatic four-cycle KM-4 difractometer (MoK_α-radiation). The structures of 1 and 2 were solved by a direct method using a package of "SHELL" programs[4] and refined by LST in anisotropic approximation. The hydrogen atoms were found from difference Fourier synthesis. The final R-factors are 0.029(1) and 0.06(2). The atomic coordinates for 1 and 2 are listed in Tables I and II. Absoption corrections have not been applied for compound 2.

TABLE I

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

Atom	X	Y	Z
N	777(3)	435(4)	1495(3)
O(1)	723(4)	−1762(4)	1865(4)
O(2)	5941(4)	4147(4)	6779(4)
C(1)	1499(4)	2305(4)	1914(4)
C(2)	2263(3)	2115(3)	2797(4)
C(3)	3017(3)	3990(3)	3219(4)
C(4)	3810(3)	4025(3)	4125(4)
C(5)	3546(3)	2180(3)	4808(5)
C(6)	4271(3)	2306(3)	5666(5)
C(7)	5290(3)	4268(3)	5904(5)
C(8)	5577(3)	6056(3)	5261(4)
C(9)	4862(3)	5940(3)	4400(4)
C(10)	15(4)	669(4)	573(4)
C(11)	413(4)	2565(5)	6(4)
C(12)	−300(4)	2639(4)	−867(3)
C(13)	−1382(3)	890(4)	−1157(3)
C(14)	−1787(3)	−917(4)	−581(4)
C(15)	−1074(3)	−1096(4)	303(4)
C(16)	6914(3)	6134(3)	7089(4)
H(1)	151(3)	380(4)	161(4)
H(2)	203(4)	70(4)	313(4)
H(3)	317(4)	545(4)	290(4)
H(5)	284(4)	82(4)	465(4)
H(6)	408(4)	104(5)	610(4)
H(8)	628(4)	739(4)	542(5)
H(9)	508(4)	721(4)	396(5)
H(11)	116(4)	380(4)	21(4)
H(12)	−3(4)	394(4)	−127(4)
H(13)	−185(4)	95(4)	−177(4)
H(14)	−258(4)	−210(4)	−78(4)
H(15)	−134(4)	−241(4)	70(4)
H(161)	729(4)	583(4)	771(4)
H(162)	630(4)	763(4)	706(4)
H(163)	780(4)	628(4)	670(5)

TABLE II

Coordinates of the non hydrogen (* 10^4) and hydrogen (* 10^3) atoms in structure 2.

Atom	X	Y	Z
		(molecule 2a)	
BR	3643(3)	3605(3)	1507(4)
O(1)	−22(3)	3826(3)	−1700(4)
O(2)	−4584(4)	3996(3)	4500(4)
N	233(4)	3781(3)	471(4)
C(1)	−222(4)	3754(3)	2272(4)
C(2)	−1010(4)	3832(3)	2097(4)
C(3)	−1447(4)	3692(3)	3979(3)
C(4)	−2249(4)	3791(3)	4139(3)
C(5)	−2663(3)	4162(3)	2304(3)
C(6)	−3434(3)	4251(3)	2538(3)
0(7)	−3856(3)	3891(4)	4557(3)
C(8)	−3433(3)	3516(4)	6387(3)
C(9)	−2681(3)	3483(3)	6165(4)
C(10)	1084(3)	3788(3)	621(4)
C(11)	1458(3)	4129(3)	2601(4)
C(12)	2230(3)	4054(4)	2827(4)
C(13)	2585(3)	3640(4)	1029(3)
C(14)	2184(3)	3325(4)	−1001(4)
C(15)	1413(3)	3319(4)	−1160(4)
C(16)	−5026(4)	3803(3)	6649(3)
H(1)	−1(4)	367(3)	382(3)
H(2)	−122(4)	399(3)	60(3)
H(3)	−120(4)	350(4)	540(4)
H(5)	−240(4)	435(5)	85(4)
H(6)	−368(4)	456(4)	131(4)
H(8)	−369(3)	328(4)	780(4)
H(9)	−241(4)	323(4)	746(4)
H(11)	119(3)	441(4)	381(4)
H(12)	251(3)	428(4)	421(3)
H(14)	245(3)	310(4)	−231(
H(15)	110(4)	300(4)	−243(4)
H(161)	−569(4)	381(4)	639(4)
H(162)	−510(5)	319(4)	678(4)
H(163)	−503(5)	421(4)	770(4)
		(molecule 2b)	
BR′	−3630(3)	−1144(4)	3184(4)
O(1)′	24(4)	−1163(4)	6931(4)
O(2)′	4654(4)	−1248(4)	386(4)
N′	−210(4)	−1174(4)	4731(4)
C(1)′	251(4)	−1256(4)	2945(4)
C(2)′	1086(3)	−1198(3)	3166(4)
C(3)′	1481(4)	−1370(3)	1244(5)
C(4)′	2253(4)	−1333(3)	1037(4)
C(5)′	2846(4)	−931(4)	2822(4)
C(6)′	3585(3)	−933(3)	2437(4)
C(7)	3878(3)	−1305(3)	409(3)
C(8)′	3346(3)	−1678(3)	−1277(4)
C(9)′	2580(3)	−1664(4)	−1024(5)
C(10)′	−1013(3)	−1133(4)	4460(5)
C(11)	−1528(3)	−1508(4)	6170(4)
C(12)′	−2292(3)	−1485(4)	5821(4)
C(13)′	−2581(3)	−1142(4)	3677(4)
C(14)′	−2036(3)	−760(3)	2066(4)

TABLE II *(Continued)*

Atom	X	Y	Z
C(15)′	− 1257(3)	− 733(3)	2407(4)
C(16)′	4964(5)	− 1506(3)	− 1702(4)
H(1)′	2(3)	− 136(3)	139(3)
H(2)′	134(4)	− 104(3)	465(3)
H(3)′	118(4)	− 154(4)	− 16(3)
H(5)′	269(4)	− 66(5)	426(3)
H(6)′	394(4)	− 66(4)	362(3)
H(8)′	352(4)	− 195(4)	− 267(3)
H(9)′	224(3)	− 189(4)	− 231(4)
H(11)′	− 134(3)	− 178(4)	758(4)
H(12)′	− 264(3)	− 170(4)	705(4)
H(14)′	− 221(3)	− 049(4)	62(3)
H(15)′	− 89(3)	− 44(4)	126(4)
H(161a)	554(4)	− 144(5)	− 159(3)
H(162b)	484(4)	− 114(5)	− 309(3)
H(163c)	479(4)	− 217(5)	− 209(3)

Bond lengths and angles in compound 1

bond	length, Å	bond	length, Å
N–O(1)	1.306(4)	N–C(1)	1.313(3)
N–C(10)	1.461(4)	O(2)–C(7)	1.361(4)
O(2)–C(16)	1.410(3)	C(1)–C(2)	1.409(4)
C(1)–H(1)	0.92(2)	C(2)–C(3)	1.328(4)
C(2)–H(2)	0.93(2)	C(3)–C(4)	1.446(4)
C(3)–H(3)	0.93(2)	C(4)–C(5)	1.433(3)
C(4)–C(9)	1.406(3)	C(5)–C(6)	1.362(4)
C(5)–H(5)	0.96(2)	C(6)–C(7)	1.395(3)
C(6)–H(6)	0.96(2)	C(7)–C(8)	1.376(3)
C(16)–H(161)	0.96(3)	C(16)–H(162)	0.96(2)
C(16)–H(163)	0.96(3)	C(8)–C(9)	1.361(4)
C(8)–H(8)	0.95(2)	C(9)–H(9)	0.96(2)
C(10)–C(11)	1.369(3)	C(10)–C(15)	1.366(3)
C(11)–C(12)	1.377(4)	C(11)–H(11)	0.96(2)
C(12)–C(13)	1.363(3)	C(12)–H(12)	0.95(2)
C(13)–C(14)	1.343(3)	C(13)–H(13)	0.94(3)
C(14)–C(15)	1.396(4)	C(14)–H(14)	0.97(2)
C(15)–H(15)	0.97(2)		
angle	**deg.**	**angle**	**deg.**
O(1)–N–C(1)	122.3(2)	O(1)–N–C(10)	115.7(3)
C(1)–N–C(10)	121.9(2)	C(7)–O(2)–C(16)	117.0(2)
N–C(1)–C(2)	123.0(2)	N–C(1)–H(1)	117.1(2)
C(2)–C(1)–H(1)	119.1(2)	C(1)–C(2)–C(3)	123.3(2)
C(1)–C(2)–H(2)	116.2(2)	C(3)–C(2)–H(2)	119.2(3)
C(2)–C(3)–C(4)	128.4(2)	C(2)–C(3)–H(3)	119.5(2)
C(4)–C(3)–H(3)	112.1(2)	C(3)–C(4)–C(5)	122.8(2)
C(3)–C(4)–C(9)	121.5(2)	C(5)–C(4)–C(9)	115.7(2)
C(4)–C(5)–C(6)	121.5(2)	C(4)–C(5)–H(5)	119.3(2)
C(6)–C(5)–H(5)	119.3(2)	C(5)–C(6)–C(7)	120.3(2)
C(5)–C(6)–H(6)	119.9(2)	C(7)–C(6)– H(6)	119.9(2)
O(2)–C(7)–C(6)	113.9(2)	O(2)–C(7)–C(8)	126.4(2)

TABLE II *(Continued)*

.Bond lengths and angles in compound 1

angle	deg.	angle	deg.
C(6)–C(7)–C(8)	119.6(2)	O(2)–C(16)–H(161)	109.5(2)
O(2)–C–C(16)–H(162)	109.5(2)	O(2)–C(16)–H(163)	109.5(2)
H(161)–C(16)–H(162)	109.5(2)	H(161)–C(16)–H(163)	109.5(3)
H(162)–C(16)–H(163)	109.5(2)	C(7)–C(8)–C(9)	120.6(2)
C(7)–C(8)–H(8)	119.7(2)	C(9)–C(8)–H(8)	119.7(2)
C(4)–C(9)–C(8)	122.4(2)	C(4)–C(9)–H(9)	118.8(2)
C(8)–C(9)–H(9)	118.8(2)	N–C(10)–C(11)	120.6(2)
N–C(10)–C(15)	117.2(2)	C(11)–C(10)–C(15)	122.1(2)
C(10)–C(11)–C(12)	118.0(2)	C(10)–C(11)–H(11)	121.0(2)
C(12)–C(11)–H(11)	121.0(2)	C(11)–C(12)–C(13)	121.1(2)
C(11)–C(12)–H(12)	119.5(2)	C(13)–C(12)–H(12)	119.5(2)
C(12)–C(13)–C(14)	120.0(2)	C(12)–C(13)–H(13)	120.0(2)
C(14)–C(13)–H(13)	120.0(2)	C(13)–C(14)–C(15)	121.0(2)
C(13)–C(14)–H(14)	119.5(2)	C(15)–C(14)–H(14)	119.5(2)
C(10)–C(15)–C(14)	117.7(2)	C(10)–C(15)–H(15)	121.1(2)
C(14)–C(15)–H(15)	121.(2)		

Bond lengths and angles in compound 2a

bond	length, Å	bond	length, Å
N–O(1)	1.302(4)	N–C(1)	1.298(4)
N–C(10)	1.496(4)	O(2)–C(7)	1.312(5)
O(2)–C(!6)	1.462(4)	C(1)–C(2)	1.410(4)
C(1)–H(1)	0.97(4)	C(2)–C(3)	1.315(4)
C(2)–H(2)	0.97(4)	C(3)–C(4)	1.443(5)
C(3)–H(3)	0.96(4)	C(4)–C(5)	1.430(5)
C(4)–C(9)	1.418(4)	C(5)–C(6)	1.337(5)
C(5)–H(5)	0.97(5)	C(6)–C(7)	1.429(4)
C(6)–H(6)	0.97(6)	C(7)–C(8)	1.423(4)
C(16)–H(161)	0.86(7)	C(16)–H(162)	0.87(6)
C(16)–H(163)	1.18(6)	C(8)–C(9)	1.391(4)
C(8)–H(8)	0.97(6)	C(9)–H(9)	0.97(6)
C(10)–C(11)	1.355(5)	C(10)–C(15)	1.406(4)
C(11)–C(12)	1.383(5)	C(11)–H(11)	0.97(6)
C(12)–C(13)	1.394(4)	C(12)–H(12)	0.97(6)
C(13)–C(14)	1.390(4)	C(13)–BR	1.886(4)
C(14)–C(15)	1.356(5)	C(14)–H(14)	0.97(6)
C(15)–H(15)	0.97(6)		

angle	deg.	angle	deg.
O(1)–N–C(1)	121.6(3)	O(1)–N–C(10)	113.1(3)
C(1)–N–C(10)	125.3(3)	C(7)–O(2)–C(16)	117.9(3)
N–C(1)–C(2)	123.9(3)	N–C(1)–H(1)	118.5(3)
C(2)–C(1)–H(1)	117.7(3)	C(1)–C(2)–C(3)	119.7(3)
C(1)–C(2)–H(2)	119.8(3)	C(3)–C(2)–H(2)	120.5(3)
C(2)–C(3)–C(4)	126.9(3)	C(2)–C(3)–H(3)	117.0(3)
C(4)–C(3)–H(3)	116.1(3)	C(3)–C(4)–C(5)	121.0(3)
C(3)–C(4)–C(9)	123.2(3)	C(5)–C(4)–C(9)	115.8(3)
C(4)–C(5)–C(6)	124.1(3)	C(4)–C(5)–H(5)	118.4(3)
C(6)–C(5)–H(5)	117.5(3)	C(5)–C(6)–C(7)	120.8(3)
C(5)–C(6)–H(6)	119.3(3)	C(7)–C(6)–H(6)	119.9(3)
O(2)–C(7)–C(6)	128.4(3)	O(2)–C(7)–C(8)	114.1(3)
C(6)–C(7)–C(8)	116.9(2)	C(7)–C(8)–C(9)	120.9(3)
C(7)–C(8)–H(8)	120.0(3)	C(9)–C(8)–H(8)	119.2(3)

TABLE II *(Continued)*

Bond lengths and angles in compound 2a

angle	deg.	angle	deg.
C(4)–C(9)–C(8)	121.4(3)	C(4)–C(9)–H(9)	119.7(3)
C(8)–C(9)–H(9)	119.0(4)	N–C(10)–C(11)	117.9(3)
N–C(10)–C(15)	116.8(4)	C(11)–C(10)–C(15)	124.7(3)
C(10)–C(11)–C(12)	117.6(3)	C(10)–C(11)–H(11)	121.6(3)
C(12)–C(11)–H(11)	120.8(3)	C(11)–C(12)–C(13)	119.1(3)
C(11)–C(12)–H(12)	120.1(2)	C(13)–C(12)–H(12)	125.1(3)
C(12)–C(13)–C(14)	121.3(3)	C(12)–C(13)–BR	120.1(3)
C(14)–C(13)–BR	123.5(3)	C(13)–C(14)–C(15)	121.0(3)
C(13)–C(14)–H(14)	120.3(3)	C(15)–C(14)–H(14)	119.5(3)
C(10)–C(15)–C(14)	116.4(3)	C(10)–C(15)–H(15)	122.1(3)
C(14)–C(15)–H(15)	121.1(3)		

Bond lengths and angles in compound 2b

bond	length, Å	bond	length, Å
N–O(1)	1.300(3)	N–C(1)	1.319(3)
N–C(10)	1.427(4)	O(2)–C(7)	1.356(4)
O(2)–C(16)	1.393(4)	C(1)–C(2)	1.462(4)
C(1)–H(1)	0.97(4)	C(2)–C(3)	1.339(5)
C(2)–H(2)	0.97(4)	C(3)–C(4)	1.357(4)
C(3)–H(3)	0.97(4)	C(4)–C(5)	1.433(3)
C(4)–C(9)	1.501(4)	C(5)–C(6)	1.359(4)
C(5)–H(5)	0.97(3)	C(6)–C(7)	1.384(3)
C(6)–H(6)	0.97(3)-	C(7)–C(8)	1.415(3)
C(16)–H(161)	0.97(4)	C(16)–H(162)	0.97(4)
C(16)–H(163)	0.97(4)	C(8)–C(9)	1.320(4)
C(8)–H(8)	0.97(4)	C(9)–H(9)	0.97(4)
C(10)–C(11)	1.397(3)	C(10)–C(15)	1.391(3)
C(11)–C(12)	1.375(4)	C(11)–H(11)	0.97(2)
C(12)–C(13)	1.388(4)	C(12)–H(12)	0.97(5)
C(13)–C(14)	1.435(4)	C(13)–BR	1.861(4)
C(14)–C(15)	1.361(4)	C(14)–H(14)	0.97(4)
C(15)–H(15)	0.97(4)		

angle	deg.	angle	deg.
O(1)–N–C(1)	122.3(3)	O(1)–N–C(10)	113.7(2)
C(1)–N–C(10)	124.0(2)	C(7)–O(2)–C(16)	119.8(3)
N–C(1)–C(2)	124.2(3)	N–C(1)–H(1)	118.3(3)
C(2)–C(1)–H(1)	117.5(3)	C(1)–C(2)–C(3)	118.1(3)
C(1)–C(2)–H(2)	120.6(3)	C(3)–C(2)–H(2)	121.3(3)
C(2)–C(3)–C(4)	128.0(3)	C(2)–C(3)–H(3)	116.5(3)
C(4)–C(3)–H(3)	115.6(3)	C(3)–C(4)–C(5)	121.4(3)
C(3)–C(4)–C(9)	125.4(3)	C(5)–C(4)–C(9)	113.2(3)
C(4)–C(5)–C(6)	123.6(3)	C(4)–C(5)–H(5)	118.6(3)
C(6)–C(5)–H(5)	117.7(3)	C(5)–C(6)–C(7)	121.5(3)
C(5)–C(6)–H(6)	119.0(3)	C(7)–C(6)–H(6)	119.6(3)
O(2)–C(7)–C(6)	128.4(3)	O(2)–C(7)–C(8)	114.7(3)
C(6)–C(7)–C(8)	116.9(2)	C(7)–C(8)–C(9)	124.4(3)
C(7)–C(8)–H(8)	118.2(3)	C(9)–C(8)–H(8)	117.4(3)
C(4)–C(9)–C(8)	120.0(3)	C(4)–C(9)–H(9)	120.0(3)
C(8)–C(9)–H(9)	119.6(4)	N–C(10)–C(11)	117.8(3)
N–C(10)–C(15)	120.3(4)	C(11)–C(10)–C(15)	121.9(3)
C(10)–C(11)–C(12)	117.6(3)	C(10)–C(11)–H(11)	123.6(3)

TABLE II *(Continued)*

Bond lengths and angles in compound 2b

angle	deg.	angle	deg.
C(12)–C(11)–H(11)	120.8(3)	C(11)–C(12)–C(13)	123.3(3)
C(11)–C(12)–H(12)	118.1(2)	C(13)–C(12)–H(12)	118.6(3)
C(12)–C(13)–C(14)	116.4(3)	C(12)–C(13)–BR	122.1(3)
C(14)–C(13)–BR	121.9(3)	C(13)–C(14)–C(15)	121.7(3)
C(13)–C(14)–H(14)	119.6(3)	C(15)–C(14)–H(14)	118.7(3)
C(10)–C(15)–C(14)	118.8(3)	C(10)–C(15)–H(15)	120.9(3)
C(14)–C(15)–H(15)	120.3(3)		

The intermolecular interaction energy (IMIE) for 1 and 2 was performed by atom-atomic potentials using the "6-exp" potential with parameters given in Reference 5.

DISCUSSION

The general view of molecules 1, 2 (compound 2 crystallizes as two independent molecules 2a and 2b) is represented in Figure 1, 2, respectively. Molecules 1 and 2 are nonplanar. Their nonplanarity is due to the turn of the methoxyphenyl fragment about the C(3)–C(4) bond by an angle of 15.9(2)° (1), 9, 7(2)°(2a), 11.0(2)° and the phenyl substitute at the nitrogen atom of the nitron group by an angle of 19.3(3)° (1), 30.8(2)° (2a), 28.8(2)° (2b) about the N–C(10) bond. In molecule 1, the angle of turn of the methoxy fragment about the O(2)–C(7) bond is less than in molecules 2a and 2b (8.4(2)° (2a), 6.9(2)° (2b)) and is equal to 4.3(2)°. The central part of molecules 1 and 2 is planar.

The geometry of nitrogen fragment of molecule 1 does not differ from the earlier reported nitrons;[1–3] it has the following parameters of bond lengths and angles:

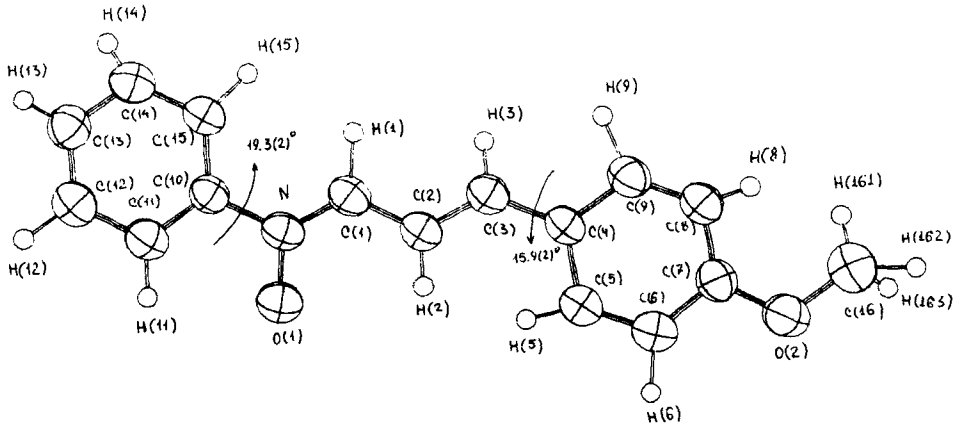


FIGURE 1 A general view of molecule I.

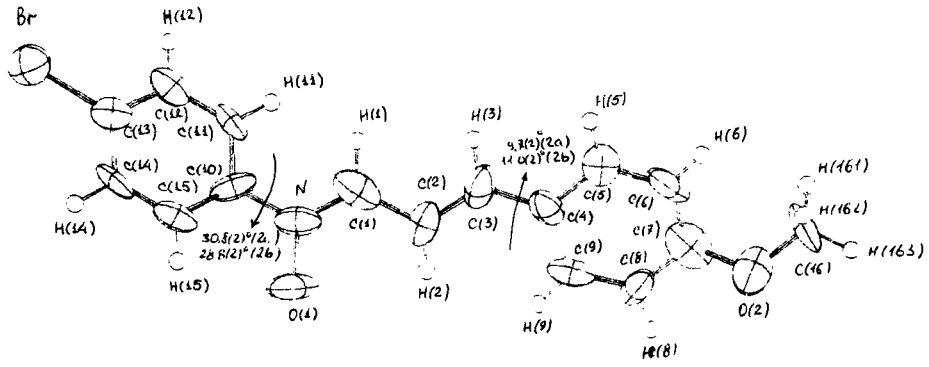


FIGURE 2 A general view of molecule II.

N–O(1) = 1.306(4), N–C(1) = 1.313(3), N–C(10) = 1.461(4) Å, O(1)NC(1) = 122.3(2)°, O(1)NC(10) = 115.7(3)°, C(1)NC(10) = 121.9(2)° (Table 3). In molecules 2a and 2b, the N–O(1) (1.302(4), 1.300(3) Å) and N=C(1) (1.298(4), 1.319(3) Å) bond lengths are within the experimental error as compared to the same lengths in molecule 1 and[1–3] (1.310, 1.306 Å). The lengths of N–C(10) bond in molecules 2a (1.496(4) Å) and 2b (1.427(4) Å) are different. In 2a this bond is longer and in 2b it is shorter than the analogous values in 1 and.[1–3] In 2b the C(1)–C(2) bond (1.462(4)Å) is much longer than in 1, 2a and than the mean value for.[1–3] Besides, in 2b the single bonds C(3)–C(4) (1.357(4) Å) and C(13)-Br (1.861(4) Å) are shortened in comparison with the analogous bonds in 1, 2a,[1–3] (Table III). The O(1)NC(10) angle in 2a (113.1(3)°) and 2b (113.7(2)°) is less than in 1 (115.7(2)°), while the C(1)NC(10) angle in 2a (125.3(3)°) and 2b (124.0(2)°) is more than in 1 (121.9(2)°).

The projection of the crystal structure of 1 on the XOZ plane is shown in Figure 3. The molecule 1 packing has isotropic character. The total structure energy is − 39.1 kkal/mol, with the van der Waals component being equal to − 29.1 kkal/mol,

TABLE III

The structure of the nitron group and angles of turn of the substituents in 1, 2; [1–3]

	N–O(1)	N=C(1)	N–C(10)	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)
1	1.306(4)	1.313(3)	1.461(4)	1.409(4)	1.328(4)	1.446(4)
2a	1.302(4)	1.298(4)	1.496(4)	1.410(4)	1.315(4)	1.443(5)
2b	1.300(3)	1.319(3)	1.427(4)	1.462(4)	1.339(5)	1.357(4)
*	1.310	1.306	1.445	1.415	1.345	1.450

C(1)NO(1)	O(1)NC(10)	C(1)NC(10)	τ(N–C(10))**	τ(C(3)–C(4))**
122.3(2)	115.7(3)	121.9(2)	19.3(3)	15.9(2)
121.6(3)	113.1(3)	125.3(3)	30.8(2)	9.7(2)
122.3(3)	113.7(2)	124.0(2)	28.8(2)	11.0(2)

* This line gives mean values of bonds lengths for.[1–3] The C(13)–Br bond is 1.885 Å.[2,3]
** Values of the torsion angles of turn along the bond.

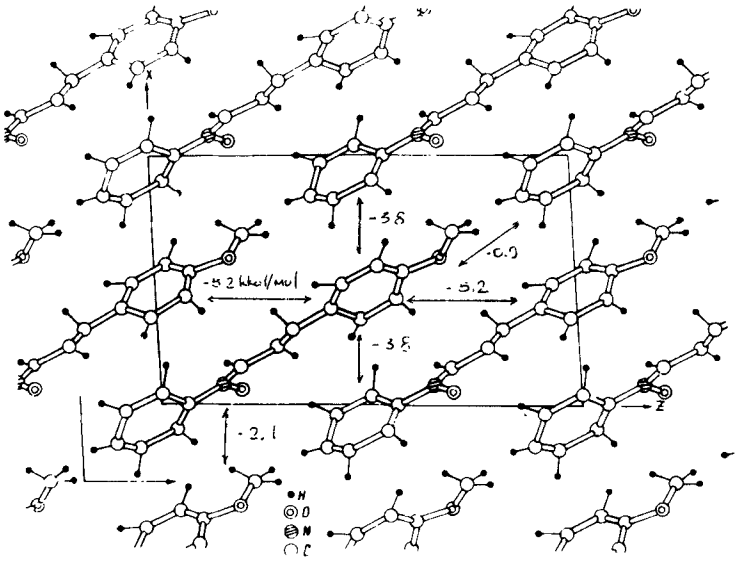


FIGURE 3 Projection of a crystal packing of molecules I on the XOZ plane.

and the coulomb component to -5.0 kkal/mol. The energy of the main conjugated interactions is given in Figure 3. The remaining energies of intermolecular interactions in crystal are not higher than -1.2 kkal/mol.

The projection of the crystal structure of 2 on the XYO plane is shown in Figure 4. No short specific intermolecular contacts are observed in crystal 2 either. The value of the Br–Br contact is 4.5 Å. The total energy of the intermolecular interaction is

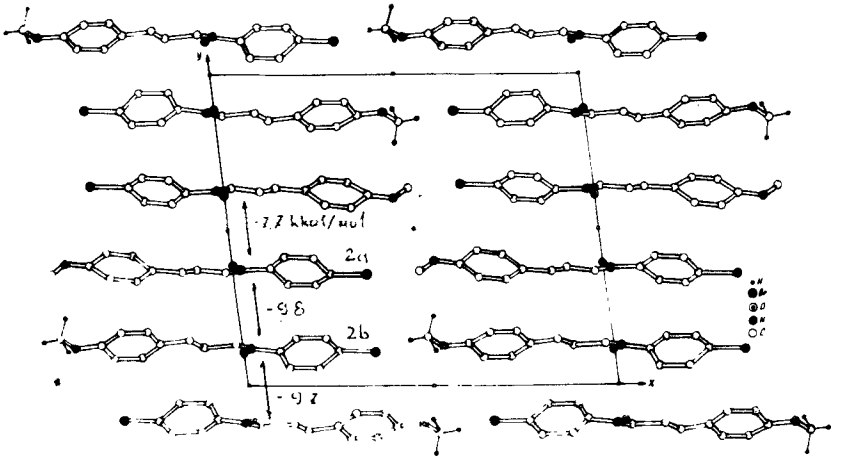


FIGURE 4 Projection of a crystal packing of molecules II on the XYO plane.

– 31.4 kkal/mol, while van der Waals interaction component is – 25.3 kkal/mol, and the energy of the Coulomb interaction is – 6.1 kkal/mol.

As distinct from the molecules of 1, the molecules 2 in crystal form layers along the "*b*" axis. Figure 4 shows the most significant energies of intermolecular interactions along the "*b*" axis. In addition both the independent molecules 2*a* (bonded translationally) and 2*b* (bonded translationally) have high energies of conjugated intermolecular interactions along the "*c*" axis, – 5.9 kkal/mol and – 6.2 kkal/mol. All the other energies of intermolecular interactions do not exceed – 2.5 kkal/mol.

The nitrons of 1 and 2, similar to the *o*-OH vinyl analogs of aldonitrons, are photosensitive in solutions. While irradiating (330–360 nm) compound 2 in ethanol, intensity of a band at 26000 cm^{-1}, corresponding to the initial nitron, decreases and intensity of absorption band at 36200 cm^{-1}, corresponding to the amide photoproduct, increases, this phenomenon being typical for nitrons. Amide photoproduct accumulates due to Beckman rearrangement from oxaziridine at the first stage of photoreaction,[7] (Fig. 5). The calculation of the electron s00pectra (INDO/S) for the initial compound 2 and its amide derivative is in a good agreement with the experimentally observed data: 28914 cm^{-1} for nitron, 36248 cm^{-1} for amide.

Photoconversions of all *o*-OH vinyl analogs of aldonitrons in solid state are due to intermolecular proton transfer and formation of colored quinoid species.[1–3] In crystals of 1 and 2, as opposed to *o*-OH vinyl analogs of aldonitrons, photoconversion can be due only to the closing of the oxaziridine three-membered heterocycle[6] characteristic of N-oxides of azomethines. In crystal such a reaction can occur if to conditions are met:

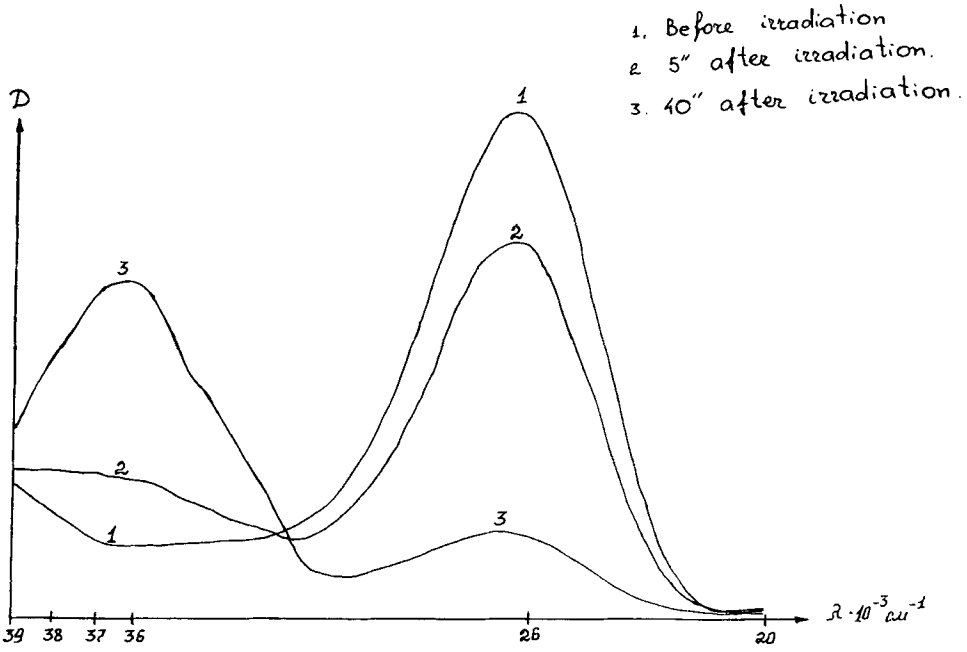


FIGURE 5 The absorption UV-spectrum of compound 2 in C_2H_5OH.

(1) a volume of a molecule formed does not exceed a volume of an initial molecule; (2) free space around an initial molecule is sufficient for its transformation into the product molecule. To study the possibilities of such a conversion in 1 and 2, we calculated the portion of the unit cell free volume, V_p, by formula:

$$V_p = V_{\text{cell}} - Z * V_{\text{mol}}$$

and the difference in the volumes of molecules of the proposed oxaziridine photoproduct and the initial nitron, ΔV(Table IV):

$$\Delta V = V_{\text{oks}} - V_{\text{mol}}$$

The oxaziridine photoproduct was modelled based on the structural data from[7] using the molecular mechanics method.[8]

As seen from the calculation data, the value of $Z * \Delta V$ for 1 (-3.6 Å^3) and 2a,b (-2.6 Å^3, -2.8 Å^3) is negative and insignificant in its absolute meaning, which points that the cyclization of 1 and 2 will be followed by decreasing of the molecule volume. However, this cyclization should lead to significant changes in the geometry of the molecule caused mainly by the fact that the nitron group carbon atom becomes sp^3 hybridized, and the electron structure of the nitrogen atom takes an sp^2 hybrid configuration.

Therefore, there must be some free volume reserve for the photoconversion to take place. It is obvious that the closer the molecules are packed in the crystal, the more hindered these reactions are. Thus it may be assumed that in the crystal of 2 where the molecules 2a and 2b form layers with appreciable energies of intermolecular interactions, this process will be more hindered than in 1, although V_p/Z (2) > V_p/Z (1). This is proved by the following fact. With the rotation of the phenyl substituent about the N–C(10) bond and the vinylmethoxyphenyl fragment about the C(1)–C(2) bond in crystal 1, the crystal structure energy (curves *a*, *b* in Fig. 6) grows slower than with the rotation of the phenyl substituent about the N–C(10) bond and the vinylmethoxyphenyl fragment about the C(1)–C(2) bond in crystal 2 (curves a, b in Fig. 6).

On the other hand, we calculated the energies of the crystal structures in the proposed cyclic photoproducts of 1 and 2 in the lattices of the initial compounds 1 and 2. In this case the mass center of the initial and final molecules was assumed to be the

TABLE IV

The free volume portion in structures 1–2, the volume of the initial and final molecules

N	Z	V_{cell} Å^3	V_{mol} Å^3	V_{ox} Å^3	V_p Å^3	$Z * \Delta V$ Å^3	k	V_p/Z Å^3
1	2	660.3	190.6	188.8	278.8	−3.6*	0.6	139.4
2a	2	1423.0	213.1	211.8	570.6	−2.6	0.6	142.7
2b	2	1423.0	212.5	211.1	570.6	−2.8	0.6	142.7

* minus indicates a decrease in the molecular volume as a result of cyclization.
$k = (Z * V_m/V_{\text{cell}})$-the coefficient of crystal packing.

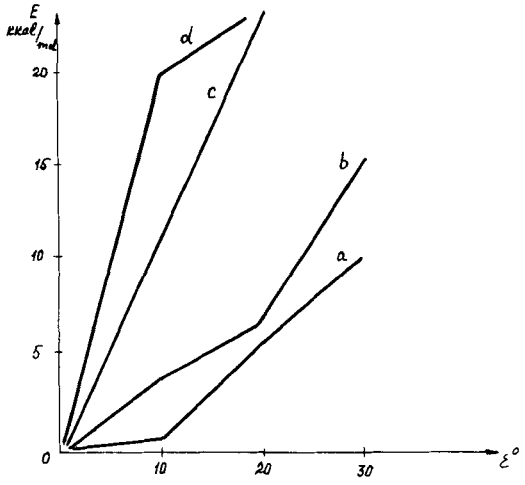


FIGURE 6 The crystal lattice energy (E) against the rotation angles of the substituents at the nitron and carbon atoms of the azomethine bond in crystals 1 and 2.

same. Then, using the "PMC" program,[9] the molecular positions (mass center coordinates and Euler angles) in unit cells were optimized. After the optimization, energy of the crystal lattice formed by the photoproduct 1 molecules was found to be -21.9 kkal/mol (van der Waals component), which confirmed the capability of the photoproduct 1 to form an independent crystal phase; the energy of the crystal lattice formed by the photoproduct 2 molecules was found to be positive.

It may be concluded that closing of the oxaziridine cycle in the crystals of 1 and 2 on UV irradiation is possible. In this case the photoproduct 1 can 0 form an independent crystal phase in the initial substance, i.e. the reaction proceeds by the principle of "single crystal-single crystal". The formation of the similar photoproduct 2 is followed by stronger stresses in the initial substance lattice and is evidently accompanied by the destruction of the molecule 2 crystal structure.

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