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Molecular and Crystal Structure of C-(2-Phenoxy-1 -Vinyl)-N-n-Bromophenyl Nitrone and C-(2-Phenoxy-1 -Vinyl)-N-Phenyl Nitrone

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Molecular and Crystal Structure of *C*-(2-Phenoxy-1-Vinyl)-*N*-*n*-Bromophenyl Nitrone and *C*-(2-Phenoxy-1-Vinyl)-N-Phenyl Nitrone

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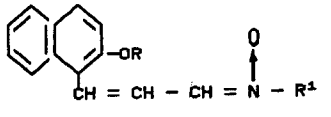
An X-ray study of the crystals of *C*-(2-phenoxy-1-vinyl)-*N*-*n*-bromophenyl nitrone (I) and *C*-(2-phenoxy-1-vinyl)-*N*-phenyl nitrone (II) has been performed. The main crystal data of I: $C_{15}H_{12}NO_2Br$, $a = 10.807(5)$ Å, $b = 10.275(5)$ Å, $c = 15.415(7)$ Å, $\beta = 129.7(2)°$, $M = 318.14$, $V = 1525(2)$ Å^3, $d_{calc} = 1.385(3)$ g/cm^3, Space gr. $P2_1/b$, $Z = 4$. The main crystal data of II: $C_{15}H_{13}NO_2$, $a = 12.760(4)$ Å, $b = 19.784(6)$ Å, $c = 9.805(4)$ Å, $M = 239.64$, $V = 2475(1)$ Å^3, $d_{calc} = 1.284(2)$ g/cm^3, Space gr. Pbna, $Z = 8$.

The crystal packing of I and II is characterized by the presence of centrosymmetric dimer associates (CDA) existing due to stable intermolecular hydrogen bonds (IMHB). Such a crystalline structure of these nitrones accounts for the possibility of intermolecular proton transfer along the O → O coordinate to form a coloured quinoid product.

1. INTRODUCTION

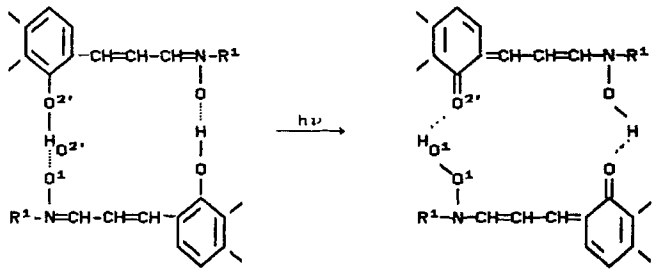
It is shown[1] that o-derivative of vinylogs of aldonitrones with R = H, R^1 = Ph (1–1) and with R = H, R^1 = *n*-MePh (1–2) form in crystals CDA where the molecules are



1–1: R = H, R^1 = Ph; 1–2: R = H, R^1 = П-MePh

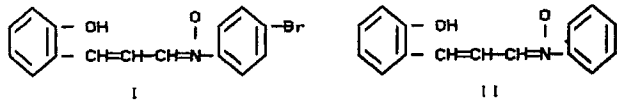
bound with stable intermolecular hydrogen bonds. This structure suggests a different way of photochemical transformation of the vinylogs of aldonitrones with an o-OH group in the aryl nucleus, which consists in a synchronous proton phototransfer along the O → O coordinate in CDA, and not in a formation of an oxaziridine heterocycle (Scheme 1).

In order to find out the peculiarities of the crystal structure and character of IMHB formation in crystals of the other hydroxy derivaties of the vinilogs of aldonitrones



SCHEME 1

X-ray investigation of *C*-(2-phenoxy-1-vinyl)-*N*-*n*-bromophenyl nitrone (I) and *C*-(2-phenoxy-1-vinyl)-*N*-phenyl nitrone (II) have been performed.



I II

2. EXPERIMENTAL

I crystallizes as red–yellow rectangular plates in monoclinic syngony. The main crystal data of I: $C_{15}H_{12}NO_2Br$, $a = 10.807(5)$ Å, $b = 10.275(5)$ Å, $c = 15.415(7)$ Å, $\beta = 129.7(2)$ Å, $M = 318.14$, $V = 1525(2)$ Å^3, $d_{calc} = 1.385(3)$ g/cm^3, Space gr. $P2_1/b$, $Z = 4$.

Integral intensities of 1839 independent reflections from crystal 1 were collected on an automated four-circle diffractometer KM-4 (MoK_α-radiation). Absorption was not considered.

II crystallizes as bright-yellow rectangular plates in orthorombic syngony. The main crystal data of II: $C_{15}H_{13}NO_2$, $a = 12.760(4)$ Å, $b = 19.784(6)$ Å, $c = 9.805(4)$ Å, $M = 239.64$, $V = 2475(2)$ Å^3, $d_{calc} = 1.284(2)$ g/cm^3, Space gr. Pbna, $Z = 8$.

Integral intensities of 1427 independent reflections from crystal II were collected on an automated three-circle diffractometer DAR (CuK_α-radiation). Absorption was not considered.

Structures I and II were determined by a direct method with a program complex "SHELL-76"[2] and refined with a full matrix least-squares technique in anisotropic approximation (non hydrogen 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 0.059 and 0.069, respectively. Atomic coordinates for I and II are given in Tables 1 and 2 respectively.

Calculation of the energy of intermolecular interactions (IMIE) was made in the framework of atom–atom approximations using "6-exp" potentials with parameters given in Reference 3.

3. RESULTS AND DISCUSSION

A general view of molecule I is shown in Figure 1. Non-planarity of I is accounted for by rotations of *n*-bromophenyl fragment about a N—C^{10} bond and the *o*-OHPh fragment about a C^3—C^4 bond by 17.8(2)° and 4.0(2)°, respectively, in opposite directions. The central vinyl-nitrone fragment deviates insignificantly from planarity, due to rotations along the C^1—C^2 bond by 2.3(2)° and along the C^2—C^3 bond by 5.7(2)°. The value of Br–Br contacts in within 4.14–4.20 Å.

A general view of molecule II is shown in Figure 2. Non-planarity of I is accounted for by rotations of phenyl fragment about a N—C^{10} bond by 35.2(2)° and the *o*-OHPh fragment about a C^3—C^4 bond by 6.8(2)°. The central vinyl-nitrone fragment, the angles of rotation about the bonds N—C^1, C^1—C^2, C^2—C^3 are 6.5(2)°, −4.7(3)°, 5.9(2)°, respectively.

TABLE 1

Coordinates of Non Hydrogen Atoms (*10^4) and Hydrogen Atoms (*10^3) in Molecule $C_{15}H_{12}NO_2Br$

	X	Y	Z
BR	4558(3)	13100(3)	1471(4)
N_1	1178(3)	11768(4)	3344(4)
O_2	1199(4)	10515(4)	3532(4)
O_1	−1610(3)	10978(3)	4890(4)
C_2	419(3)	12606(3)	3495(4)
C_3	−370(3)	12303(3)	3928(3)
C_4	−1063(4)	13263(4)	4092(4)
C_5	−1832(3)	13261(4)	4586(3)
C_6	−2045(3)	12162(3)	5014(3)
C_7	−2694(3)	12294(4)	5539(4)
C_8	−3196(4)	13486(3)	5633(4)
C_9	−3036(4)	14574(3)	5183(3)
C_{10}	−2374(3)	14459(3)	4679(3)
C_{11}	2012(2)	12141(4)	2940(4)
C_{12}	3119(3)	11273(4)	3082(4)
C_{13}	3904(3)	11580(3)	2676(3)
C_{14}	3599(3)	12743(3)	2125(4)
C_{15}	2539(4)	13610(3)	2009(4)
C_1	1760(4)	13330(4)	2423(3)
H_2	68(2)	1345(2)	351(1)
H_3	−32(3)	1137(2)	422(2)
H_6	−84(1)	1410(2)	397(2)
H_7	−265(2)	1160(1)	590(2)
H_8	−366(2)	1364(2)	610(2)
H_9	348(1)	1552(1)	524(2)
H_{11}	−238(2)	1521(2)	426(2)
H_{12}	317(1)	1041(2)	339(2)
H_{14}	474(1)	1112(2)	293(1)
H_{15}	213(2)	1428(1)	150(2)
H	81(2)	1389(1)	221(1)
H_{02}	−151(2)	1047(2)	525(2)

TABLE 2

Coordinates of Non Hydrogen Atoms (*10^4) and Hydrogen Atoms (*10^3) in Molecule $C_{15}H_{13}NO_2$

	X	Y	Z
N_1	2549(3)	−794(2)	1856(4)
O_2	2774(3)	−795(2)	557(3)
O_1	5693(3)	570(2)	1143(3)
C_2	3013(4)	−401(2)	2709(4)
C_3	3855(3)	38(2)	2412(4)
C_4	4319(4)	388(2)	3419(4)
C_5	5237(3)	821(2)	3424(4)
C_6	5487(4)	1167(2)	4620(5)
C_7	6327(4)	1573(2)	4756(5)
C_8	6985(4)	1634(2)	3672(5)
C_9	6783(4)	1305(2)	2446(5)
C_{10}	5914(3)	893(2)	2315(4)
C_{11}	1768(3)	−1278(2)	2248(4)
C_{12}	1737(4)	−1891(3)	1596(5)
C_{13}	1003(4)	−2360(3)	1922(5)
C_{14}	291(4)	−2234(3)	2939(5)
C_{15}	320(4)	−1622(3)	3566(5)
C_1	1059(4)	−1130(2)	3273(5)
H_2	270(1)	−38(1)	347(1)
H_3	419(1)	3(1)	146(1)
H_5	402(1)	37(1)	439(1)
H_6	505(1)	110(1)	521(1)
H_7	649(1)	189(1)	544(1)
H_8	756(1)	194(1)	386(1)
H_{11}	720(1)	130(1)	168(1)
H_{12}	224(1)	−189(1)	92(1)
H_{13}	95(1)	−282(1)	151(1)
H_{14}	−22(1)	−259(1)	322(1)
H_{15}	−12(1)	−153(1)	418(1)
H	103(1)	−57(1)	365(1)
H_{02}	626(1)	58(1)	45(1)

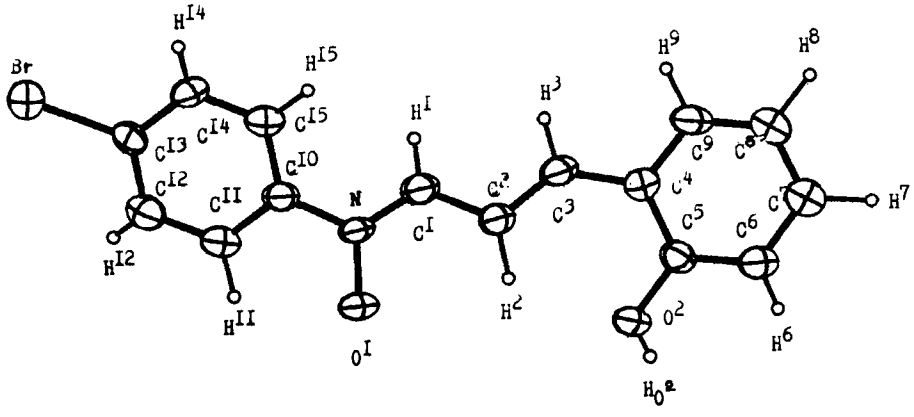


FIGURE 1 A general view of molecule I.

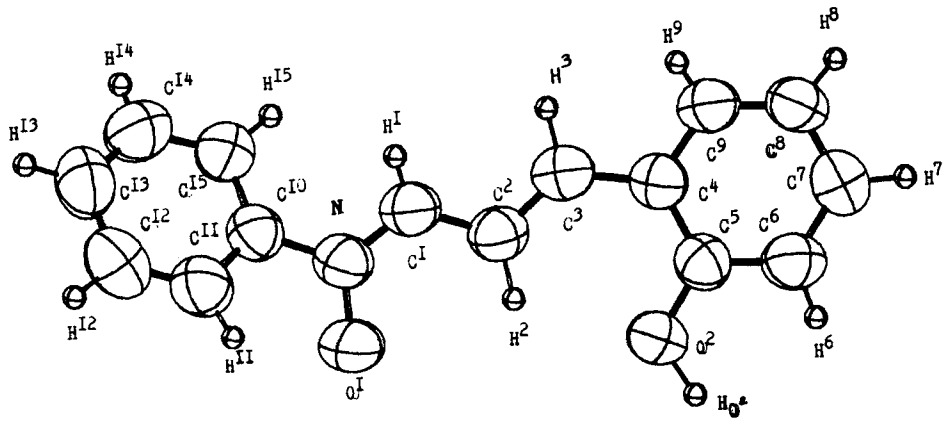


FIGURE 2 A general view of molecule II.

TABLE 3

	$N^1—O^1$	$>C^1=N^1$	$N^1—C^{10}$	$C^1N^1O^1$, deg.	$O^1N^1C^{10}$, deg.	$C^1N^1C^{10}$, deg.
I	1.310(4)	1.308(3)	1.432(4)	121.5(2)	115.2(2)	123.3(2)
1-1	1.308(3)	1.312(3)	1.454(4)	121.7(4)	115.5(5)	122.8(3)
II	1.306(3)	1.286(4)	1.435(4)	122.3(2)	114.5(2)	123.3(2)
1-2	1.313(7)	1.313(10)	1.451(11)	124.0(7)	112.9(6)	122.9(6)
[4]	1.266 ÷	1.270 ÷	1.438 ÷	120.3 ÷	113.4 ÷	118.0 ÷
[5]	÷ 1.308	÷ 1.357	÷ 1.511	÷ 126.3	÷ 116.0	÷ 123.0

Continuation of Table 3

N	Torsion angles (deg.)				
	$C^{11}C^{10}NC^1$	$NC^1C^2C^3$	$C^1C^2C^3C^4$	$C^2C^3C^4C^5$	$C^{10}NC^1C^2$
I	17.8(2)	2.3(2)	5.7(2)	4.0(3)	3.9(2)
1-1	22.9(2)	2.2(2)	3.5(2)	18.1(2)	4.4(2)
II	35.2(2)	4.5(2)	5.9(2)	6.8(2)	4.7(2)
1-2	39.3(2)	2.6(2)	0.0(0)	13.5(2)	0.0(0)

The nitrone groups in both molecules are planar. The distribution of bond lengths and angles in the indicated group for I and II are the following: $N—O^1 = 1.310(4)$, 1.306(3); $N—C^1 = 1.308(3)$, 1.286(4); $N—C^{10} = 1.432(4)$, 1.435(4) Å; $O^1NC^1 = 121.5(2)°$; 122.2(2)°; $O^1NC^{10} = 115.2(2)°$, 114.5(2)°; C^1NC^{10} 123.3(2)°, 123.3(3)°. A rotation of the hydroxylic group along the $C^5—O^2$ bond is 12.7(3)° and 19.1(3)° for I and II, respectively.

Table 3 gives geometric data of I and II as compared with the earlier studied nitrones 1-1 and 1-2 and the literature data on the characteristic values of the nitrone group. From Table 3 it is clear that I and II have inconsiderable geometric differences in the nitrone systems presented here. On the one hand, the angles of rotation of the substituents about the $N—C^{10}$ bond in I and II are greater than in 1-1 and 1-2, on the other hand, Table 3 shows the bond length of $N—C^{10}$ in I and II is shortened.

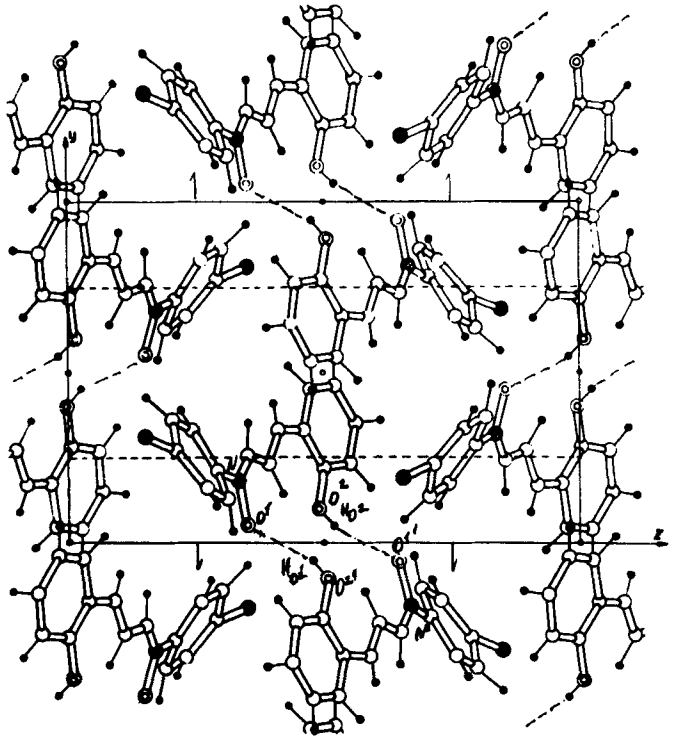


FIGURE 3 Projection of a crystal packing of molecules I on the OYZ plane.

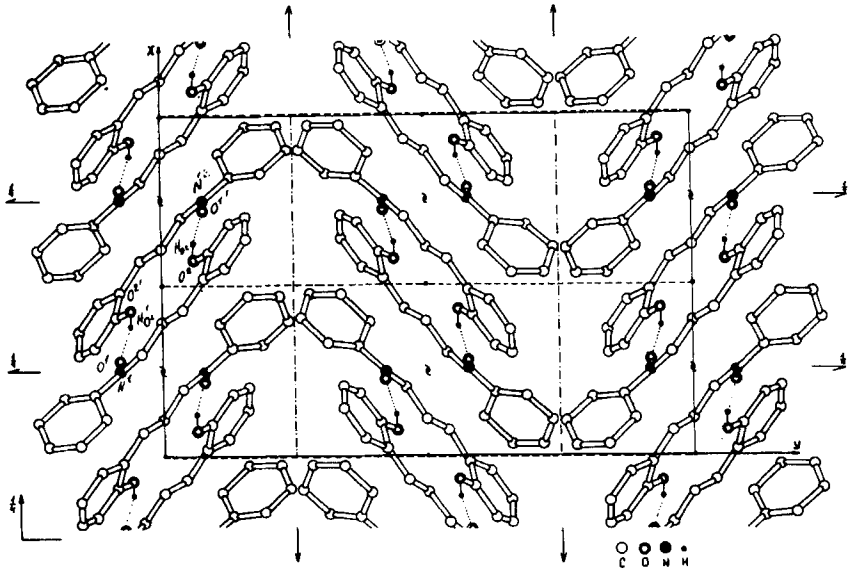


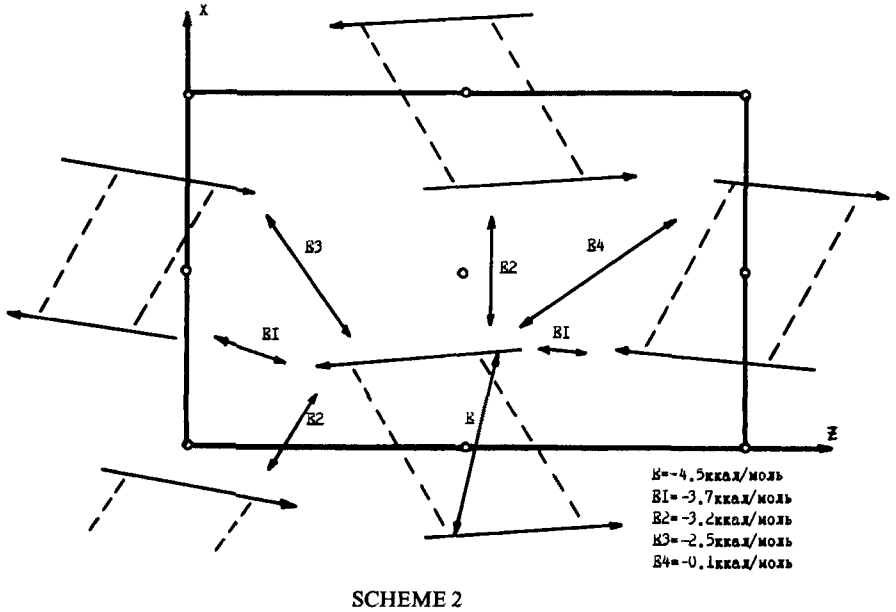
FIGURE 4 Projection of a crystal packing of molecules II on the XYO plane.

TABLE 4

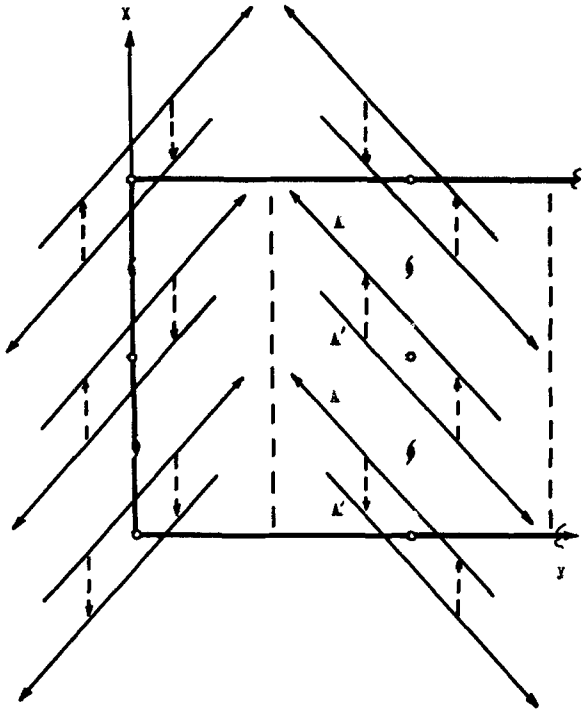
Compound	$O^1..O^{2'}$	$H_{02'}...O^1$	$O^1H_{02'}O^{2'}$	$H_{02'}O^{2'}N$
1	2.662	1.964	165.0°	133.2°
1–1	2.658	1.530	156.6°	123.7°
2	2.567	1.567	165.0°	137.8°
1–2	2.580	1.420	180.0°	140.0°

The presence of centrosymmetric dimer associates analogous to Reference 1 (Figure 3,4) is a characteristic feature of the crystal packing of compounds I and II. CDA of compound I is formed by IMHB: $O^1..H_{02'} = 1.964(3)$ Å, $O^1...O^{2'} = 2.662(4)$ Å, $O^1H_{02'}O^{2'} = 165.0(2)°$, $H_{02'}O^1N$ 133.2(3)°. The angle between direction $O^2—H_{02'}$ and the plane passing through atoms O^1, C^1, C^{10} is 21.5(2)°. The main characteristics of IMHB in the CDA of compound II: $O^1..H_{02'} = 1.567(3)$ Å, $O^1...O^{2'} = 2.567(4)$ Å, $O^1H_{02'}O^{2'} = 165.8(2)°$, $H_{02'}O^1N = 137.2(2)°$. The angle between direction $H_{02'}—O^2$ and the plane passing through atoms O^1, C^1, C^{10} is 22.6(2)°. Table 4 lists geometric data on IMHB for I and II as compared with 1–1 and 1–2. It is clear from this table that in compound 1–2 the hydrogen bond $H_{02'}...O^2$ is shorter than in II although the value of contact $O^1...O^{2'}$ is greater. Such a correction between the above values is due to the fact that in 1–2 IMHB has a more linear value of angle $O^1H_{02'}O^{2'} = 180°$ than in II: $O^1H_{02'}O^{2'} = 165°$.

The projection of crystal lattices I on plane OXZ and of II on plane XYO are shown in Figures 3,4, respectively. The total energy of the crystal packing in I and II is −28.0 and −24.8 kcal/mole, respectively, not taking into account the IMHB energy. Analogous to 1–1 and 1–2, the molecules in the dimer associates in crystal structures I and II are packed by "head-to-tail" (Schemes 2 and 3) but, as distinct from the latter,



SCHEME 2



SCHEME 3

TABLE 5

Compound	$O^1..O^{2'}$	$H_{01'}...O^{2'}$	$O^1H_{01'}O^{2'}$	$H_{01'}O^2C^5$
I	2.698	2.16	114°	121°
II	2.597	2.00	116°	131°

do not form molecular stacks and three-dimension frameworks. It is confirmed by the energies of − 6.1 kcal/mole, and the energies of intermolecular interactions between the nearest molecules from the neighbour dimer associates in I: E1 = − 3.7, E2 = − 3.2, E3 = − 2.5 kcal/mole in their values are comparable with the energy between the *A* and *A'* molecules in CDA equal to − 4.5 kcal/mole (Scheme 2). Meanwhile in 1–1, for example, the energy between the molecules in a dimer associate is − 6.1 kcal/mole, and the intermolecular interaction energy in one of the directions is − 11.9 kcal/mole in Reference 1.

The fact that the structure of CDA in the crystals of nitrones I and II is analogous to that of CDA in crystals 1–1 and 1–2 suggest an analogous mode of their photochemical transformation in the solid state, which is associated with a synchronous proton phototransfer along the O→O coordinate to form coloured quinoud products. Geometric modelling of an transfer in dimer associate I and II points to a marked weakening of IMHB in the phototransformation products: the hydrogen bond length is

increased to 2.00 Å in I and to 2.16 Å in II, and respectively, the $O^1 \ldots O^{2'}$ contacts increase, on the one hand, and angle $O^1 H_{01} O^{2'}$ is significantly distorted to 114°, on the other hand, which should hinder a reverse proton transfer and stabilize the photoproduct structure (Table 5 and Scheme 1).

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