Characteristic features of photochemical conversions of *C*-(2-furyl-5-nitro)-*N*-phenyl- and *C*,*N*-di(*p*-bromophenyl)nitrones in liquid and crystal phases

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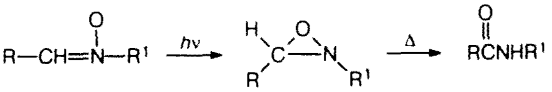
Photoconversions of *C*-(2-furyl-5-nitro)-*N*-phenylnitrone (**1**) and *C*,*N*-di(*p*-bromophenyl)nitrone (**2**) were studied in solutions with different polarity. The UV spectrum of **1**, unlike that of **2**, shows a long-wavelength absorption band, which is observed only in polar solutions. This band corresponds to the intermediate product of the photochemical conversion of compound **1**. Based on the results of quantum-chemical calculations, a scheme of probable photoconversion of nitrone **1** in polar solvents and the molecular structure of the intermediate product were suggested. Based on the data of X-ray structural analysis of compounds **1** and **2** and the results of calculations of model compounds, it was demonstrated that solid-phase photoconversion, which is associated with the formation of the oxaziridine heterocycle, can occur.

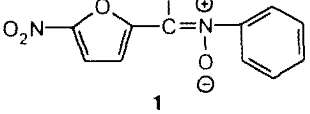
Key words: nitrones, molecular structure, X-ray structural analysis, quantum chemistry, absorption spectra.

It is known[1] that isomerization to unstable oxaziridines immediately from the low-lying excited singlet state followed by rearrangement with the formation of the final products (amides) of the photoreaction is the photochemical conversion typical of nitrones in the liquid phase.

Scheme 1



In this work, photoconversions of *C*-(2-furyl-5-nitro)-*N*-phenylnitrone (**1**) and *C*,*N*-di(*p*-bromophenyl)nitrone (**2**) in solutions with different polarity were studied by X-ray structural analysis, UV spectroscopy, and quantum chemistry. It was found that, unlike nitrone **2**, photoconversion of compound **1** in polar solvents affords a stable intermediate product, which is characterized by an intense absorption band in the region of 17000—18000 cm^{-1}. The characteristic features of liquid-phase and solid-phase photoconversions of nitrones **1** and **2** and of some model compounds were studied.



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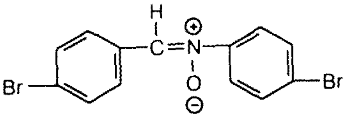

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Experimental

***C*-(2-Furyl-5-nitro)-*N*-phenylnitrone (1).** A solution of NH_4Cl (6.42 g) in H_2O (50 mL) was added to a solution of nitrobenzene (12.3 g) in 95% ethanol (50 mL), and the mixture was cooled in an ice bath. Powdered Zn (15.7 g) was added portionwise (3 g) with stirring to the mixture. The reaction mixture was stirred for 25 min. Then a solution of 5-nitrofurfurol (9.9 g) in CH_3COOH (50 mL) was added. The mixture was stirred for 30 min and then poured into toluene (200 mL). After washing with a saturated $NaHCO_3$ solution (150 mL) and H_2O (150 mL), toluene was removed by distillation *in vacuo* with heating. The hot residue was added to cyclohexane (200 mL) and cooled. The precipitate was filtered off. The yield of the compound was 5.2 g (44.7%), m.p. 178 °C. Found (%): C, 56.97; H, 3.51; N, 12.12. $C_{11}H_8N_2O_4$. Calculated (%): C, 56.89; H, 3.45; N, 12.07.

***C*,*N*-Di(*p*-bromophenyl)nitrone (2)** was prepared using the same procedure as in the synthesis of **1** from *p*-bromonitrobenzene and *p*-bromobenzaldehyde. The yield was 38.9%, m.p. 235 °C. Found (%): C, 43.98; H, 2.60; N, 3.98. $C_{13}H_9NOBr_2$. Calculated (%): C, 43.94; H, 2.54; N, 3.94.

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Table 1. Coordinates of nonhydrogen atoms (×10^4) and hydrogen atoms (×10^3) for the $C_{11}H_8N_2O_4$ molecule (**1**)

Atom	*x*	*y*	*z*
O(1)	4662 (3)	1779 (2)	983 (2)
O(2)	3595 (2)	430 (3)	3529 (3)
O(3)	2846 (3)	−471 (2)	4877 (2)
O(4)	2326 (3)	0 (2)	3427 (3)
N(1)	4758 (2)	1333 (4)	2106 (2)
N(2)	2748 (2)	−31 (2)	3838 (3)
C(1)	4414 (2)	932 (3)	2908 (2)
C(2)	3902 (3)	969 (2)	2585 (3)
C(3)	3630 (2)	1350 (2)	1568 (3)
C(4)	3133 (3)	1046 (3)	1863 (2)
C(5)	3134 (3)	496 (2)	3037 (3)
C(6)	5280 (3)	1234 (2)	2449 (1)
C(7)	5334 (3)	1712 (2)	3612 (3)
C(8)	5934 (2)	1620 (3)	3870 (2)
C(9)	6271 (3)	1104 (2)	2987 (2)
C(10)	6110 (3)	621 (2)	1829 (3)
C(11)	5609 (2)	696 (3)	1547 (3)
H(1)	520 (4)	223 (4)	413 (5)
H(3)	603 (4)	205 (4)	477 (4)
H(4)	661 (4)	111 (3)	317 (4)
H(7)	635 (4)	19 (3)	123 (3)
H(8)	549 (4)	22 (3)	78 (3)
H(9)	452 (3)	40 (3)	372 (4)
H(10)	376 (3)	193 (4)	86 (4)
H(11)	285 (4)	126 (4)	139 (4)

Compound **1** crystallized from toluene as pale-rose rectangular plates belonging to the orthorhombic system. The principal crystallographic data are as follows: $C_{11}H_8N_2O_4$, a = 27.007 (6), b = 7.209 (4), c = 10.900 (5) Å, M = 232.20, V = 2120 (1) Å^3, d_{calc} = 1.450 g cm^{-3}, Z = 8, space group *Pbca*.

Compound **2** crystallized from ethanol as yellow plates belonging to the monoclinic system. The principal crystallographic data are as follows: $C_{13}H_9NOBr_2$, a = 24.990 (8), b = 6.180 (4), c = 3.984 (3) Å, β = 85.5 (2)°, M = 355.00, V = 614 (1) Å^3, d_{calc} = 1.920 g cm^{-3}, Z = 2, space group $P2_1/a$.

Intensities of 1525 (**1**) and 1601 (**2**) independent reflections with $I > 2\sigma(I)$ were measured on an automated four-circle KM-4 diffractometer (Mo Kα radiation). The structures were solved by direct methods using the SHELX program package[2] and refined anisotropically (nonhydrogen atoms) by the full-matrix least-squares method. Hydrogen atoms were located from difference Fourier syntheses. The final values of the R factors were 0.055 (**1**) and 0.061 (**2**). Atomic coordinates for molecules **1** and **2** are given in Tables 1 and 2, respectively.

Molecule **2** occupies a special position (a center of symmetry) and, hence, is statistically disordered. It was first assumed that molecule **2** is centrosymmetrical and contains two N→O groups. However, refinement by the full-matrix least-squares method demonstrated that the oxygen atom had anomalously large thermal parameters, namely, when the R factor was 0.095, the diagonal elements were 0.146, 0.1470, and 0.153. Therefore, the atoms of the nitrone group were included in the refinement with occupancies of 0.5. These occupancies were also refined. The final values of the occupancies of the O, N, and C(1) atoms were 0.53, 0.53, and 0.52, respectively. The thermal parameters of the oxygen atom were 0.079, 0.093, and 0.168. The final value of the R factor was 0.061, which is indicative of the validity of the model. The position of the H(1) atom was calculated from geometric considerations.

Table 2. Coordinates of nonhydrogen atoms (×10^4) and hydrogen atoms (×10^3) for the $C_{13}H_9NOBr_2$ molecule (**2**)

Atom	*x*	*y*	*z*
Br(1)	2040 (4)	9559 (3)	4084 (4)
Br(2)	−2040 (4)	20441 (3)	−4084 (4)
N	233 (4)	15235 (3)	−0177 (4)
O	462 (3)	17021 (4)	−1650 (4)
C(1)	−233 (3)	14765 (4)	0177 (4)
C(2)	−639 (3)	16183 (4)	−0943 (4)
C(3)	−1158 (4)	15461 (3)	−0479 (4)
C(4)	−1578 (3)	16689 (3)	−1374 (4)
C(5)	−1467 (3)	18650 (4)	−2858 (3)
C(6)	−959 (3)	19430 (4)	−3248 (3)
C(7)	−541 (4)	18160 (3)	−2365 (3)
C(8)	639 (4)	13817 (4)	0943 (4)
C(9)	541 (4)	11840 (4)	2365 (4)
C(10)	959 (4)	10570 (4)	3248 (3)
C(11)	1467 (3)	11350 (3)	2858 (3)
C(12)	1578 (3)	13310 (3)	1374 (4)
C(13)	1158 (3)	14539 (4)	0479 (4)
H(1)	−34 (4)	131 (4)	−106 (4)
H(3)	−126 (4)	141 (4)	74 (3)
H(4)	−196 (4)	161 (4)	−93 (5)
H(6)	−89 (4)	208 (4)	−487 (5)
H(7)	−20 (5)	189 (4)	−249 (4)
H(9)	20 (4)	112 (5)	249 (4)
H(10)	89 (4)	92 (5)	487 (4)
H(12)	196 (5)	139 (5)	93 (4)
H(13)	126 (4)	159 (4)	−74 (4)

The UV absorption spectra were recorded on a Specord M-40 spectrometer with the use of a reference cell. Samples were prepared as solutions with required concentrations in solvents with different polarity, namely, in heptane, ethanol, and acetonitrile (in the 40000—14000 cm^{-1} region), in benzene and toluene (in the 35000—14000 cm^{-1} region), and in acetone (in 30000—14000 cm^{-1} the region).

Theoretical spectra of various model compounds were calculated by the INDO/S method. The geometries of the molecules were optimized by the semiempirical AM1 and PM3 methods (MOPAC 6.0) and by the *ab initio* method (the STO-3G basis set, GAMES).

The energy of pairwise intermolecular interactions was calculated in the atom-atom approximation with the use of the 6-exp potentials.[3]

Results and Discussion

The overall views of molecules **1** and **2** are shown in Fig. 1. Unlike molecule **2**, molecule **1** is nonplanar. The angle of rotation of the phenyl substituent about the N(1)—C(6) bond is 31.6 (2)°. The bond lengths and bond angles of the nitrone fragment of **1** agree (to within the experimental error) with the published data[4] on the nitrones studied previously. The N—O(1), N—C(Ph), and N=C(1) bond lengths are 1.292 (4), 1.309 (4), and 1.460(5) Å, respectively. The C(1)NO(1), O(1)NC(Ph), and C(1)NC(Ph) angles are 123.1(2), 116.6(2), and 120.3(2)°, respectively. Molecule **2** is planar. The geometry of the molecule is not discussed in detail because of its disorder.

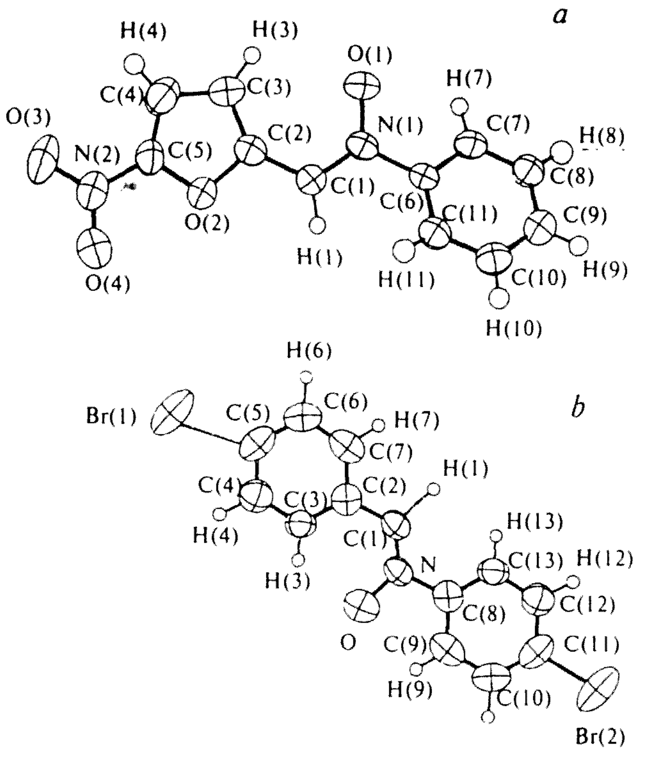


Fig. 1. General views of molecules **1** (*a*) and **2** (*b*).

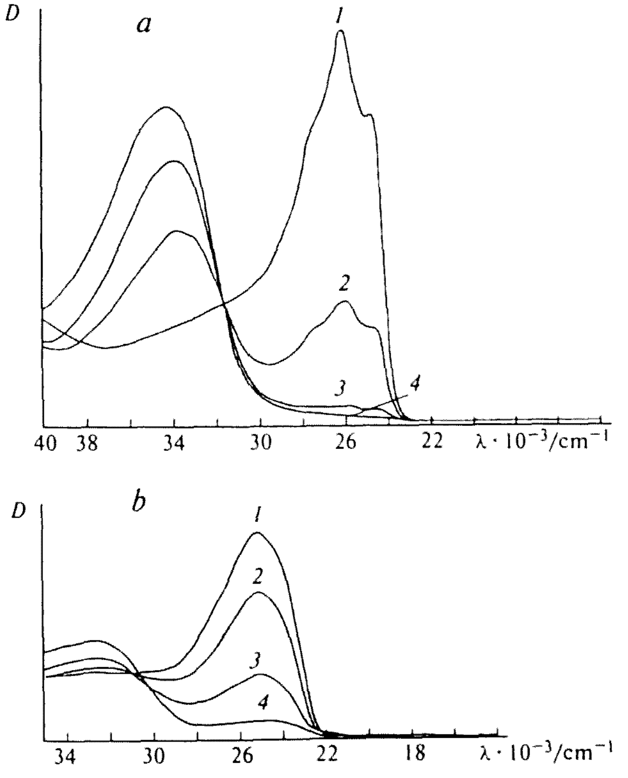


Fig. 2. UV absorption spectra of compound **1** in *n*-heptane (*a*) and benzene (*b*) before (*1*) and after (*2*—*4*) irradiation. Duration of irradiation/s: 30 (*2*), 90 (*3*), and 225 (*4*).

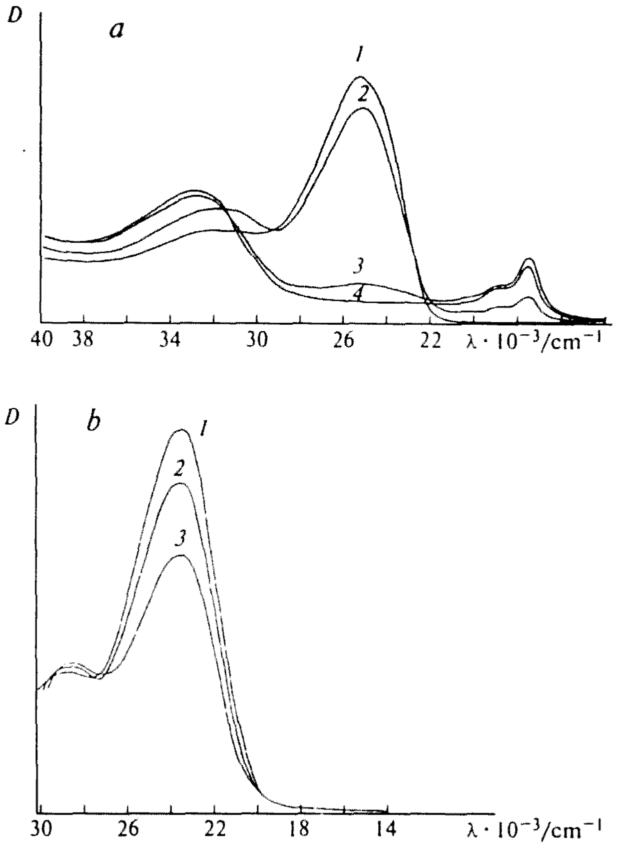
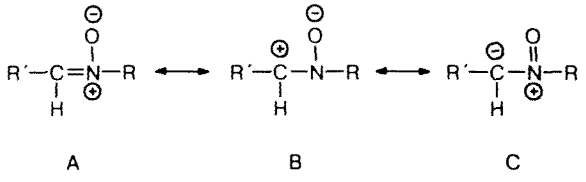


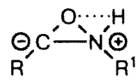
Fig. 3. UV absorption spectra of compound **1** in acetonitrile (*a*) and compound **2** in ethanol (*b*) before (*1*) and after (*2*—*4*) irradiation. Duration of irradiation/s: *a*: 45 (*2*), 225 (*3*), and 825 (*4*); *b*: 10 (*2*) and 65 (*3*).

The initial UV spectra of compound **1** (Figs. 2 and 3) and **2** (Fig. 3) in solvents with different polarity are characterized by two major absorption bands in the regions of 25000—26000 and 32000—34000 cm^{-1}. The UV spectrum of compound **2** was recorded only in ethanol (Fig. 3, *b*). The electronic absorption spectrum of molecule **1** calculated by the quantum-chemical method (INDO/S) with the use of the experimental geometry of molecule **1** (λ_1 30083 cm^{-1} and λ_2 39564 cm^{-1}) differs substantially from the spectra measured in various solvents. When the contributions of the mesomeric forms B and C[5] to the structure of **1** (λ_1 25530, λ_2 34100 cm^{-1} and λ_1 27302, λ_2 31839 cm^{-1}) are taken into account, this agreement is noticeably improved.



When solutions of nitrone **1** in nonpolar solvents (*n*-heptane (Fig. 2, *a*) and benzene (Fig. 2, *b*)) are irradiated with UV light (λ 360 nm), a decrease in the intensity of the long-wavelength absorption band (λ 26000 cm^{-1}), an increase in the intensity of the absorption band in the region of ~34000 cm^{-1}, and a weak bathochromic shift of this band are observed, which are typical of nitrones. According to the published data,[1] this photoconversion may be associated with the formation of a cyclic oxaziridine photoproduct.

When solutions of nitrone **1** in polar solvents (acetone, toluene, ethanol, and acetonitrile) are irradiated with UV light, analogous changes are observed in the absorption spectra along with a long-wavelength band at ~17000 cm^{-1} (Fig. 3, *a*). In highly polar acetonitrile, this band is complex. This absorption band cannot be assigned to the initial nitrone or to the final amide photoproduct, and therefore, it may be suggested that this band corresponds to the intermediate product of the Beckmann rearrangement. This intermediate product is a substituted oxaziridine, in which the hydrogen atom shifts from the carbon atom toward the nitrogen atom. Formation of the final amide is associated with the intramolecular shift of the hydrogen atom, which can occur both through the shortest pathway (C→N) and through the oxygen atom (C→O→N). With the aim of elucidating the mechanism of this process, we carried out quantum-chemical calculations (the INDO/S method) of model compounds **3**, **4**, and **5**. The most probable sites for the location of hydrogen atoms were determined from the maps of the distribution of electrostatic potential for the oxaziridine ring in the ground state (Fig. 4): **3** (λ_1 16176 and λ_2 27718 cm^{-1}), **4** (λ_1 19987 and λ_2 27327 cm^{-1}), and **5** (λ_1 19047 and λ_2 23326 cm^{-1}).



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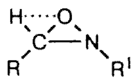

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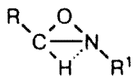

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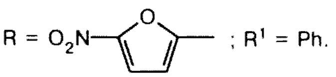

The results of calculations demonstrated that none of the structures is the intermediate form of photoconversion of nitrone **1**. Apparently, all these structures make particular contributions to the actually occurring intermediate state.

Stabilization of such intermediate forms is possible for nitrone **1** because of its particular molecular structure. The nitrofuran substituent is a strong acceptor, and stabilizes the structure with the negative charge on the C(1) atom.

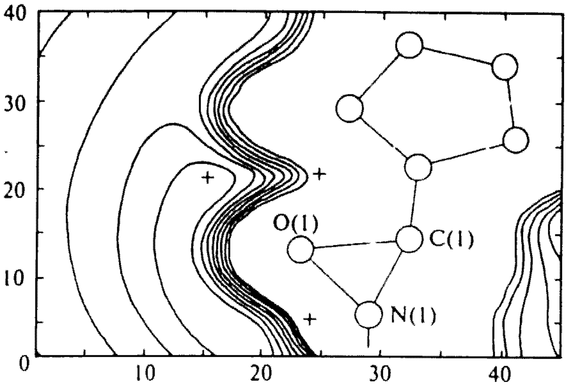

Fig. 4. Map of electrostatic potential distribution for oxaziridine photoproduct **1**.

We have also studied the possibility of photoconversion in crystals of **1** and **2**. The crystal structure of compound **1** is characterized by the absence of short intermolecular contacts. The projection of the crystal packing of compound **1** onto the XYO plane is shown in Fig. 5, *a*. The total energy of the crystal packing is −23.0 kcal mol^{-1}. The pairwise interactions between molecules that are related by a twofold screw axis and that are packed in stacks along the crystallographic *b* axis, make the major contribution to the energy (−9.4 kcal mol^{-1}). The projection of the crystal packing of compound **2** is shown in Fig. 5, *b*. The total energy of the crystal packing is −24.7 kcal mol^{-1}. Molecules **2**, which are related by translation along the *Z* axis, are packed in stacks in which the energy of intermolecular interactions is −11.9 kcal mol^{-1}. In addition, the energies of pairwise interactions between adjacent molecules along the *Y* axis are −12.1 and −11.6 kcal mol^{-1}, which is indicative of the formation of layers in the structure of **2**.

With the aim of studying whether photoconversion of the oxaziridine ring in the crystals of **1** and **2** can occur, we calculated the portion of the free volume of the unit cell V_p and the difference in the volumes (ΔV) of the molecules of the proposed oxaziridine photoproduct (V_{ox}) and the initial nitrone (V_{mol}) according to the following equations:

$$V_p = V_{cell} - Z \cdot V_{mol}, \quad \Delta V = V_{oks} - V_{mol},$$

where V_{cell} is the total volume of the unit cell.

The proposed oxaziridine photoproducts formed from **1** and **2** were simulated based on structural data[4] with full optimization using the PM3 method (MOPAC 6.0).

For compounds **1** and **2**, ΔV (−2.6 Å^3 and −3.3 Å^3, respectively) have small negative magnitudes. This indicates that cyclization of **1** and **2** should be accompanied by a slight increase in the molecular volume. However, in this case, a substantial change in the geometry of the molecule should occur, associated primarily with the fact that the carbon and nitrogen atoms of the nitrone

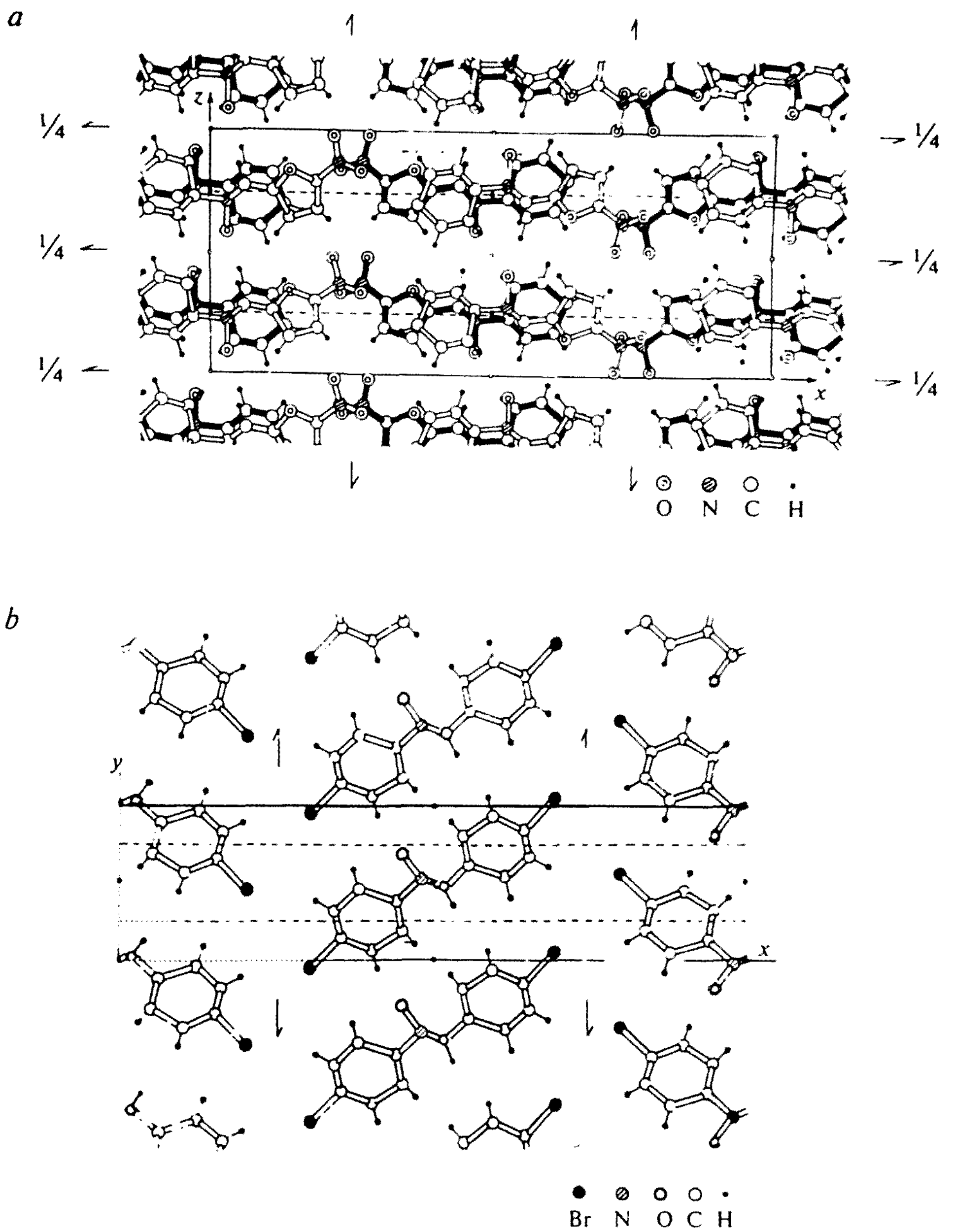

Fig. 5. Projections of the crystal packings of **1** (*a*) and **2** (*b*).

group are sp^3 hybridized and adopt tetrahedral and pyramidal configurations, respectively. Hence, this photoconversion requires a certain reserve of the free volume in crystals. The value of V_p/Z (108.9 Å^3 (1) and 113.6 Å^3 (2)) corresponds to the free volume of the unit cell per molecule. Evidently, the closer the molecular packing, the more hindered these reactions in the crystal. Therefore, it can be suggested that in the crystals of **2**, in which molecules are packed in layers and the energy of intermolecular interactions is considerable, this process is more hindered than in **1**. This is confirmed by the fact that when formation of the oxaziridine ring in the crystals of **1** and **2** was simulated, the lattice energy changed. In crystals of **1**, the lattice energy (Fig. 6, curves *a* and *b*) even decreased, whereas in crystals of **2**, the lattice energy increased sharply (Fig. 6, curves *c* and *d*) due to the short intermolecular contacts between the "guest" and "host" molecules that occur as a consequence of the layer structure. The decrease in the energy of the crystal structure of **1** is caused by the characteristic features of the crystal packing. The results of *ab initio* quantum-chemical calculations of molecule **1** with full optimization demonstrated that the nitrofuran substituent and the nitrone group are in a single plane, whereas the phenyl fragment forms an angle of 32.2° with this planar moiety of the molecule, which is

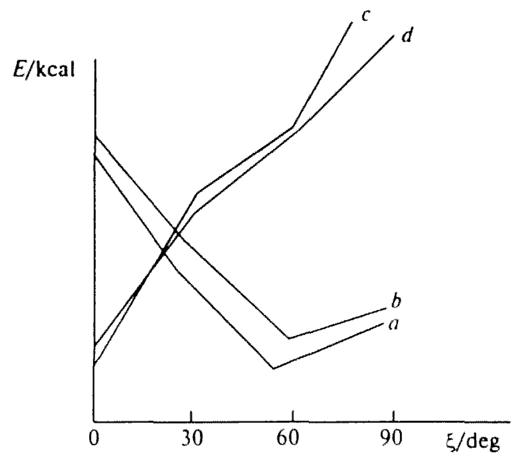

Fig. 6. Changes in the energies of the crystal structures of **1** and **2** when formation of the oxaziridine photoproduct was simulated. Angles ξ correspond to the angles of rotation of the substituents about the N—C(Ph) and C(1)—C(2) bonds (Figs. 1 and 2) in nitrones **1** and **2**. *E* is the lattice energy.

in agreement with the results of X-ray structural analysis. In other words, the crystal structure is completely determined by the optimum molecular structure of **1**. However, molecules **1** are arranged in stacks so that the twisted phenyl fragment is located between two planar fragments, while the planar fragment is located between two twisted fragments (Fig. 5, *a*). In both cases, if these substituents rotate, they become parallel to the adjacent fragments of the stack, *i.e.*, intermolecular contacts increase. Therefore, the crystal structure of **1** is more favorable for the formation of the cyclic photoproduct.

We also calculated the energies of the crystal structures of the supposed cyclic photoproducts **1** and **2** in the crystal lattices of the initial compounds on the assumption that the centers of mass of the initial and final molecules coincide. Then the positions of the molecules in the unit cells (coordinates of the centers of mass and the Euler angles) were optimized using the PMC program.[6] After optimization, the energy of the crystal lattice formed by molecules of photoproduct **1** was -21.9 kcal mol^{-1} (the van der Waals component), which indicates that photoproduct of **1** can form its own crystal phase in the lattice of the initial compound. The energy of the crystal lattice formed by molecules of photoproduct **2** was positive, which indicates that photocyclization of **2** in the initial crystal lattice is hindered. The experimental study of the photochemical properties of compounds **1** and **2** in the crystal phase will be performed later on.

Therefore, both in solution and in the crystalline state compounds **1** and **2** undergo photochemical conversions of the same type accompanied by the formation of the oxaziridine three-membered ring. An intermediate product of this photorearrangement with displaced hydrogen atom of the azomethine group was found for compound **1**. When crystals of **1** and **2** are irradiated with UV light, formation of the oxaziridine ring is also possible. In this case, photoproduct of **1** can form its own crystal phase in the crystal lattice of the initial nitrone, *i.e.*, the reaction can follow the pattern "single crystal→single crystal". An analogous reaction in the crystal structure of **2** is energetically unfavorable and would be accompanied by substantial hindrance in the crystal structure of the initial nitrone.

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