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Quantum Yield of Photo-rearrangement of Nitrones

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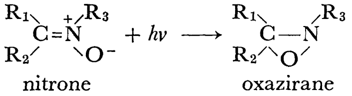
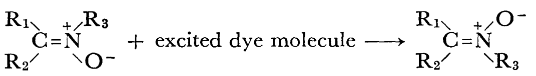
Fifteen nitrones, *N*-butylidenecyclohexylamine *N*-oxide, *N*-benzylidenemethylamine *N*-oxide, *N*-diphenylmethylenemethylamine *N*-oxide, *N*-benzylidenaniline *N*-oxide, and its derivatives, were irradiated with light in solution, each at its longest-wavelength absorption band. Each nitrone isomerized to the corresponding oxazirane. The quantum yield of this photo-rearrangement, Φ, was measured. For each nitrone, the value of Φ is larger in cyclohexane solution than in ethanol solution. In the series of *N*-benzylidenaniline *N*-oxide and its *para*-substituted derivatives, the substituent lowers Φ, and the more electron-donating or the more electron-withdrawing the substituent is, the smaller is Φ. These facts are explained on the basis of a hypothesis that Φ should increase with the change in the π-bond order between the carbon and oxygen atoms of the nitrone group upon the lowest-energy electron excitation, $\Delta P_{\mathrm{C,O}}$, calculated by the simple MO method.

It has been reported that nitrones isomerize to oxaziranes by light absorption,[2–7] while photosensitization by dye molecules results in the geometrical isomerization about the C=N bond.[7]





We have concluded previously that nitrone molecules in the lowest excited singlet state isomerize to the corresponding oxaziranes by oxygen atom rearrangement and that nitrone molecules excited to a triplet state as a result of energy transfer from triplet dye molecules undergo the *cis-trans* isomerization.[6,7]

In the present paper it is elucidated how the groups R affect the quantum yield of the photochemical nitrone→oxazirane rearrangement.

Experimental

The nitrones used in this work are as follows: *N*-butylidenecyclohexylamine *N*-oxide (I), *N*-benzylidenemethylamine *N*-oxide (II), *N*-diphenylmethylenemethylamine *N*-oxide (α-phenyl-II), *N*-benzylidenaniline *N*-oxide (α,*N*-diphenylnitrone, III; see Fig. 1), and its derivatives, which are listed in Table 1 and are hereafter referred to with the entry numbers in this table. The synthesis and some physical properties of the nitrones except 1, 3, 5, and 15[8] were described in previous papers.[9,10]

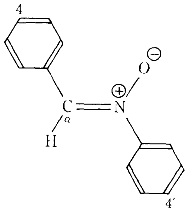


Fig. 1. α,*N*-Diphenylnitrone (*N*-benzylidenaniline *N*-oxide).

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[1] To whom any correspondence should be addressed.

[2] M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957).

[3] J. Splitter and M. Calvin, *ibid.*, **23**, 651 (1958).

[4] R. Bonnett, V. M. Clark and A. Todd, *J. Chem. Soc.*, **1959**, 2102.

[5] L. S. Kaminsky and M. Lamchen, *Chem. Commun.*, **1965**, 130; *J. Chem. Soc., C*, **1966**, 2295; M. Lamchen and T. W. Mittag, *ibid.*, **1968**, 1917.

[6] K. Shinzawa and I. Tanaka, *J. Phys. Chem.*, **68**, 1205 (1964).

[7] K. Koyano and I. Tanaka, *ibid.*, **69**, 2545 (1965).

[8] The authors are indebted to Dr. T. Kubota of Shionogi Research Laboratory, Shionogi and Co., Ltd. for kindly supplying the specimens of nitrons 3 (mp 106.5—108°C) and 5 (mp 221—222°C). Nitrone 1 (mp 34°C) was synthesized by the usual method,[10] and nitrone 15 (mp 216—217°C) was prepared by following the procedure described by F. Barrow and E. D. Griffiths (*J. Chem. Soc.*, **119**, 212 (1921)).

[9] K. Koyano and H. Suzuki, *Tetrahedron Lett.*, **1968**, 1859.

[10] K. Koyano and H. Suzuki, This Bulletin, **42**, 3306 (1969).

Ultraviolet absorption spectra were measured with a Hitachi Spectrophotometer EPS2U at room temperature. Cyclohexane and ethanol were used as solvents. Cyclohexane was purified by being passed through silica gel and distilled. Ethanol of guaranteed reagent grade was used without further purification.

The procedure of the irradiation experiment is quite similar to that described in a previous paper.[6] Three different light sources were used: (a) a 253.7 nm light source, a low pressure mercury lamp without filter; (b) a 313.0 nm light source, a high pressure mercury lamp with a combination of filters of cobalt - nickel sulfate solution and a glass which completely absorbs light below 300 nm; (c) a 365.0 nm light source, a high pressure mercury lamp with a combination of filters of Toshiba UVD1 and a glass. For each nitrone the light source was selected so that the light was absorbed by the nitrone at its longest-wavelength absorption band. The irradiation was carried out at room temperature. The intensity of the incident light was measured by potassium ferrioxalate actinometry.[11] The ratio of the decrease in the number of nitrone molecules to the number of photons absorbed was taken as the quantum yield of the photo-rearrangement.

Results and Discussion

Absorption Spectra and the Quantum Yield. The ultraviolet absorption spectra of the nitrones in solution changed markedly on irradiation, as exemplified by Fig. 2. The products are considered to be oxaziranes since their absorption bands appear at much shorter wavelength than those of the nitrones, indicating the break of the π bond between the α-carbon and the nitrogen atom. The formation of oxaziranes from nitrones 2, 3, 4, and 5 was confirmed by the fact that the products liberated iodine from acid solution of potassium iodide.[12,13]

In Table 1 are listed the values of the wavenumber ($\nu_{\max}$) and molar extinction coefficient ($\varepsilon_{\max}$) at the peak of the longest-wavelength absorption bands of the nitrones, the quantum yield of the photo-rearrangement (Φ), and the wavelength at the peak of the absorption bands of the products ($\lambda_{\max}$). There are some correlations between $\nu_{\max}$ and Φ as follows.

(i) The values of Φ for the nitrones except 11 are larger in cyclohexane solution than in ethanol solution, and the values of $\nu_{\max}$ for most of the nitrones are smaller in cyclohexane solution than in ethanol solution.

(ii) The values of Φ and $\nu_{\max}$ for nitrone 1 are larger than the corresponding values for the other nitrones. In each solvent, a nitrone having a higher $\nu_{\max}$ value has a larger Φ value than does a nitrone having a lower $\nu_{\max}$ value. There seems to be no clear relation between $\varepsilon_{\max}$ and Φ. The introduction of the second phenyl group to the α-carbon atom decreases the value of $\varepsilon_{\max}$ to about a half, but

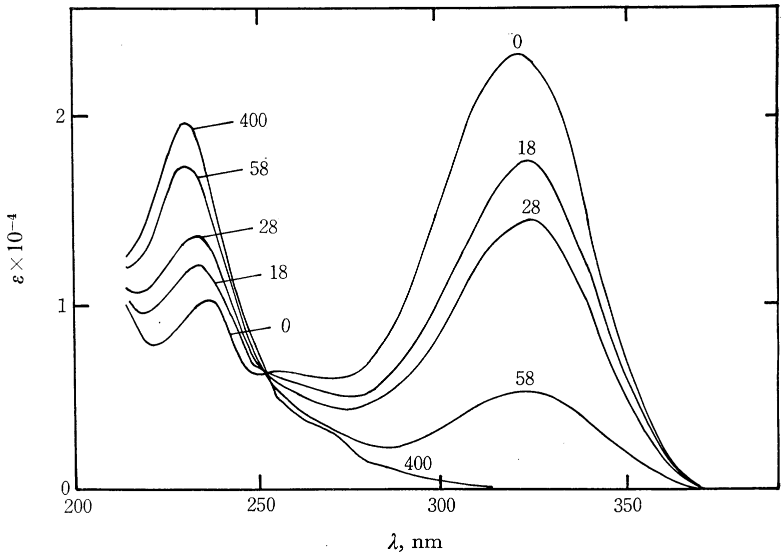

Fig. 2. The electronic absorption spectrum of *N*-(*p*-chlorobenzylidene)-aniline *N*-oxide (nitrone 7) in ethanol at room temperature and its change caused by irradiation with 313 nm light. The numbers represent the irradiation time in seconds.

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[11] C. A. Parker, *Proc. Roy. Soc.* (London), **220A**, 104 (1953).

[12] The oxaziranes were so unstable that they could not be isolated.

[13] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York (1949), p. 100.

TABLE 1. THE FIRST ABSORPTION MAXIMA OF NITRONES, THE QUANTUM YIELDS OF THE PHOTO-REARRANGEMENT OF THE NITRONES, AND THE ABSORPTION MAXIMA OF THE PRODUCTS

No.	Nitrone[a]	Absorption maximum In Cy[b] ν_{max} kK	ε_{max} $\times 10^{-4}$	In Et[b] ν_{max} kK	ε_{max} $\times 10^{-4}$	Quantum yield In Cy[b]	In Et[b]	Product In Cy[b] λ_{max} nm	In Et[b] λ_{max} nm
1	I	40.5	0.81	42.5	0.87	0.49[c]	0.42[c]	<210	<210
2	II	33.4	1.90	34.3	1.89	0.49[d]	0.36[d]	<210	<210
3	α-Phenyl-II	32.7	0.72	34.1	0.67	0.48[d]	0.33[d]	<210	<210
4	III	31.3	1.86	31.8	2.07	0.52[d]	0.36[d]	<220	<220
5	α-Phenyl-III	31.3	1.17	32.1	1.13	0.40[d]	0.24[d]	<210	<210
6	4-Methyl-III	30.6	2.10	31.4	2.35	0.43[d]	0.35[d]	229	229
7	4-Chloro-III	30.6	2.22	31.2	2.34	0.23[d]	0.24[d]	232.5	231
8	4-Bromo-III	30.4	2.32	31.0	2.44	0.25[d]	0.22[d]	237	236
9	4-Hydroxy-III	30.0[f]	2.00[f]	29.9	2.49		0.03[e]		241
10	4-Methoxy-III	29.9	2.11	30.2	2.41	0.16[e]	0.11[e]	240	239
11	4-Dimethylamino-III	26.9	2.40	26.0	3.21	0.13[e]	0.16[e]	274	269
12	4-Cyano-III	29.7	2.73	30.2	2.68	0.50[d]	0.34[d]	236.7	236.5
13	4-Methoxycarbonyl-III	29.5	2.62	30.2	2.75	0.39[d]	0.28[d]	240	240
14	4-Nitro-III	27.6	1.76	28.1	1.95	0.19[e]	0.09[e]	261	265
15	4-Nitro-4′-dimethylamino-III			23.5	2.12		0.01[e]		261

a) I, α-propyl-*N*-cyclohexylnitrone (*N*-butylidenecyclohexylamine *N*-oxide); II, α-phenyl-*N*-methylnitrone (*N*-benzylidenemethylamine *N*-oxide); III, α,*N*-diphenylnitrone (*N*-benzylidenaniline *N*-oxide).
b) Cy, cyclohexane; Et, ethanol.
c) Irradiated with 253.7 nm light.
d) Irradiated with 313.0 nm light.
e) Irradiated with 365.0 nm light.
f) In benzene.

does the values of Φ only slightly. (Compare nitrones 3 and 5 with 2 and 4, respectively.)

(iii) The value of Φ and ν_{max} for α,*N*-diphenylnitrone (nitrone 4) are larger than those for the 4-substituted derivatives (nitrones 6—15). In the case where the substituent is electron-donating, the more electron-donating the substituent is, the smaller are the values of Φ and ν_{max}. Thus, the decreasing order of Φ and ν_{max} is $CH_3 > Cl \approx Br > CH_3O > (CH_3)_2N$, and this is in accordance with the increasing order of the absolute value of the Hammett σ constant. In the case where the substituent is electron-withdrawing, the values of Φ and ν_{max} decrease in the order $CN > CH_3COO > NO_2$. This order is the increasing order of the electron-withdrawing property of the substituent, that is, the increasing order of the Hammett σ constant. The values of Φ and ν_{max} for nitrone 15 are the lowest of all. The relation between Φ and ν_{max} is shown in Fig. 3. From the fact that both the electron-donating and the electron-withdrawing substituents decrease Φ, it is evident that the reactivity of the nitrone group ($C{=}N^+{-}O^-$) can not be interpreted in terms of the polarity of the group or the electron density of the atoms involved.

Simple MO Calculation. The reactivity of nitrones can be elucidated in terms of simple molecular orbitals. The molecular orbitals of the nitrone group were calculated by the use of parameters $\alpha_C=\alpha+0.5\beta$, $\alpha_N=\alpha+1.6\beta$, $\alpha_O=\alpha+1.2\beta$, and $\beta_{CN}=\beta_{NO}=\beta$. These parameter values are the values used by Kubota and Yamakawa in simple MO calculation on the π electron system of *N*-benzylidenalkylamine *N*-oxides, that is, the α-phenylnitrone π electron system.[14] The results are given in Table 2. In the ground state MO's ϕ_1 and

TABLE 2. THE SIMPLE MOLECULAR ORBITALS OF THE NITRONE GROUP ($C{=}\overset{+}{N}{-}\overset{-}{O}$)*

MO	Energy	Coefficients of AO's C	N	O
ϕ_1	$\alpha+2.7129\beta$	0.3527	0.7806	0.5159
ϕ_2	$\alpha+0.8927\beta$	−0.5990	−0.2352	0.7654
ϕ_3	$\alpha-0.3056\beta$	0.7188	−0.5791	0.3846

* The parameter values used: $\alpha_C=\alpha+0.5\beta$, $\alpha_N=\alpha+1.6\beta$, $\alpha_O=\alpha+1.2\beta$, and $\beta_{CN}=\beta_{NO}=\beta$.

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[14] T. Kubota and M. Yamakawa, This Bulletin, **36**, 1564 (1963).

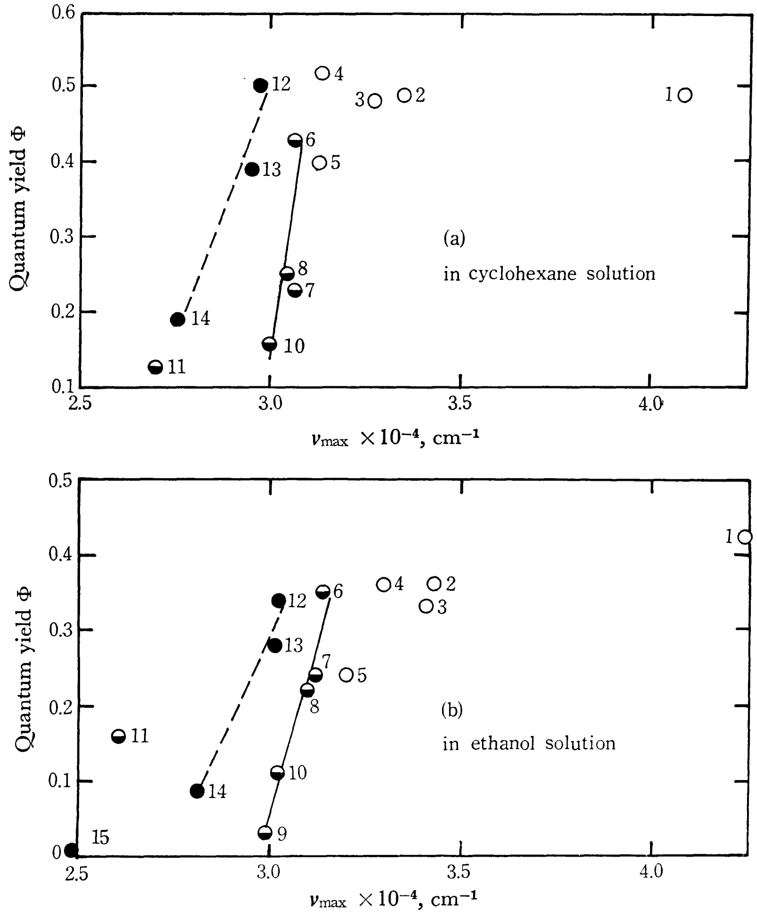
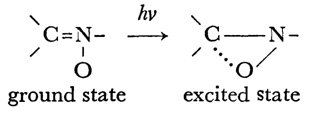


Fig. 3. The relation between Φ and ν_{max}: (a) in cyclohexane; (b) in ethanol. ◒, for 4-X-α,*N*-diphenylnitrones in which X is an electron-donating substituent; ●, for those in which X is an electron-withdrawing substituent; ○, for the other nitrones. The numbers are the entry numbers of the nitrones in Table 1.

ϕ_2 are filled with electrons.

The π-bond order of the C=N bond, P_{CN}, is calculated to be 0.832 in the ground state and 0.275 in the excited state where one electron has been excited from ϕ_2 to ϕ_3. The π-bond order of the N–O bond, P_{NO}, is 0.445 in the ground state and 0.403 in the excited state. The π-bond order of the hypothetical bond between the chemically non-bonded carbon and oxygen atoms, $P_{C,O}$, is -0.553 in the ground state and 0.182 in the excited state. Thus, on the excitation, P_{CN} decreases largely, P_{NO} decreases slightly, and $P_{C,O}$ increases largely. This tendency remains unchanged when the values of parameters α_N and α_O are changed in the ranges between $\alpha+1.5\beta$ and $\alpha+3.0\beta$ and between $\alpha+1.0\beta$ and $\alpha+2.0\beta$, respectively. The photo-rearrangement of nitrones to oxaziranes is safely interpreted as the result of the decrease in bonding character of the C=N bond and the large increase in bonding character of the hypothetical C···O bond caused by light absorption.



Correlation of the Quantum Yield with the Change in the π-Bond Order. The longest-wavelength absorption bands of the nitrones are attributed approximately to the one-electron excitation from the highest occupied π orbital to the lowest vacant one. The energy of this excitation is denoted by ΔE, and the changes in the π-bond orders associated with this excitation are denoted by ΔP. The effects of solvent and substituent on Φ can be interpreted in terms of the change in the $\Delta P_{C,O}$ value, and those on ν_{max} can be interpreted in terms of the change in the ΔE value.

(a) As the value of α_O becomes negatively arger, the value of $\Delta P_{C,O}$ decreases and the value

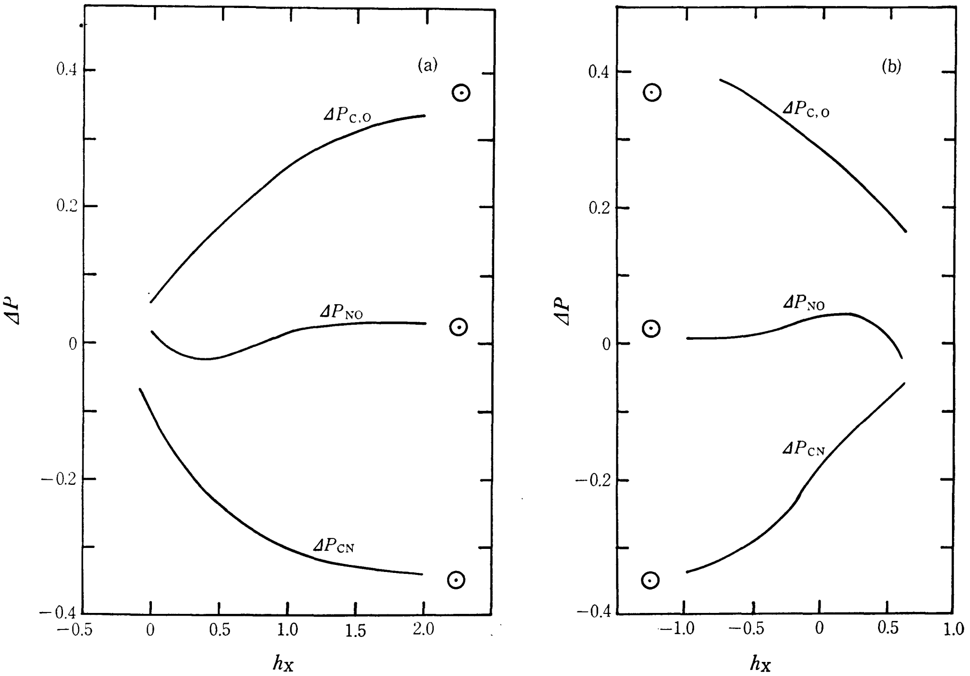


Fig. 4. The relations between ΔP's and h_X in the 4-X-α,*N*-diphenylnitrone π electron system: (a) in the case where X is an electron-donating substituent; (b) in the case where X is an electron-withdrawing substituent. The marks ⊙ represent ΔP's for the unperturbed α,*N*-diphenylnitrone π electron system.

of ΔE increases. The formation of a hydrogen bond has been found between the solvent alcohol and nitrone molecules, the oxygen atom of the nitrone group acting as a proton acceptor.[15] The value of the Coulomb integral for a hydrogen-bonding oxygen atom should be larger than that for a non-hydrogen-bonding oxygen atom. This can interpret well the solvent effects on Φ and ν_{max}. The possible increase in the energy dissipation rate due to hydrogen bond formation in ethanol solution may also decrease the quantum yield.

(b) The simple molecular orbitals were calculated for the 4-X-α,*N*-diphenylnitrone π electron system by using various values for parameter h_x in the Coulomb integral of the substituent X, $\alpha_x = \alpha + h_x\beta$. In the case where X is an electron-donating substituent, 18 electrons participate in the π electron system, and the lowest-energy-electron excitation takes place from the 9th to the 10th orbital. In this case a smaller value of h_x correponds to a stronger electron-donating power of X. On the other hand, in the case where X is electron-withdrawing, it is assumed that 16 electrons participate in the π electron system. In this case, the lowest-energy electron excitation takes place from the 8th to the 9th orbital, and a larger value of h_x cor-

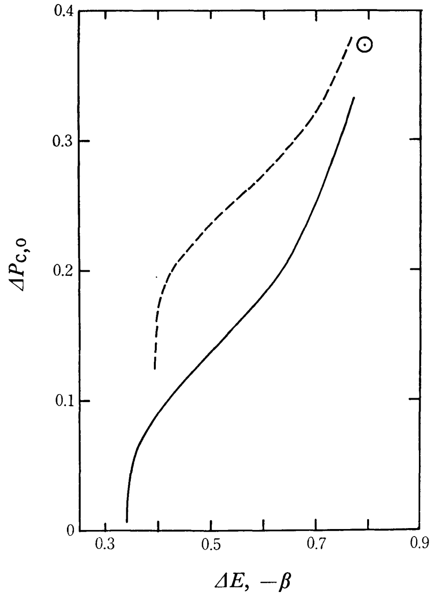


Fig. 5. The relation between $\Delta P_{C,O}$ and ΔE in the 4-X-α,*N*-diphenylnitrone π electron system. The solid line represents the relation in the case where X is electron-donating, and the broken line represents the relation in the case where X is electron-withdrawing. The mark ⊙ is for the case where X is absent.

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[15] T. Kubota, M. Yamakawa and Y. Mori, This Bulletin, **36**, 1552 (1963).

responds to a stronger electron-withdrawing power of X.

The relations between ΔP's and h_x are shown in Fig. 4.[16] As is seen in this figure, the value of $\Delta P_{C,O}$, which is positive in the range shown in the figure, is almost at its maximum when X is absent, and decreases as the effect of X increases, whether it is electron-donating or electron-withdrawing. This explains well the effect of X on Φ.

The value of ΔE decreases as the value of h_x decreases when X is electron-donating, and as the value of h_x increases when X is electron-withdrawing. This means that the first absorption band should shift to longer wavelength as the 4-substituent becomes more electron-donating or more electron-withdrawing, in accordance with the observation. The relation between $\Delta P_{C,O}$ and ΔE is shown in Fig. 5. This relation corresponds to the relation between Φ and ν_{max} shown in Fig. 3.

In nitrone 15, which has an electron-donating substituent at the 4-position and an electron-withdrawing substituent at the 4′-position, both the values of $\Delta P_{C,O}$ and ΔE must be small.

(c) The variation in the value of Φ in the series of α,*N*-diphenylnitrone and its 4-substituted derivatives has so far been explained well by saying that the value of Φ decreases as the value of $\Delta P_{C,O}$ decreases. The values of $\Delta P_{C,O}$ for the α,*N*-diphenylnitrone, α-phenylnitrone, and nitrone group π electron systems are 0.370, 0.508, and 0.735, respectively. Therefore, the value of Φ would be expected to increase rapidly in this sequence. In fact, however, the values of Φ for nitrones 1 and 2 are not much different from the values for nitrone 4. Thus, in this series of nitrones, it appears that the value of Φ does not monotonously increase with the value of $\Delta P_{C,O}$, but approaches a limiting value of about 0.5. There seem to be some fast processes which deactivate excited nitrone molecules and thereby depress Φ.

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[16] The energies of the lowest vacant and highest occupied orbitals of α,*N*-diphenylnitrone are calculated to be $\alpha-0.1830\beta$ and $\alpha+0.6103\beta$, respectively. In Fig. 4, in the case where X is electron-donating (case a) values larger than -0.1830 were taken for h_x, and in the case where X is electron-withdrawing (case b) values smaller than 0.6103 were taken for h_x. The case a where the value of h_x is sufficiently large and the case b where the value of h_x is sufficiently small correspond to the case where the α,*N*-diphenylnitrone π electron system is not perturbed by the substituent X.