Nature of the Longest Wavelength Absorption Bands of *N*-Substituted Maleimides*

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In spite of the considerable progress in recent years in understanding the absorption spectra of many π-electron systems, not much knowledge has been obtained as to the spectra of cyclic imides derived from anhydrides. For example, the absorption spectra of several imides have been reported in some papers without any theoretical consideration of the nature of each band.[1] The present paper will study the effects of *N*-substitution on the electronic spectra of maleimide derivatives from both the theoretical and experimental points of view.

Experimental

The compounds used for the measurement of the absorption spectra were obtained in the same way as reported in the previous paper in which the infrared spectra of the carbonyl groups of maleimide and its *N*-substituted derivatives were discussed.[2]

The spectra were measured with a Hitachi model EPS-2U recording spectrophotometer.

Experimental Results and Discussion

The absorption spectra of the compounds investigated are shown in Figs. 1 and 2 as measured in *n*-hexane. Since the main interest was concentrated on the longest wavelength absorption band of each compound, the highly intense bands in the shorter wavelength region are not shown in the figures. These high intensity bands are due to electronic transitions of a nature different from that discussed in this paper. The same could be said about the medium intensity band of *N*-(*p*-methoxyphenyl)-maleimide at 275 mμ, which shows less solvent effect than does the lower intensity band at 350 mμ, as will be discussed later. Also excluded from the present discussion are the bands with some fine structures around 260 mμ in the spectra of those compounds with a phenyl group as the constituent of their substituents. Obviously the bands are due to the transitions localized at the phenyl group, not to the characteristics of cyclic imides.

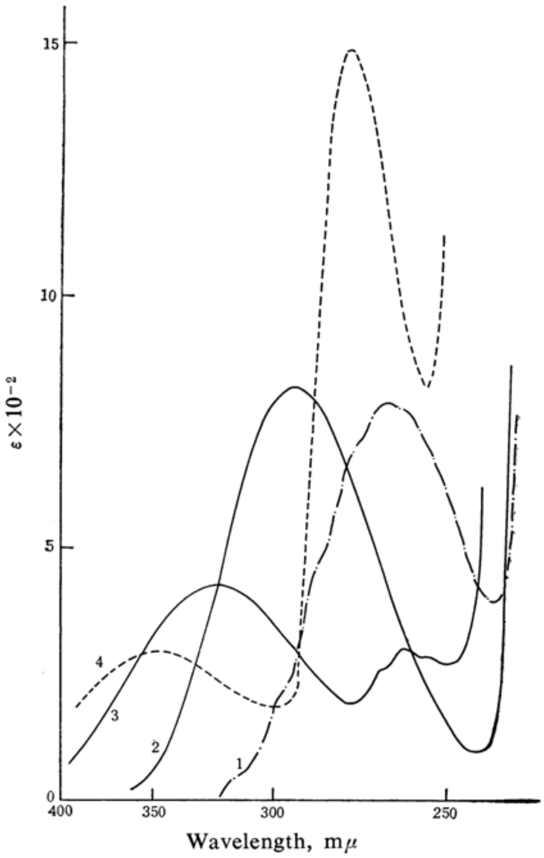

Fig. 1. Electronic absorption spectra of maleimide and its *N*-substituted derivatives in *n*-hexane.

1 Maleimide
2 *N*-Ethylmaleimide
3 *N*-Phenylmaleimide
4 *N*-(*p*-Methoxyphenyl)-maleimide

The longest wavelength absorption bands in question are classified into four groups according to their intensities and the wavelengths of the absorption maxima. The corresponding *N*-substituents of the four groups are found to be as follows:

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[1] a) W. R. Roderick, *J. Am. Chem. Soc.*, **79**, 1710 (1957); b) M. P. Grammaticakis, *Compt. rend.*, **251**, 1790 (1960); c) C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83**, 4586 (1961); d) C. M. Lee and W. D. Kumler, *J. Org. Chem.*, **27**, 2055 (1962).

[2] T. Matsuo, This Bulletin, **37**, 1844 (1964).

Group 1: hydrogen,
Group 2: ethyl, cyclohexyl and benzyl,
Group 3: phenyl, *p*-tolyl and *p*-chlorophenyl, and
Group 4: *p*-methoxyphenyl.

The groups are numbered in the order of the increasing wavelength, or of the decreasing intensity, of the absorption maximum of the band concerned.

The difference between the classes given above becomes more evident when a comparison is made in terms of their solvent effects, shown in Figs. 3, 4 and 5. The solvent effect is also summarized in Table I. A strong bathochromic shift is observed for group 1 when the measurement is made in polar solvents. The bathochromic effect is very small or almost negligible in the case of group 2. The effect of the polar solvent becomes hypsochromic in group 3, and this same effect is further pronounced in group 4.

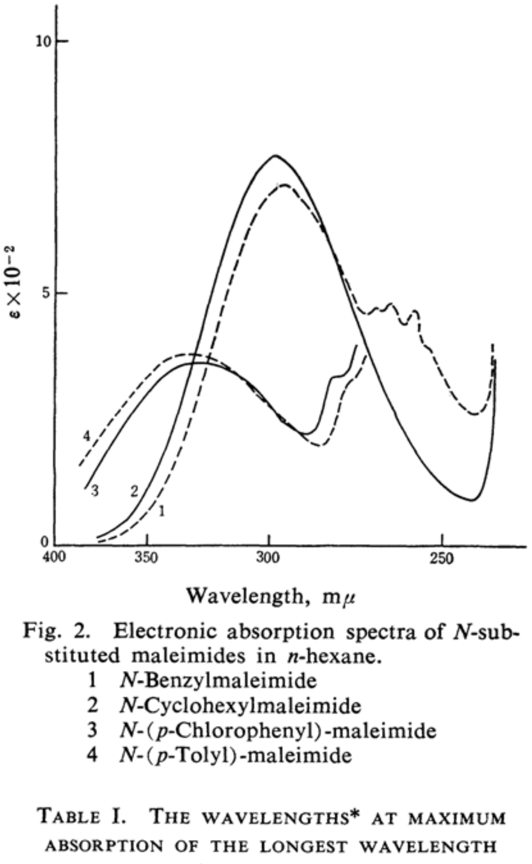


Fig. 2. Electronic absorption spectra of *N*-substituted maleimides in *n*-hexane.
1 *N*-Benzylmaleimide
2 *N*-Cyclohexylmaleimide
3 *N*-(*p*-Chlorophenyl)-maleimide
4 *N*-(*p*-Tolyl)-maleimide

Table I. The wavelengths* at maximum absorption of the longest wavelength bands of *N*-substituted maleimides in various solvents

Substituent	*n*-Hexane	Acetonitrile	Ethanol	Methanol
Hydrogen	265	272	274	275
Ethyl	294	296		300
Cyclohexyl	299	302		
Benzyl	296	296		
Phenyl	322	307	298	
p-Chlorophenyl	327	311		
p-Tolyl	330	312		
p-Methoxyphenyl	348	317		

* In mμ units.

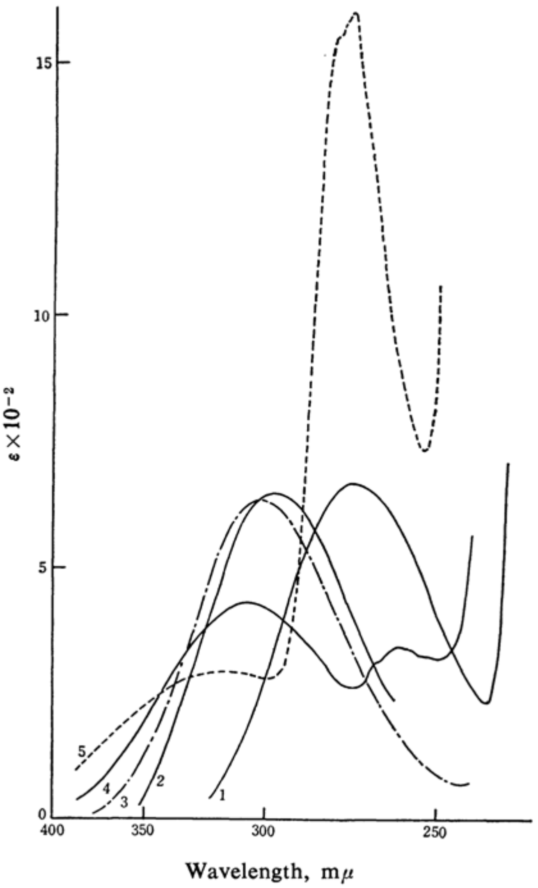
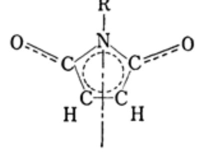


Fig. 3. Electronic absorption spectra of maleimide and its *N*-substituted derivatives in acetonitrile.
1 Maleimide
2 *N*-Etylmaleimide
3 *N*-Cyclohexylmaleimide
4 *N*-Phenylmaleimide
5 *N*-(*p*-Methoxyphenyl)-maleimide

Attempts were made to interpret the above experimental results by means of the Hückel LCAO-MO theory. The calculations were made by assuming a C_{2v} symmetry and parameters for the imide system:



$$\alpha_{\dot{O}}=\alpha_C+h_{\dot{O}}\beta$$
$$\alpha_{\ddot{N}}=\alpha_C+h_{\ddot{N}}\beta$$
$$\beta_{CO}=k_{CO}\beta$$
$$\beta_{CN}=k_{CN}\beta$$

The effect of the expansion of conjugated systems on their energy levels was first examined by using the coplanar, axial structures and parameters shown in Fig. 6. When the substituent, R, is an aryl group, a new highest-occupied π-electron level appears. The lowest unoccupied energy level, on the other hand, is not affected at all, since the orbital is localized at the carbonyl groups and at the double bond connecting them. A decrease in the energy difference between the highest-occupied and the lowest-unoccupied levels results, therefore, when an aryl group is attached to the nitrogen atom. The decrease in the separation of the two π-electron energy levels argees qualitatively with the trend observed in the behavior of the longest-wavelength absorption bands of the four groups described above. This agreement, however, is not the true answer to the present problem, as may be seen by the following arguments. First of all, the oscillator strength of the pure $\pi \rightarrow \pi^*$ transition implied by the energy diagram may be expected to be much larger

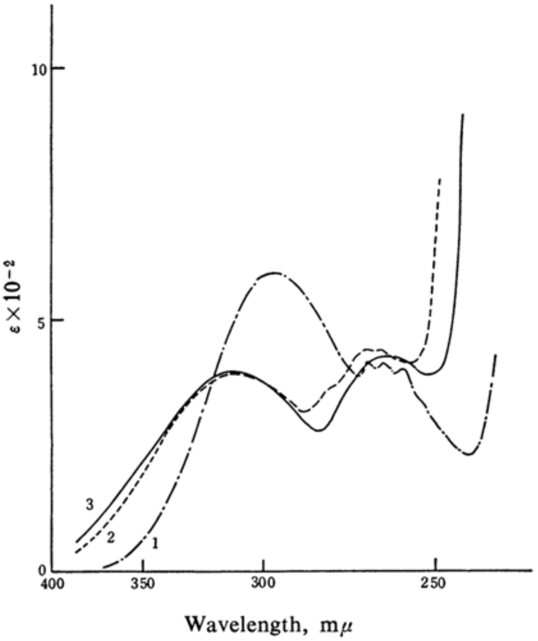


Fig. 4. Electronic absorption spectra of *N*-substituted maleimides in acetonitrile.
1 *N*-Benzylmaleimide
2 *N*-(*p*-Chlorophenyl)-maleimide
3 *N*-(*p*-Tolyl)-maleimide

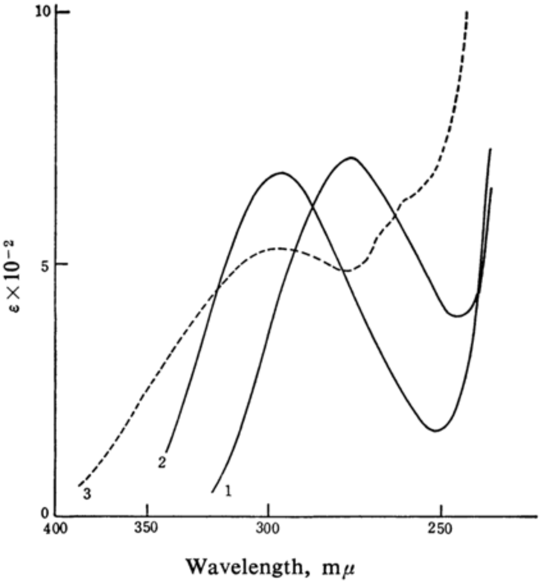
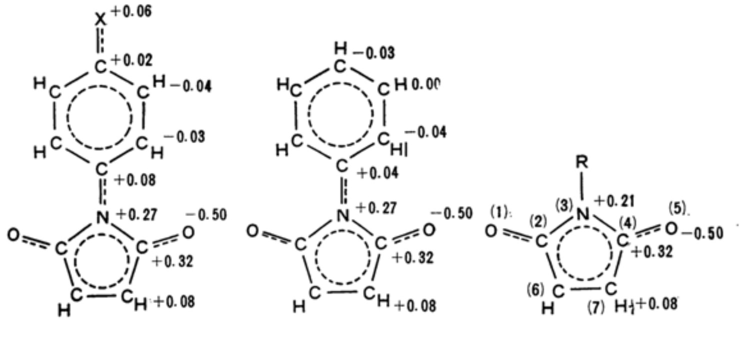


Fig. 5. Electronic absorption spectra of (1) maleimide (in methanol), (2) *N*-ethylmaleimide (in methanol), and (3) *N*-phenylmaleimide (in ethanol)



(I) (II) (III)

Fig. 6(a). The charge distributions in *N*-(*p*-methoxyphenyl)-maleimide (I), *N*-phenylmaleimide (II), and *N*-alkylmaleimide (III), as calculated by the Hückel LCAO method under the assumptions of coplanar, axial structures and the following parameters,
$h_{\dot{O}} = k_{CO} = 1.0$, $h_{\ddot{N}} = 1.5$, $k_{CN} = 0.8$, $h_{\ddot{X}} = 2.0$ and $k_{CX} = 0.8$.
The parameters were chosen from the values recommended in the table given by Streitwieser.³⁾

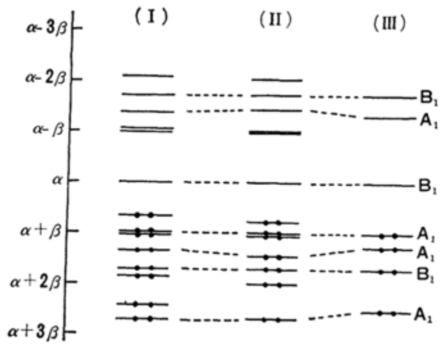


Fig. 6(b). The energy levels of the systems given in Fig. 6(a).

than the largest observed values (of the order of 10^{-2}) for the longest-wavelength absorption bands of *N*-alkylmaleimides. In the case of *N*-arylmaleimides, the molecular orbital of the highest-occupied π-electron energy level is localized at the aryl group. Therefore, the transition from that level to the lowest-unoccupied energy level has a strong character of charge-transfer absorption. An appreciable bathochromic shift may be expected, then, when the absorption band is measured in polar solvents. The experimental results are just the opposite of this prediction. In short, the absorption band in question can not be explained as due to a pure $\pi\rightarrow\pi^*$ transition.

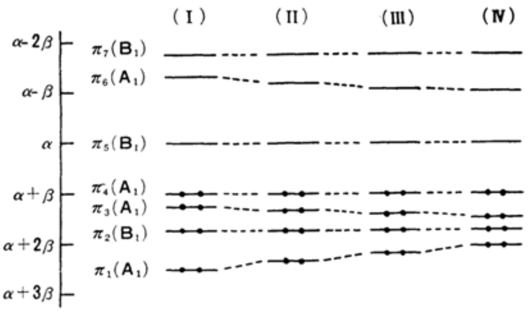


Fig. 7. The energy levels for maleimide systems as calculated by the use fo various k_{CN} values.
(I) : $k_{CN}=0.8$ (II) : $k_{CN}=0.6$
(III) : $k_{CN}=0.4$ and (IV) : $k_{CN}=0.2$.
See the caption for Fig. 6(a) for the rest of the parameters used in the calculation.

TABLE II. CHARGE DENSITIES CALCULATED FOR MALEIMIDE SYSTEMS WITH VARIOUS k_{CN} VALUES*

Atom	$k_{CN}=0.8$	$k_{CN}=0.6$	$k_{CN}=0.4$	$k_{CN}=0.2$
N	+0.21	+0.13	+0.06	+0.02
O	−0.50	−0.48	−0.47	−0.46
$C_{C=O}$	+0.32	+0.33	+0.33	+0.33
$C_{C=C}$	+0.08	+0.10	+0.11	+0.12

* See the caption for Fig. 7 for the rest of parameters used in the calculation.

The extent of the contribution of the nitrogen atom to the conjugated system was examined explicitly in the next calculations. In the cases of *N*-substituted phthalimides, their dipole moments indicate that the hybridization of the nitrogen orbital for the N–R bond changes from sp^3 to sp^2 types as the substituent is changed from hydrogen to methyl and then to phenyl groups.[4] Correspondingly, the orbital for the lone pair electrons of the nitrogen atom changes from a sp^3 to a pure p orbital in the order of the substituents given above. The same situation may be expected for *N*-substituted maleimides. In the Hückel LCAO-MO method, the above change in the hybridization of atomic orbitals corresponds to a modification of the parameters to be used in the calculations. In order to minimize any further complications, only k_{CN} was varied in examining the effect of the isolation of the nitrogen atom from the conjugated system. The results are summarized in Fig. 7 and Table II. It shoud be noted that the electron densities at the nitrogen and oxygen atoms decrease and increase respectively as the k_{CN} value increases. The increased electron density at the oxygen atom raises the energy level, *En*, of the lone pair electrons on the atom. Therefore, an interpretation of the absorption band as being due to the $n\rightarrow\pi^*$ transition of the carbonyl groups becomes possible, even though the lowest unoccupied level is not affected for the first approximation. Assuming that the nitrogen and the four carbon atoms make a completely coplanar system and that k_{CN} is linearly proportional to the overlap integral, the k_{CN} value is estimated to decrease approximately by a factor of 0.7 as a change is made from pure p to sp^3 orbitals for the nitrogen atom. A further reduction in k_{CN} is expected if the nitrogen atom rises a little above the plane made by the carbonyl groups and the double bond. A close examination of the lowest unoccupied level reveals that it is also affected by the delocalization of the electrons of the nitrogen atom, as will be shown below. The molecular orbital of this level is:

$$\psi_5=\frac{1}{\sqrt{6}}(\phi_1-\phi_2+\phi_4-\phi_5-\phi_6+\phi_7) \qquad (1)$$

and its energy is given by:

$$E_5=\int\psi H\psi\mathrm{d}\tau=\alpha_C+\frac{1}{3}(h\dot{o}-1)\beta+\frac{2}{3}(1-k_{CO})\beta \qquad (2)$$

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[3] A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley & Sons, Inc., New York (1961), p. 135.

[4] a) H. Lumbroso and R. Dabard, *Bull. soc chim. France*, **1959**, 749; b) A. Arcoria, H. Lumbroso and R. Passerini, ibid., **1959**, 754.

The delocalization of the electrons to carbonyl groups increases the contribution of an ionic structure where the oxygen atom is bonded to the carbon atom through a single bond. Therefore, k_{CO} becomes less than when the contribution of the ionic structure is small. The increased electron density at the oxygen atom in the ionic structure causes a reduction in the value of $h_{\dot{O}}$ which appears in Eq. 2. The net results of these corrections are minor, however, in comparison with the change in *En*. Therefore, the increase in k_{CN}, or the contribution of the ionic structures, makes the separation between *En* and E_5 narrower than before after all.

The results obtained above agree qualitatively with the observed shift of the wavelength of the absorption band under discussion when the before-mentioned group is advanced from 1 to 4. However, neither the difference in the solvent effects of the four groups nor the relatively large intensities of the absorptions can be explained by a simple $n \rightarrow \pi^*$ transition of the carbonyl groups. Thus, it is clear that some modification of the above discussion are required. This modification is brought about quite naturally when the interaction between the $n \rightarrow \pi^*$ and other transitions of the system is taken into consideration.

A fairly large number of β,γ-unsaturated ketones have been known to show extraordinarily strong $n \rightarrow \pi^*$ transitions.[5,6] According to Labhart and Wagniere, the high intensities observed for these $n \rightarrow \pi^*$ transitions are due to a perturbation of the absorptions by the $\pi \rightarrow \pi^*$ transitions through the overlap of the oxygn 2p lone-pair orbital with the β-carbon $2p_\pi$ orbital.[6] Quite similar situations may be expected for the maleimide derivatives under discussion. Using Mulliken's table[7] and the geometry assumed for maleimide as shown in Fig. 8, the overlap integral between the oxygen 2p orbital and the nitrogen sp^3 orbital has been calculated to be 0.013. The overlap becomes small as the nitrogen orbital approaches a pure p orbital corresponding to the presumed cases of *N*-arylmaleimides. The nitrogen orbital, on the other hand, plays an important role in the π-electronic system of the imide group. As is shown in Table III, a large contribution of the nitrogen atomic orbital, to the third energy level π_3 of the imide systems given in Fig. 7 is observed. Therefore, a considerable interaction between the two transitions, n-π^* and $\pi_3 \rightarrow \pi^*$, may be expected when a noticeable overlap exists between the oxygen 2p orbital and the nitrogen orbital. Unfortunately, the $\pi_3 \rightarrow \pi^*$ transition could not be identified in the present experiment. The oscillator strength of the corresponding absorption band, however, is estimated theoretically to be of the order of 10^{-1}, since it is a possible $\pi \rightarrow \pi^*$ transition. Therefore, the overlap between the oxygen 2p lone-pair orbital and the nitrogen orbital as estimated above is large enough to explain the intensification of the $n \rightarrow \pi^*$ transition of the carbonyl groups by the perturbation. Furthermore, the $\pi_3 \rightarrow \pi^*$ transition has a strong charge-transfer absorption character as is obvious from an inspection of the molecular orbitals concerned. Therefore, it is quite natural that a bathochromic shift is observed for the longest-wavelength absorption band of maleimide and its *N*-alkyl substituted derivatives when the spectra are measured in polar solvents. The overlap described above decreases rapidly as the nitrogen orbital approaches a pure p orbital. A decrease in intensity and a change in solvent effect are

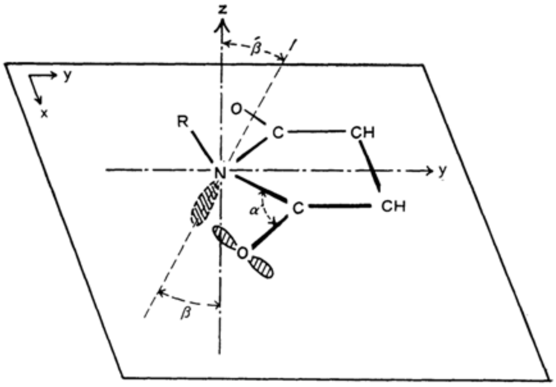

Fig. 8. Steric arrangement of atoms and the orbitals assumed for maleimide and its *N*-alkylsubstituted derivatives. The oxygen 2p orbitals are in the xy plane. The N—R bond and the nitrogen orbital as indicated by the shadowed area are directed up and down, respectively, from the xy plane. The following bond distance and bond angles were assumed in the calculation described in the text.

$r_{CN} = r_{CO} = 1.25$ Å, $\alpha = 125°$, and $\beta = 35°$

TABLE III. THE COEFFICIENTS FOR ATOMIC ORBITALS IN THE THIRD MOLECULAR ORBITAL π_3 SHOWN IN Fig. 7

Atom	$k_{CN}=0.8$	$k_{CN}=0.6$	$k_{CN}=0.4$	$k_{CN}=0.2$
N	−0.709	−0.781	−0.863	−0.952
O	0.346	0.304	0.242	0.146
$C_{C=O}$	0.097	0.104	0.099	0.069
$C_{C=C}$	0.346	0.304	0.242	0.146

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[5] R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, **1956**, 2302.

[6] H. Labhart and G. Wagniere. *Helv. Chim. Acta*, **42**, 2219 (1959).

[7] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

expected, accordingly, for the longest-wavelength absorption band of *N*-arylmaleimide.

In the case of *N*-arylmaleimide, an interaction of the oxygen 2p orbital with the π orbital on the phenyl group must also be taken into consideration. This type of interaction is expected to have a small effect upon the longest-wavelength absorption for the following two reasons. The overlap between the oxygen lone-pair orbital and the π orbital of the phenyl group is strongly dependent on the twisting angle, θ, of the phenyl group around the C_2 axis, as is shown in Fig. 9. For the best situation, where θ is 90°, the overlap between the oxygen 2p orbital and the highest-occupied orbital of the phenyl group is estimated to be 0.01 or so. Actually, the phenyl group does not stay at the perpendicular position relative to the imide plane. Thus, the real or average value of the overlap integral is less than 0.01. Secondly, moment of the transition from the π orbitals on the phenyl group to π^* is expected to be small when θ is different from zero. Therefore, the $\pi \rightarrow \pi^*$ transition under discussion is not intensified very much by the perturbation through the interaction of the oxygen lone-pair orbital with π orbitals of the phenyl group.

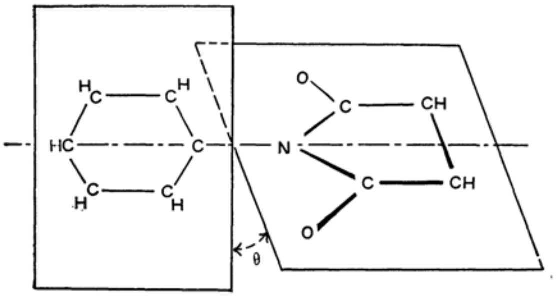

Fig. 9. Orientation of the plane of phenyl group with respect to the imide plane. The angle of twisting is indicated by θ.

In conclusion, the longest-wavelength absorption bands of *N*-substituted maleimides are found to be essentially due to the $n \rightarrow \pi^*$ transition of the carbonyl group. When the hydrogen on the nitrogen atom is replaced by alkyl and aryl groups, the nitrogen lone-pair electrons delocalize more and more to the carbonyl groups and the absorption bands in question shift to longer wavelengths. In the case of maleimide, the $n \rightarrow \pi^*$ transition is perturbed strongly by the $\pi \rightarrow \pi^*$ transition of the cyclic imide system, and an appreciable intensification of the absorption band and its bathochromic shift in the polar solvents result. The perturbation decreases rapidly in the order of *N*-alkyl- and *N*-arylmaleimides, and the absorption approaches a pure $n \rightarrow \pi^*$ transition.

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