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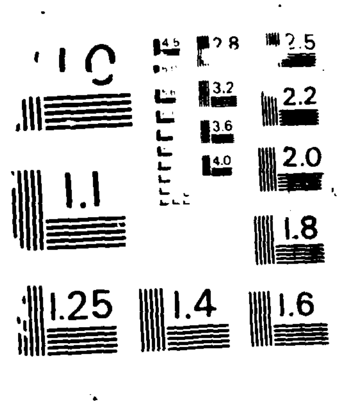

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LASER FLASH PHOTOLYSIS OF A METHYLENE 4,4'-DIPHENYLDIISOCYANATE (MDI) BASED POLYURETHANE AND MODEL CARBAMATES

by

C. E. Hoyle, Y. G. No, K. G. Malone, S. F. Thames and D. Creed

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Transient species in the laser flash photolysis of solutions of methylene 4,4'-diphenyldiisocyanate (MDI) based polyurethanes and small molecule models have been detected. One of the transient species, a substituted anilinyl radical, is not quenched by oxygen while a second transient is extinguished by the introduction of oxygen. Based on the spectral results, a plausible mechanism is offered for the primary photochemical reactions of MDI based polyurethanes.

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Laser Flash Photolysis of a Methylene 4,4'-diphenyldiisocyanate (MDI) Based Polyurethane and Model Carbamates

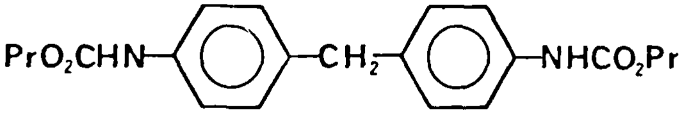
The photolytic degradation of polyurethanes based on aromatic diisocyanates continues to receive a considerable amount of attention (1-7). Indeed, there have been a number of schemes proposed to account for their photolytic degradation, each having its own merit (1-7). This communication is designed to provide basic insight into the nature of the transient intermediates produced during the primary photochemical reactions of the aryl carbamate chromophores in a methylene 4,4'-diphenyldiisocyanate (MDI) based polyurethane in solution. The results for the MDI polyurethane are interpreted by comparison with appropriate mono- and biscarbamate small molecule models. The polyurethane used in this study (hereafter designated MDI-PUE) was prepared by reacting methylene 4,4'-diphenyldiisocyanate (MDI) with poly(tetramethylene ether glycol, MW 1000) and then extending with 1,4-butanediol.

Figure 1 (curve a) shows the transient absorption spectrum of a nitrogen saturated 5.5 X 10^{-3} g/dL solution of MDI-PUE in tetrahydrofuran (THF) obtained on an Applied Photophysics, Ltd. kinetics spectrometer at a delay time of 2.0 μs after firing a laser pulse from a krypton fluoride excimer laser (λ_{ex} = 248 nm; ~ 10 ns pulse width; 80 mJ/pulse). The ground state absorbance of the polymer was 1.1 at 248 nm, and the transient spectrum was generated by analyzing transient decay curves recorded every 6 nm from 300 to 500 nm. The prominent features of the transient absorption spectrum in Figure 1, curve a, are the four bands with maxima at 310 nm, 355 nm (broad), 370 nm, and >390 nm (very weak diffuse absorbance band). Curve b in Figure 1 shows the transient spectrum of an air saturated THF solution of MDI-PUE (5.5 X 10^{-3} g/dL). Oxygen completely extinguishes the peak at 370 nm, but has less of an effect on the peaks at 310 nm and the absorbance band above 390 nm. The effect of air on the 355 nm band is difficult to interpret since it falls so close to the bands at 370 nm which is heavily quenched by oxygen. The oxygen effect at 370 nm is confirmed by lifetime quenching results which will be presented in a full paper.

Now we must ask, what species are responsible for the transient absorbance spectrum in Figure 1, curve a. This question can best be answered by first considering the laser flash photolysis of several small molecule models. The transient absorption spectra recorded 2.0 μs after the laser flash of both aniline (5.1 X 10^{-4} M) and propyl N-phenylcarbamate (5 X 10^{-4} M) in nitrogen saturated THF are shown in Figures 2 and 3. [Essentially identical spectra were obtained in air saturated THF.] For both aniline and propyl N-phenylcarbamate, a distinct peak is present at 310 nm as well as a broad band above 390 nm. In the case of propyl N-phenylcarbamate an additional broadening is observed between 340 nm and 360 nm with a maximum around 355 nm. Land and Porter (8) have assigned the strong peak at 310 nm and the weak broad band absorbance centered around ~ 400 nm in the flash photolysis of aniline in non-protic solvents to the allowed and forbidden transitions of the anilinyl radical formed by N-H bond cleavage. Thus, the peak at 310 nm and the broad band above 390 nm in Figure 2 (aniline) and Figure 3 (propyl N-phenylcarbamate) can be assigned to an anilinyl radical which should be relatively non-reactive with oxygen, especially in a solvent with readily abstractible hydrogens. In the case of propyl N-phenylcarbamate, the anilinyl radical must be formed by direct homolytic cleavage of the nitrogen-carbon bond in the carbamate moiety. Based on the results for aniline and propyl N-phenylcarbamate, it is appropriate to ascribe the 310 nm and broad band absorbance above 390 nm in the transient spectrum of MDI-PUE (Figure 1) to an anilinyl type radical. The detection of anilinyl radicals in the laser flash photolysis of MDI-PUE is in agreement with earlier identification (9) of an anilinyl radical (detected by ESR) in the photolysis of an MDI based polyurethane. Our results are also consistent with formation of reported (1,2,4) photo-Fries and substituted aniline photoproducts which have been reputed to form by a primary N-C bond cleavage in the carbamate moiety followed by rearrangement and/or separation of the resultant radicals.

Identification of the 355 nm band for MDI-PUE and propyl N-phenylcarbamate is less obvious than for the 310 nm peak and the broad band absorbance above 390 nm. We know from the historic work of Porter and co-workers (8) that anilinyl radicals are readily formed via a photolytically induced nitrogen-hydrogen bond cleavage of N-substituted anilines. It is thus reasonable to suspect that a nitrogen-hydrogen bond cleavage will occur for N-aryl carbamates to produce a carboxy substituted anilinyl radical which, since it is a substituted anilinyl radical, would have a red-shifted (from 310-320 nm) absorbance, perhaps with a peak around 355 nm.

Having furnished, based on model compounds, what seems to be a plausible assessment of three of the four bands in the transient absorption spectrum of MDI-PU (Figure 1, curve a), identification of the 370 nm peak remains. Consider the bispropylcarbamate model (BP-MDI) of MDI shown below.



BP-MDI

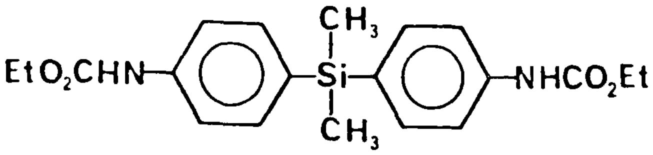
It possesses, in addition to the two phenyl carbamate groups, a disubstituted methylene carbon. In addition, it should be noted that the transient spectra of propyl N-(p-tolylcarbmate), although not shown, also has bands with maxima around 310 nm and above 390 nm. As in the case of propyl N-phenylcarbamate, the transient spectrum of propyl N-(p-tolylcarbamate) shows no maximum at 370 nm. Thus, any additional bands in the transient spectrum of BP-MDI can be attributed to the presence of the central methylene carbon. Bearing this in mind, the transient absorption spectrum of BP-MDI in Figure 4 (λ_{ex} = 248 nm; 2.7 X 10^{-5} M in nitrogen degassed THF taken at a delay of 2.0 μs) shows a distinct peak at ~ 370 nm in addition to the structural features found in the transient spectrum of propyl N-phenylcarbamate (Figure 3). The 370 nm peak is completely quenched in the presence of oxygen. The possibility of the 370 nm transient resulting from an excited triplet was eliminated by failure to diminish its intensity with cis-piperylene, an effective triplet quencher. Although at this time we can offer no absolute identification of the species responsible for the 370 nm peak, we can conclude from its absorption maximum (well above 300 nm) that it results from a radical centered on an atom attached to the phenyl ring, for instance a diarylmethyl radical ($\mathrm{Ar\hat{C}HAr}$). Porter and Windsor (10) have shown that unsubstituted diphenylmethyl radicals have an absorbance maximum at 335 nm and are readily formed upon direct photolysis of diphenylmethane in paraffin solution by a C-H bond cleavage. We have reproduced on our instrument the transient absorption spectrum of the unsubstituted diphenylmethyl radical in THF and obtain an absorbance maximum around 340 nm. It is certainly plausible that substitution of carbamate groups at the para positions could red shift the absorbance maximum of the diphenylmethyl radical to around 370 nm. The following additional points are compatible with, although do not provide unconditional evidence for, a diarylmethyl structure:

1. Diarylmethyl radicals should react readily with oxygen: this is consistent with the results in Figure 1 (curve b).

2. The expected peroxy radical product between a diarylmethyl radical and oxygen should eventually, upon hydrogen abstraction from the solvent, yield a hydroperoxide. Such hydroperoxides centered on the diaryl substituted methylene carbon have indeed been reported to form upon photolysis (1) of MDI based polyurethanes.

3. Recent radical abstraction experiments in our lab (11) also strongly suggest the generation of a diarylmethyl radical.

In order to test the vaildity of assigning the 370 nm peak to a diarylmethyl radical, a dimethyl substituted diarylsilane biscarbamate ($SiMe_2MDI$) analog of MDI was synthesized (see structure below).



$SiMe_2MDI$

This compound cannot possibly form a diarylmethyl radical. In accordance with this expectation, the transient absorption spectrum (Figure 5) of this compound (λ_{ex}=248 nm; 2.6 X 10^{-5} M in nitrogen degassed THF taken at a delay of 2.0 μs) has no peak at 370 nm and thus provides additional support for assignment of the

370 nm peak in the transient spectrum of the model BP-MDI (Figure 4) and polyurethane MDI-PUE (Figure 1) to the diarylmethyl radical. Results for a number of other model biscarbamates are also consistent with diarylmethyl radical formation. Conclusive identification of the species responsible for the 370 nm peak is pendant on additional work in progress.

In summary, the transient absorbance spectrum of the bispropylcarbamate model BP-MDI (Figure 4) and the polyurethane MDI-PUE in (Figure 1) are essentially identical. Combined with data for aniline and propyl N-phenylcarbamate models (Figures 2 and 3), a tentative mechanism has been postulated for at least a portion of the primary photochemical reactions of MDI based polyurethanes in solution. Finally, it should be pointed out that care must be taken when extension of transient measurements in solution is made to polyurethane films since the lifetimes of radicals generated may be substantially altered. In addition, certain pathways for reactions of radicals in solution may be absent in the solid phase. Laser flash photolysis of polyurethane films will thus be the subject of a future investigation.

In order to substantiate the preliminary results presented in this brief communication, we recently completed a laser flash photolysis study in which independently generated hydrogen abstracting t-butoxy radicals are employed to produce transients from model arylcarbamates and MDI-based polyurethanes. A thorough kinetic analysis of polyurethane laser flash photolysis based on these results will be published as a full paper in the near future. In addition, detailed time resolved decay profiles and radical decay times will be presented for all radical species discussed in this paper.

Acknowledgement

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11. To be published.

Figure Captions

Figure 1. Transient absorption spectra (2.0 μs) of MDI-PUE in THF (a) Nitrogen saturated (b) Air saturated.

Figure 2. Transient absorption spectrum (2.0 μs) of aniline in nitrogen saturated THF.

Figure 3. Transient absorption spectrum (2.0 μs) of propyl N-phenylcarbamate in nitrogen saturated THF.

Figure 4. Transient absorption spectra (2.0 μs) of BP-MDI in THF (a) Nitrogen Saturated (b) Air Saturated.

Figure 5. Transient absorption spectrum (2.0 μs) of $SiMe_2MDI$ in nitrogen saturated THF.

Fig (1)

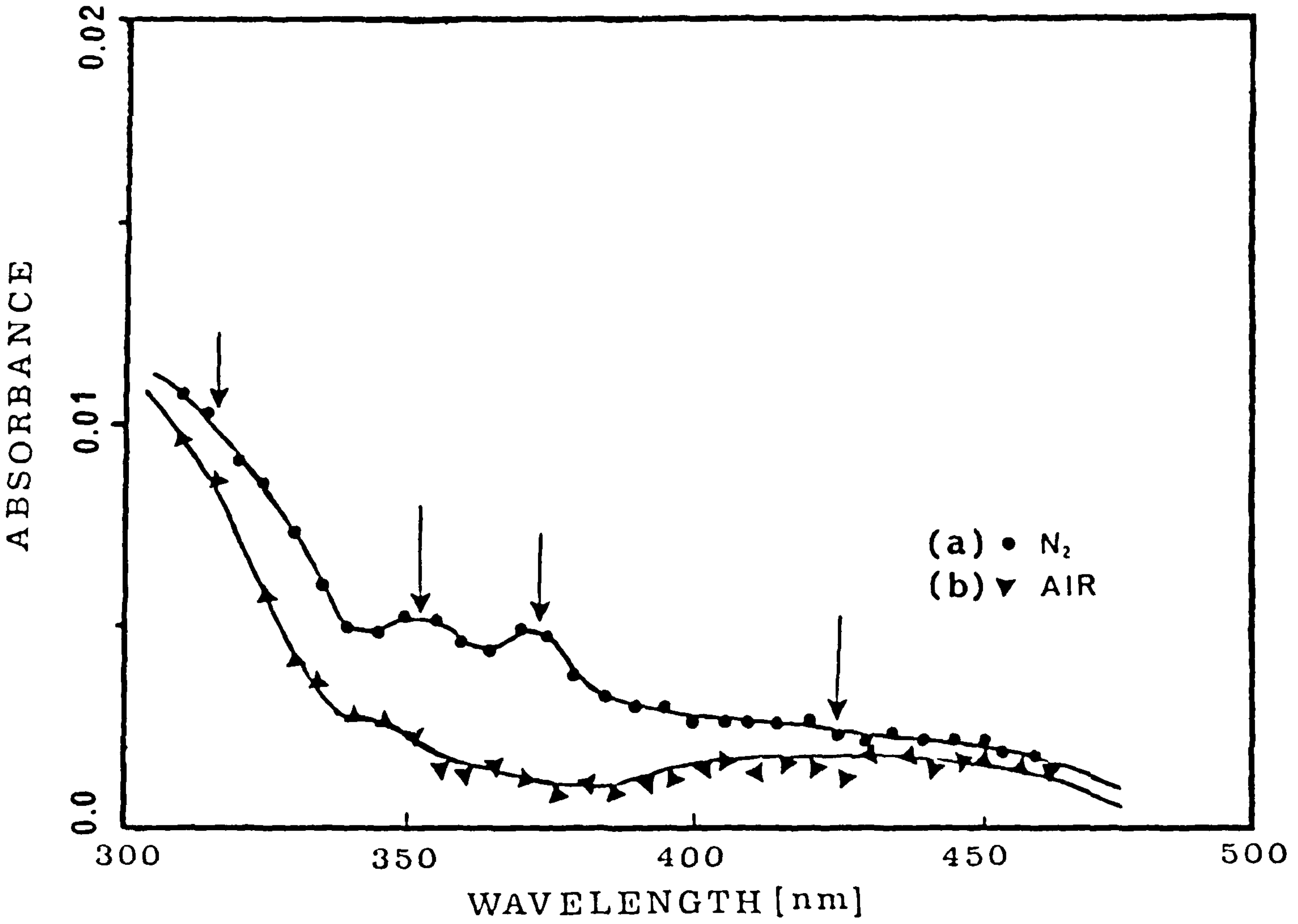

0.02
0.01
0.0
ABSORBANCE
300
350
400
450
500
WAVELENGTH [nm]
(a) ● N_2
(b) ▼ AIR

Fig 2

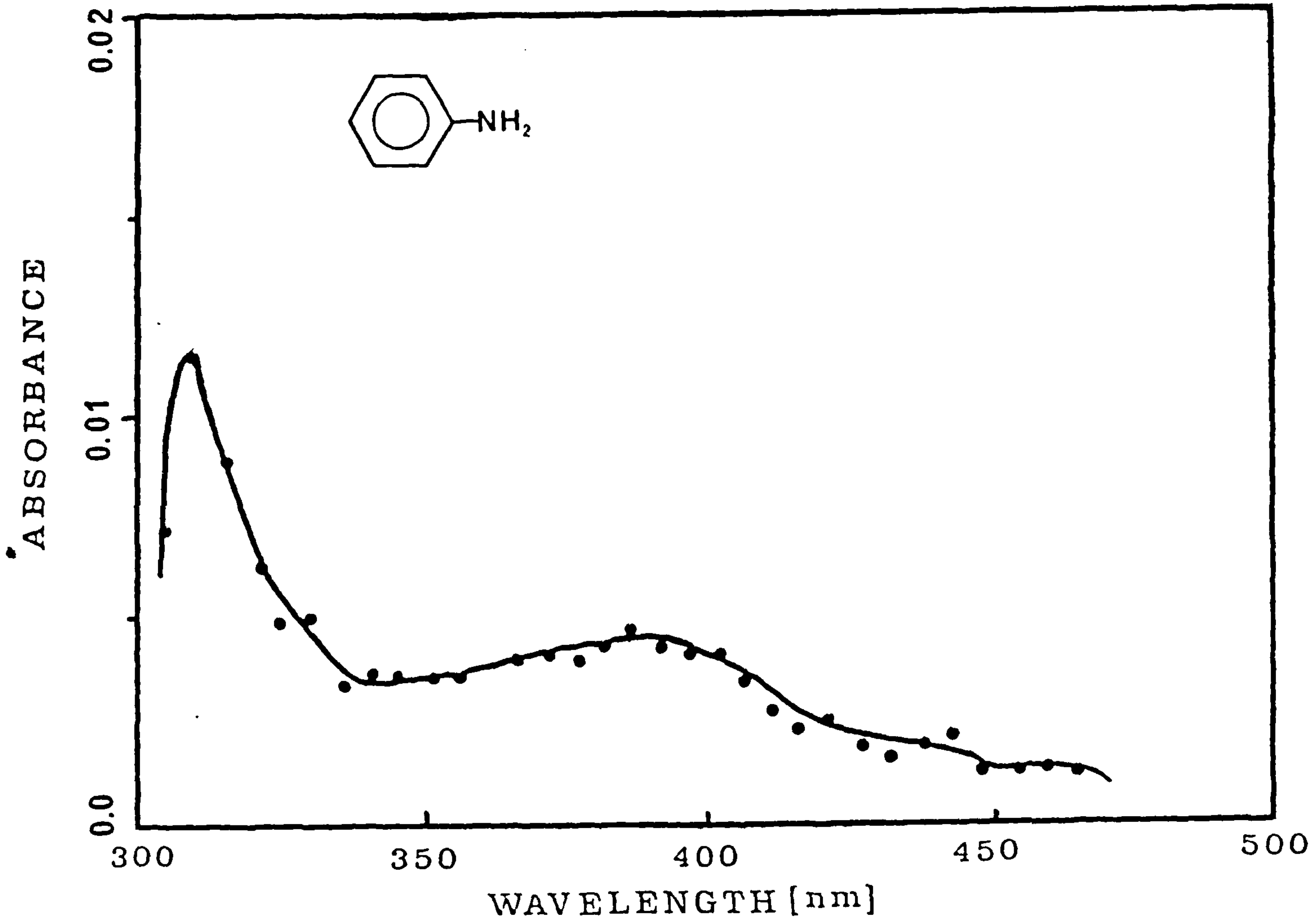


Fig. 3

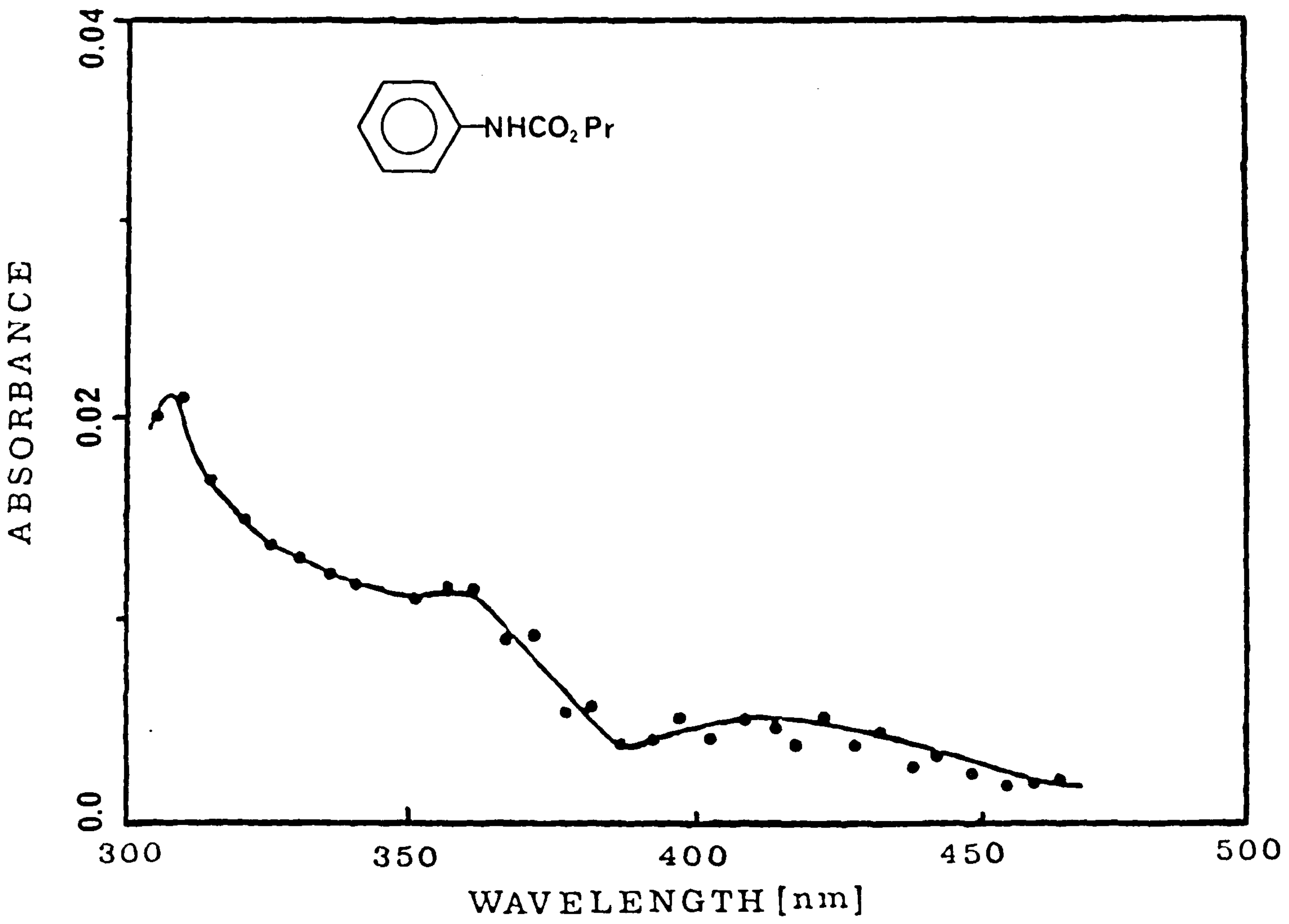
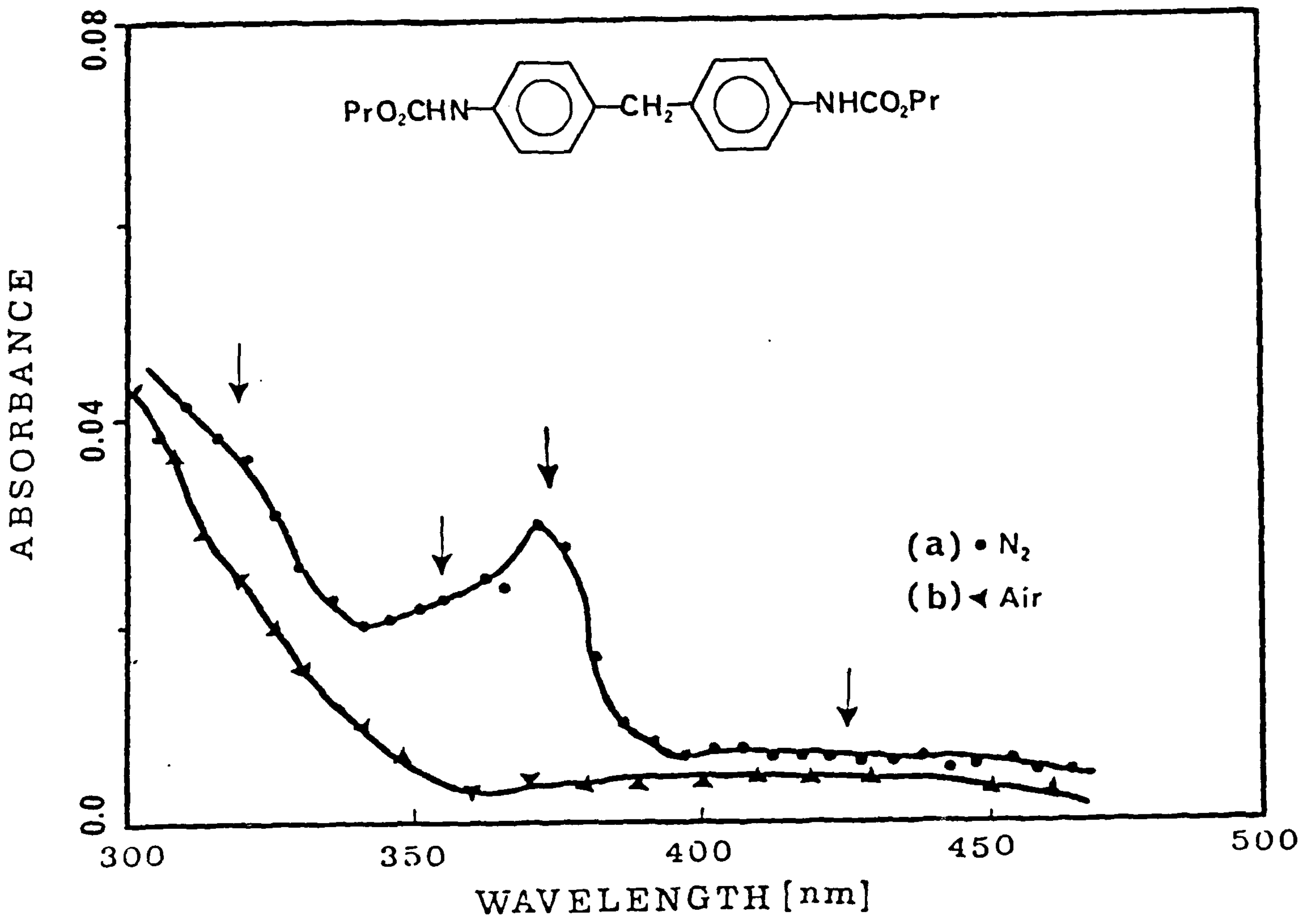
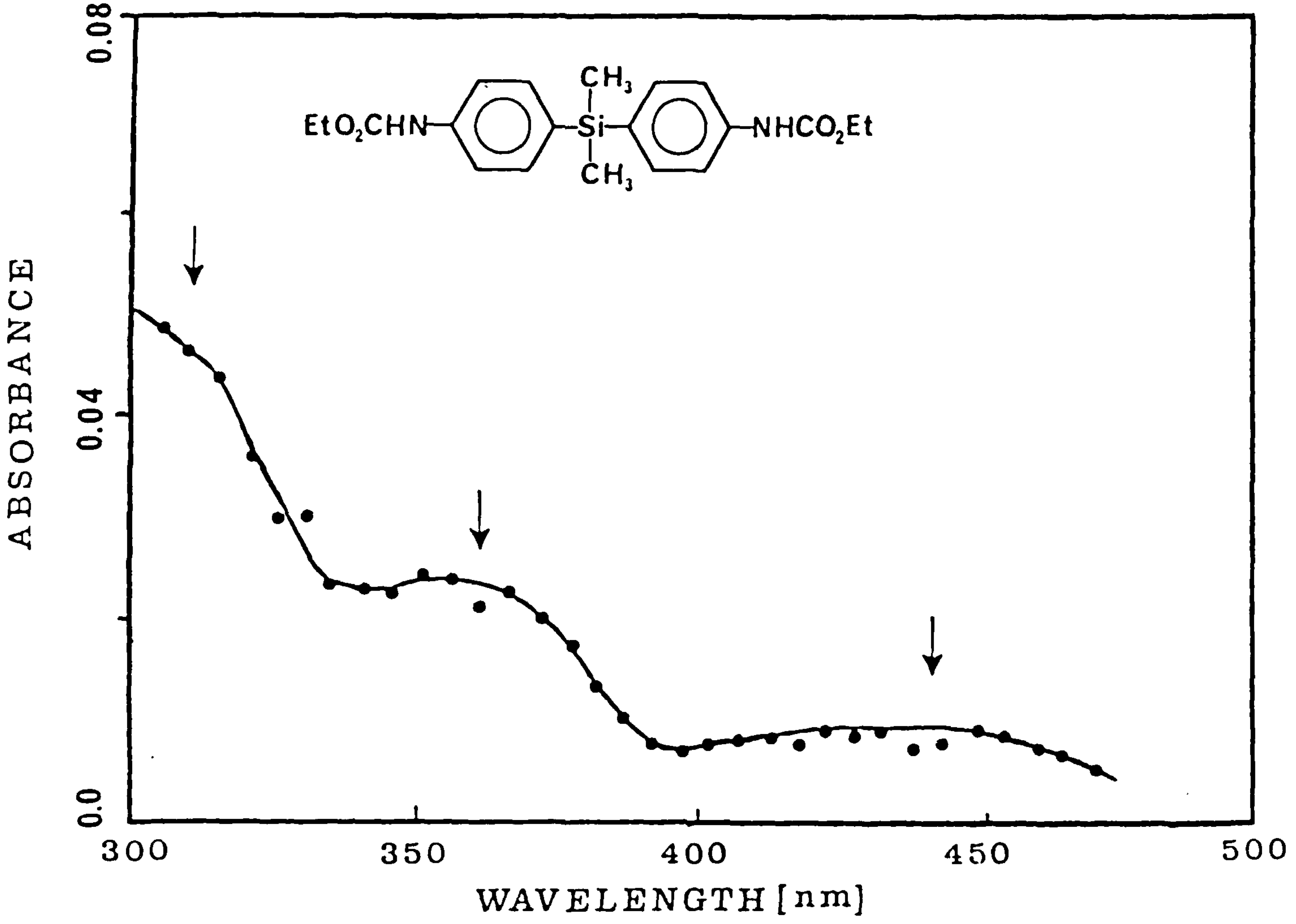

NHCO$_2$Pr
ABSORBANCE
0.04
0.02
0.0
300
350
400
450
500
WAVELENGTH [nm]

Fig. 4



PrO$_2$CHN–C$_6$H$_4$–CH$_2$–C$_6$H$_4$–NHCO$_2$Pr
(a) ● N$_2$
(b) ◀ Air
ABSORBANCE
0.08
0.04
0.0
300
350
400
450
500
WAVELENGTH [nm]

Fig 5


EtO2CHN
CH3
Si
CH3
NHCO2Et
ABSORBANCE
0.0
0.04
0.08
300
350
400
450
500
WAVELENGTH [nm]

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