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Metalloporphyrins. III.[1] Photoinduced Acylamination of Zinc Porphyrins by Use of Acyl Azides

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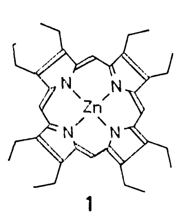
Visible light irradiation of a solution of zinc octaethylporphin (ZnOEP) in the presence of acyl azide gives zinc complex of 5-acylamino-2,3,7,8,12,13,17,18-octaethylporphin together with a small amount of zinc complex of 21-acylamino-2,3,7,8,12,13,17,18-octaethylporphin. Zinc 5,10,15,20-tetraphenylporphin (ZnTPP) is coverted into zinc complex of 21-acylamino-5,10,15,20-tetraphenylporphin in a similar way. The pyrolysis of the *N*-acylaminated ZnOEP affords the rearrangement product in addition to ZnOEP, while *N*-acylaminated ZnTPP is converted into ZnTPP on heating. The spectroscopic properties of these photoproducts are given.

Photochemical studies on metalloporphyrins have hitherto been focused on their photoreduction and photooxidation in particular in relation to the function of photosynthetic pigments and the degradation of biological macrocycles. Little work has been done regarding other photochemical reactions of the macrocyclic ligands.[2] During the course of an investigation on the fluorescence quenching of metalloporphyrins, acyl azide was found to effectively quench the emission of zinc octaethylporphin (ZnOEP) (**1**), the fluorescence intensity decreasing gradually during the course of measurement. These observations prompted us to study the photolysis of ZnOEP–acyl azide system.[3] This paper describes the photoinduced acylamination at the *meso*-position and at the pyrrolic nitrogen of the macrocycle resulting from the sensitized decomposition of acyl azide. This type of photochemical conversion was extended to zinc tetraphenylporphin (ZnTPP) (**2**), yielding *N*-acylaminated ZnTPP. This seems to be a first example of the photoinduced substitution on metalloporphyrins.

Results and Discussion

When a dichloromethane solution of ZnOEP was irradiated with light of wavelength>450 nm in the presence of a slight excess of aromatic acyl azide under argon stream, the color of the solution immediately darkend. The irradiation period was dependent upon the nature of acyl azide; an electron-withdrawing group except nitro group on benzoyl residue accelerates the photolysis (Table 1). The reaction was followed by TLC, and two photolytic products were isolated by preparative TLC. The red major product showing larger R_f-value has typical visible bands of metal complexes and the CO stretching vibration owing to amide



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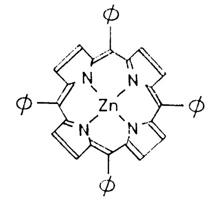

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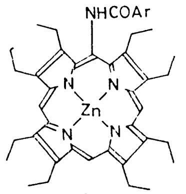

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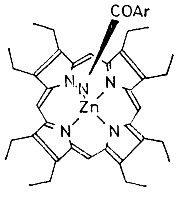

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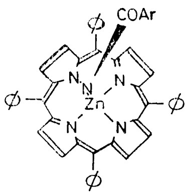

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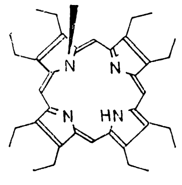

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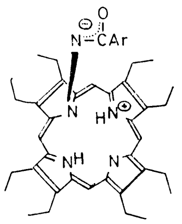

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TABLE 1. *meso*-ACYLAMINOOCTAETHYLPORPHINATOZINC (**3**)

	Ar	Mp (dec)	Irradiation time (h)	Yield[a)]	Elementary analyses (%) Found C	Found H	Found N	Calcd C	Calcd H	Calcd N
3a	C_6H_5	307—309 °C	4	58%	71.65	6.80	9.54	71.99	6.89	9.97
3b	*p*-$MeOC_6H_4$	295—301	6	50	69.91	6.98	9.14	70.70	6.88	9.38
3c	*p*-ClC_6H_4	324—325	2	61	63.57	6.40	9.16	68.79	6.44	9.32
3d	*p*-CNC_6H_4	305—307	0.2	59	70.76	6.40	10.86	71.18	6.52	11.33
3e	*p*-$NO_2C_6H_4$	298—299	14	55	67.60	6.20	10.56	67.73	6.53	11.03
3f	*m*-$NO_2C_6H_4$	277—279	15	65	67.31	6.14	10.42	67.73	6.53	11.03
3g	α-Naphthyl	283—286	2	47	72.92	6.89	9.18	73.55	6.70	9.14
3h	Cinnamoyl	296—306	1	43	72.64	6.88	9.27	72.69	6.92	9.43

a) A small amount of ZnOEP recovered unchanged on photolysis is not taken into consideration.

group (Table 2). From the NMR spectra the amide group can be ascribed to the *meso*-substituent of the macrocyclic ligand, since the ethyl protons are no longer equivalent and three *meso*-protons are observed in the intensity ratio 1:2.[4,5] Appearance of new NMR proton signals due to aryl ring derived from acyl azide as well as the elementary analyses suggest that ZnOEP is substituted by ArCONH– or ArNHCO– group at the *meso*-position (Table 1 and 3). The structure having the former group for the major product (**3**; Ar=Ph) was unequivocally elucidated by identification of the photoproduct from ZnOEP–benzoyl azide system with the authentic sample prepared by the benzoylation of *meso*-aminooctaethylporphin,[5] followed by metallization.

The NMR spectra of the minor photoproducts chelated by zinc (Table 4) show the presence of four *meso*-protons in the intensity ratio 2:2 and the remarkable high field shift of the aryl protons derived from acyl azide, indicating that acylimino (ArCON) or its isomer (ArNCO) is bound to the pyrrolic nitrogen of ZnOEP (Table 5). Determination of the structure having the former group (**4**) was made by IR spectral analysis of the photoproduct starting from ZnOEP-*p*-cyanobenzoyl azide; $\bar{\nu}_{CN}$ at 2232 cm^{-1} is in line with that of *p*-cyanobenzoyl-*p*-toluide (**5**) and *N'*,*N'*-dimethylhydrazide (**6**) at 2233 cm^{-1} rather than that of *N*,*N*-dimethyl-*N'*-(*p*-cyanophenyl)urea (**7**) at 2223 cm^{-1}. The shift of the amide carbonyl frequency to lower wavelength at *ca.* 1610 cm^{-1} of this type of compound can be interpreted in terms of the bond formation between zinc and the acylamino nitrogen[6] (Table 6). The metal complexes exist as neutral species, in contrast to *N*-alkylporphins which require counter anion like halogenide

Table 2. Visible and infrared spectra of zinc *meso*-acylaminooctaethylporphins (**3**)

	λ_{max} nm ($\varepsilon \times 10^{-4}$) in CH_2Cl_2	$\bar{\nu}_{max}$ cm^{-1} in KBr
3a	412(42.0), 504(0.26), 540(1.95), 578(1.60)	3400, 1655, 1503
3b	412(46.0), 504(0.24), 540(1.71), 578(1.33)	3300, 1645, 1520
3c	412(40.6), 504(0.27), 540(1.90), 578(1.58)	3300, 1643, 1520
3d	412(43.5), 504(0.22), 540(1.93), 578(1.62)	3400, 2233, 1660, 1510
3e	411(40.0), 503(0.34), 541(1.86), 579(1.53)	3400, 1660, 1528, 1343
3f	412(38.5), 505(0.25), 541(1.88), 579(1.61)	3400, 1640, 1532, 1350
3g	414(40.5), 504(0.29), 542(2.02), 580(1.60)	3400, 1660
3h	412(43.5), 504(0.27), 541(2.07), 578(1.70)	3280, 1665, 1625

Table 3. NMR spectra of *meso*-acylaminooctaethylporphinatozinc (**3**)

	Solvent[a]	*meso*-H	Aryl-H	Ring-H
3a	DC	10.02 (s, 3H),	7.7—8.0 (m, 3H)	
3b	TFA	10.91, 11.02	7.67 (d, 2H, 9 Hz) 8.73 (d, 2H, 9 Hz)	−3.01 (2H), −4.13 (2H)
3c	TFA	10.88, 10.98	8.05 (d, 2H, 10.5 Hz)	−2.90 (2H), −4.00 (2H)
3d	DC	10.11 (s, 2H), 10.20 (s, 2H)	7.79 (d, 2H, 5.5 Hz), 8.57 (d, 2H, 5.5 Hz)	
3e	DC	9.97 (s, 2H), 10.10 (s, 2H)	8.55 (s, 4H)	
3f	TFA	10.90, 11.00	8.23 (m, 1H) 9.00—9.46 (m, 2H) 9.60—9.90 (m, 1H)	−2.86 (2H), −3.95 (2H)
3g	TFA	10.73, 10.91	7.79—9.05 (m, 7H)	−2.70 (2H), −3.98 (2H)
2h	TFA	10.56, 10.70	7.2—8.2 (m, 6H) 8.62 (d, 1H, 15 Hz)	−2.90 (2H), −4.08 (2H)

a) DC; chloroform-*d*. TFA; trifluoroacetic acid.

Table 4. *N*-Acylaminooctaethylporphins (**10**) and their zinc complexes (**4**)

	Ar		Elementary analyses (%)					
			Found			Calcd		
			C	H	N	C	H	N
10a	C_6H_5	Free base	79.40	7.85	10.31	78.96	7.87	10.72
4c	*p*-ClC_6H_4	Zn salt	68.49	6.82	9.03	68.79	6.44	9.32
4d	*p*-CNC_6H_4	Zn salt	70.79	6.81	10.89	71.18	6.52	11.33
10d	*p*-CNC_6H_4	Free base	77.53	7.52	11.98	77.82	7.43	12.39
10h	Cinnamoyl	Free base	79.09	7.90	10.21	79.47	7.86	10.31

to form the metal complexes.[7-12] Another metal complex of this type of anomalous coordination has been reported.[13]

The photochemical acylamination on porphyrin ring has been extended to ZnTPP (**2**) (Table 7). The structure of the zinc complex of the photoproduct has been clarified by NMR spectra (Table 8). Protons attributable to acyl group derived from acyl azide undergo considerable high field shift as in the case of **4**. The number of β-pyrrolic protons remains eight; two singlets for four protons and an AB quartet for four protons. The zinc macrocycles show similar polarization of the amide CO and the cyano group like **4**, supporting the structure (**8**) (Table 9).

The structure of the photoproducts in the present work demonstrates the resemblance of the photolysis to the nitrene reaction. The reactions of nitrene or carbene with metalloporphyrins investigated so far fall into four categories, although no photochemically induced reaction has been reported; *a*) insertion at the *meso*-position,[14,15] *b*) addition on the pyrrolic nitrogen atom,[7-9,16] *c*) addition to the β,β-double bond of pyrrolic ring to give cyclopropane derivatives,[7,15,17] and *d*) formation of a metal-carbon bond.[18] The *meso*-acylaminated photoproducts (**3**) seem to be formed by reaction *a*), and the *N*-acylaminated macrocycles (**4**) and (**8**) by reaction *b*). The azacyclopropane derivative according to reaction *c*) has not yet been isolated in the photolysis of ZnOEP–acyl azide.

The photolysis of zinc porphyrin–acyl azide system is of synthetic value for the introduction of a functional group at the *meso*-position of the symmetrical macrocycles and particularly for the preparation of *N*-substituted macrocycles which are attracting attention as regards structural problems and chemical reactivity. Since the *N*-acylaminated porphins are the first example of the macrocycle bearing *N*-substituent other than alkyl, the NMR spectra and chemical reactivity of **4** and **8** have

Table 5. NMR spectra of *N*-acylaminooctaethylporphins (**10**) and their zinc complexes (**4**) in $CDCl_3$

	CH_3CH_2	CH_3CH_2	*meso*-H	Acyl-H	Ring-H
10a	1.51 (t, 6H) 1.91 (t, 6H) 2.00 (t, 12H)	*ca.* 4.18	10.66 (s, 2H) 10.71 (s, 2H)	3.16—3.39 (m, 2H) 5.40—5.75 (m, 2H) 6.06—6.37 (m, 1H)	−0.98 (2H)
4c	1.43 (t, 6H) 1.95 (t, 18H)	*ca.* 4.16	10.39 (s, 2H) 10.52 (s, 2H)	*ca.* 3.90 (2H) 5.79 (d, 2H, 8 Hz)	
10c	1.50 (t, 6H) 1.88 (t, 6H) 1.93 (t, 6H) 1.96 (t, 6H)	*ca.* 4.18	10.52 (s, 2H) 10.55 (s, 2H)	3.11 (d, 2H, 8 Hz) 5.42 (d, 2H, 8 Hz)	
4d	1.46 (t, 6H) 1.98 (t, 18H)	*ca.* 4.18	10.42 (s, 2H) 10.56 (s, 2H)	*ca.* 4.03 (2H) 6.12 (d, 2H, 8 Hz)	
10d	1.52 (t, 6H) 1.88 (t, 6H) 1.93 (t, 6H) 1.98 (t, 6H)	*ca.* 4.18	10.57 (s, 2H) 10.61 (s, 2H)	3.28 (d, 2H, 8 Hz) 5.78 (d, 2H, 8 Hz)	−1.36 (2H)
10h	1.54 (t, 6H) 1.90 (t, 6H) 1.96 (t, 6H) 2.00 (t, 6H)	*ca.* 4.18	10.54 (s, 4H)	5.35 (m, 2H) 6.6—6.9 (m, 3H) 3.01 (d, 1H, 15 Hz)	

Table 6. Visible and infrared spectra of *N*-acylaminooctaethylporphins (**10**) and their zinc complexes (**4**) in dichloromethane

	λ_{max} ($\varepsilon \times 10^{-4}$) in nm	$\bar{\nu}_{max}$ in cm^{-1}
10a	401(10.8), 530(0.74), 566(1.28), 612(0.26)	1610, 1560
4c	410(19.0), 530(0.94), 563(1.57), 606(1.02)	1610, 1560
4d	410(17.1), 530(0.83), 563(1.18), 606(0.84)	2232, 1615, 1550
10d	402(11.5), 529(0.77), 565(1.27), 610(0.30)	2229, 1608
10h	404, 526, 562, 605	1645, 1590, 1560

Table 7. 21-Acylamino-5,10,15,20-tetraphenylporphinatozinc (**8**)

	Ar	Irradiation time (h)	Yield (%)	Elementary analyses (%)					
				Found			Calcd		
				C	H	N	C	H	N
8c	p-ClC_6H_4	15	69	73.19	4.23	7.98	73.63	3.88	8.43
8d	p-CNC_6H_4	15	62	75.51	4.08	9.87	75.94	3.93	10.23
8h	Cinnamoyl	12	67	77.07	4.35	8.32	77.31	4.29	8.51

a) Based on the consumed ZnTPP.

Table 8. NMR spectra of zinc complexes of 21-acylamino-5,10,15,20-tetraphenylporphin (**8**) in $CDCl_3$

	Acyl-H	β-Pyrrole-H
8c	3.93 (d, 2H, 8 Hz), 5.87 (d, 2H, 8 Hz)	7.88 (s, 2H), 9.05 (d, 2H, 4.5 Hz), 9.27 (d, 2H, 4.5 Hz), 9.03 (s, 2H)
8d	4.05 (d, 2H, 8 Hz), 6.15 (d, 2H, 8 Hz)	7.85 (s, 2H), 9.45 (d, 2H, 4.5 Hz), 9.65 (d, 2H, 4.5 Hz), 9.43 (s, 2H)
8h	2.51 (d, 1H, 15.8 Hz), 4.68 (d, 1H, 15.8 Hz), 5.9—6.2 (m, 2H) 6.6—6.9 (m, 2H)	— , 9.02 (d, 2H, 4.5 Hz), 9.23 (d, 2H, 4.5 Hz), 9.00 (s, 2H)

Table 9. Visible and infrared spectra of zinc complexes of 21-acylamino-5,10,15,20-tetraphenylporphin (**8**)

	λ_{max} ($\varepsilon \times 10^{-4}$) nm in CH_2Cl_2	$\tilde{\nu}_{max}$ cm^{-1} (KBr)
8c	438(28.5), 559(0.79), 587(1.17), 609(1.41)	1616
8d	437.5(28.9), 555(0.76), 587(1.18), 608(1.29)	2234, 1614
8h	438.5(26.2), 558(0.80), 587(1.10), 610(1.33)	1638, 1598

been studied in detail. First the magnetic shielding effect of the macrocycles on the protons of *N*-acylamino group should be mentioned. Storm and Corwin showed that a plot of the incremental shift of *N*-alkyl substitutent (Δ in ppm) *vs.* the square of the reciprocal of the distance (r in Å) of the alkyl group from the current loop gives a straight line.[19] *N*-Acylamino group of **4** and **8** is approximately perpendicular to the plane of the macrocycles, as in the case of metal-free and metal containing *N*-alkylporphyrins (Fig. 1).[13,20-22] When the distance of protons on acyl including cinnamoyl group from the plane is estimated in the same way as in the work of Storm and Corwin, a plot of Δ between *N*-acylaminoporphin and the corresponding acyl amide as the reference compound against r^{-2} is found to give a straight line coinciding with the line for *N*-alkyl porphin (Fig. 2).

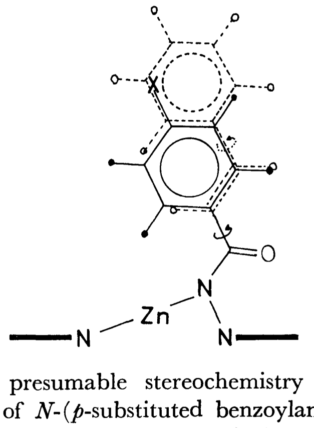


Fig. 1. The presumable stereochemistry of the zinc complexes of *N*-(p-substituted benzoylamino)porphin (full line) and *N*-(cinnamoylamino)porphin (broken line).

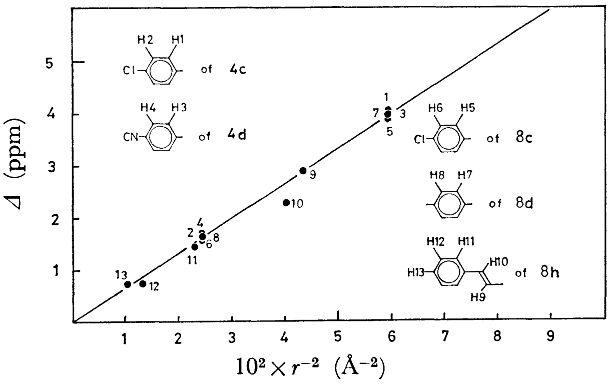


Fig. 2. A plot of the difference in chemical shift (Δ) between zinc complexes of *N*-acylaminoporphin and the corresponding acyl amide against the square of the reciprocal of the distance of the acyl protons from the current loop (r). This line is obtained by Storm and Corwin for *N*-alkyletioporphyrin-II.[19] The number of the plot refers to the acyl proton sketched in the Figure.

It was found that **4** and **8** are readily demetallized even when a solution of the complexes in dichloromethane was passed through a silica gel column. The anomalous instability of the zinc chelation reflects the sp^3 character of the pyrrolic nitrogen bounded by the acylamino group. The stronger basicity of this nitrogen may accelerate the removal of zinc. The metal-free *N*-acylaminooctaethylporphins give characteristic spectroscopic data. The CO frequency of the acylamino group shows a considerable shift to lower wavenumber at *ca.* 1610 cm^{-1} (Table 6), indicating a strong polarization of the CO bond. The visible spectra are no longer similar to those of *N*-methyloctaethylporphin (**9**) having four visible bands but resemble that of monocation of **9** (Fig. 3). This suggests that the metal-free *N*-acylaminoporphin possesses the betaine structure (**10**) which has a strong polarized acylamino residue and monocationic macrocyclic system. Furthermore, two magnetically equivalent protons attributable to the ring protons support the structure. The unusually good solubility of this compound in methanol is also consistent with the polar structure.

The thermal decomposition of *N*-alkylated porphyrins leads to *a*) elimination of the alkyl,[7,23] *b*) isomerization to *meso*-alkylporphin,[16] *c*) migration of the alkyl to the β-pyrrolic position,[7,20] and *d*) formation of a novel macrocyclic system, homoporphyrin.[16] It was found that *N*-acylaminoporphyrins and their zinc complexes show similar pyrolytic behavior. When the crystals of **4d** were heated above 200 °C, ZnOEP and 3d were isolated in the ratio 1:2.1. The thermal conversion was also carried out in boiling *o*-dichloroben-

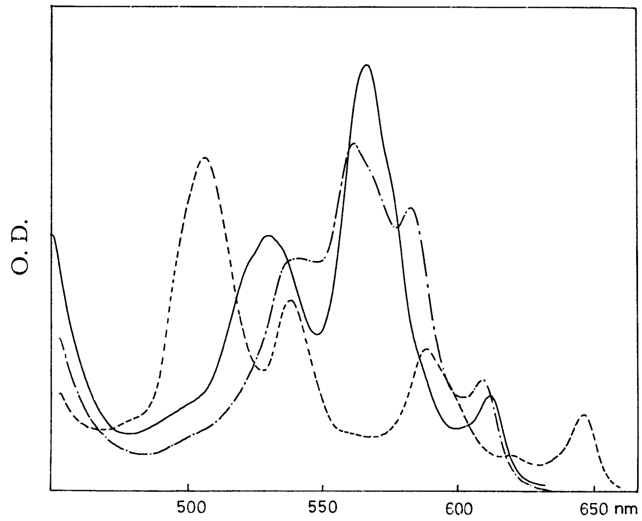
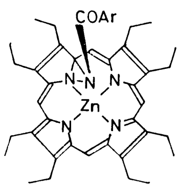


Fig. 3. The visible electronic absorption spectsa of *N*-benzoylaminooctaethylporphin (**10a**) in CH_2Cl_2 (——), *N*-methyloctaethylporphin (**9**) in CH_2Cl_2 (----), and **9** in CH_2Cl_2 containing acetic acid (—·—·—·—).



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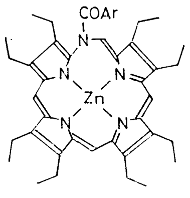

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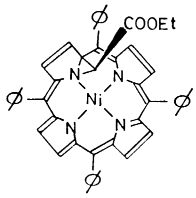

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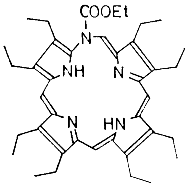

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zene whithin a few minutes. The thermolysis of **10d** required more drastic conditions, giving OEP and the free base of **3d** in the product ratio 1 :0.1. **8d** decomposed smoothly on heating in boiling *o*-dichlorobenzene.

The rearrangement of **4** to **3** occurs presumably through the diaziridine (**11**) and the azahomoporphyrin (**12**) as in the case of *N*-alkylporphyrins.[16] Although the aziridine intermediate (**13**) corresponding to **11** has been isolated in the thermal conversion of *N*-ethoxycarbonylethyltetraphenylporphinatonickel,[16] rapid ring contraction of **12** to the *meso*-substituted porphyrin takes place either upon heating or chelation.[14] Observation of the isosbestic points in the spectral change of **4d** and **8d** in boiling toluene suggests that both **11** and **12** are extremely short-lived.

Experimental

All melting points are not corrected. Visible, IR, and NMR spectra were recorded on a Hitachi type 323 spectrophotometer, and Hitachi EPI-3G spectrophotometer, and a JEOL C-60 HL type nuclear magnetic spectrometer, respectively. The preparative TLC was carried out with use of silica gel plates activated at 130 °C for 3 h.

Materials. Zinc octaethylporphin was recrystallized from toluene, and determination of its purity was made by means of visible spectrum and TLC on silica gel using benzene–hexane as an eluent. Commercial tetraphenylporphinatozinc (Strem Chemicals Inc.) was used without purification. Acyl azides were purified by passing a dichloromethane solution through a short column of silica gel, followed by recrystallization.

5-Benzoylamino-2,3,7,8,12,13,17,18-octaethylporphin. 5-Amino-2,3,7,8,12,13,17,18-octaethylporphin[5] (12.1 mg) was dissolved in 1 ml dry pyridine, and 50.0 mg of benzoyl chloride was added to the solution under stirring. A color change, violet→blue→olive green→violet, was observed. After 40 min stirring, the solution was poured into chloroform–water and the chloroform layer was separated, washed with dil acetic acid (×1), water (×3) and dried over anhydrous magnesium sulfate. After the solvent has been evaporated, the residue was chromatographed on silica gel plates with use of dichloromethane as an eluent. A red band was collected, and the product was extracted with dichloromethane containing methanol and recrystallized from dichloromethane–hexane. Red violet needles (6 mg) of mp 312—313 °C with decomposition was obtained. Found: C, 79.21; H, 8.10; N, 10.25%. Calcd for $C_{43}H_{49}N_5$: C, 78.96; H, 7.87; N, 10.72%. $\bar{\nu}_{max}$ (KBr): 3280 and 1643 cm^{-1}. λ_{max} in CH_2Cl_2: 405, 502, 536, 570, and 623 nm. Treatment with zinc acetate in chloroform–methanol gave the zinc complex.

Photolysis of Octaethylporphinatozinc in the Presence of Acyl Azide. To a solution of ZnOEP (120 mg) in 200 ml dichloromethane was added 1.5 molar amount of acyl azide, and the solution was irradiated with a 450 W high pressure mercury arc filtered with a Corning filter C. S. No.3—69 under argon bubbling and efficient stirring. The photolysis was followed by TLC and visible spectra. The irradiated solution was evaporated under reduced pressure, and the residue was chromatographed on silica gel plates with use of chloroform or dichloromethane–acetone as an eluent. The chromatogram was complex, two red bands being collected. The main red band having larger R_f-value gave red violet crystals of 5-acylamino-2,3,7,8,12,13-17,18-octaethylporphinatozinc (**3**) which were recrystallized from dichloromethane–methylcyclohexane. Identification of the benzoylamino derivative (**3a**) as well as its metal-free macrocycle with the authentic samples prepared as above was performed by TLC, IR, and visible spectra. The results are summarized in Table 1. The visible and IR spectra are given in Table 2. Methyl protons of ethyl group at the β-pyrrole positions undergo deshielding in the NMR spectra. The *meso*-protons are also influenced by the introduction of the *meso*-substitutent, being split into two signals in the intensity ratio 1 :2. When the spectra are measured in trifluoroacetic acid, **3** is demetallized to form the dication and exhibits four ring NH protons in the intensity ratio 2 :2. All the NMR signals are characteristic to *meso*-substituted octaethylporphin.[24] The protons of aroyl group show down field shift ($\Delta = ca.$ 0.8 ppm for protons at the *ortho*-position of phenyl) as a result of magnetic anisotropy of the porphyrin ring system. The acylamino group is thus positioned within the loop of the macrocycles. It is noteworthy that cinnamoylamino group in **3h** is in the *trans*-configuration (J=15 Hz); no sensitized isomerization of the cinnamoyl group exists during the course of photolysis.

The second product with smaller R_f-value was in some cases isolated in a demetallized state and recrystallzied from dichloromethane–methylcyclohexane. Treatment of the metal-free products with zinc acetate gave zinc complexes which were found to be demetallized during the chromatographic work-up. This anomalous instability of the zinc complex indicates that the demetallization takes place not during the course of photolysis but on the chromatographic separation. When purified dichloromethane was used as an eluent, the zinc complexes were isolated from the photoproducts by TLC on silica gel. The demetallization must be caused by trace amount of acidic impurity in the eluent. The second TLC fraction was treated with zinc acetate, washed with water, and evaporated to dryness to give 20-acylamino-2,3,7,8,12,13,17,18-octaethylporphinatozinc (**4**) which was recrystallized from chloroform–methylcyclohexane. The results are given in Table 4. NMR, and visible and IR spectra are given in Tables 5 and 6, respectively.

Photolysis of 5,10,15,20-Tetraphenylporphinatozinc–Acyl Azide. A solution of ZnTPP (200 mg) and 5 molar amount of acyl azide in 100 ml of dichloromethane was irradiated in the same way as in the case of ZnOEP. The resulting dark brown solution was evaporated to dryness, and the residue was chromatographed on a silica gel column with use of dichloromethane as an eluent. After eluting recovered ZnTPP, the eluent turned into a dichloromethane–acetone mixture (100:1 v/v). An emerald-green fraction was obtained and evaporated to dryness. TLC of the residue on silica gel revealed that the fraction is composed of two products. The one with larger R_f-value having $\lambda_{\max}$ at 438, 554, 586, 609, and 636 nm was converted, on treatment with hydrochloric acid, into the other with smaller R_f-value having $\lambda_{\max}$ at 433, 460, 550, 590, and 649 nm. The latter was reversely converted into the former on treatment with zinc acetate. Accordingly, the residue of the mixture was treated with zinc acetate in chloroform–methanol, followed by washing with water and drying with anhydrous sodium sulfate. 21-Acylamino-5,10,15,20-tetraphenylporphinatozinc (**8**) was recrystallized from dichloromethane–hexane as dark blue crystals. The results are given in Table 7. NMR, and visible and IR spectra are given in Tables 8 and 9, respectively.

Pyrolysis of N*-Acylaminoporphyrins and the Zinc Complexes.* The crystals of 21-(*p*-cyanobenzoylamino)-2,3,7,8,12,13,17,18-octaethylporphinatozinc (**8d**) were heated at *ca.* 200 °C for a short time and chromatographed on a silica gel column with use of dichloromethane as an eluent. The first red fraction was identified with ZnOEP by TLC and visible spectrum. The second red fraction was identified with 5-(*p*-cyanobenzoylamino)-2,3,7,8,12,13,17,18-octaethylporphinatozinc (**3d**) (TLC and visible spectrum). The product ratio of ZnOEP to **3d** was determined spectrophotometrically to be 1 : 2.1. The crystals of the metal-free 21-(*p*-cyanobenzoylamino)-2,3,7,8,12,13,17,18-octaethylporphin (**10d**) were heated at *ca.* 270 °C, and the products were separated and identified to be OEP and 5-(*p*-cyanobenzoylamino)-2,3,7,8,12,13,17,18-octaethylporphin (TLC and visible spectrum). The product ratio of OEP to the rearranged product was 1 : 0.1. The pyrolytic product of 21-(*p*-cyanobenzoylamino)-5,10,15,20-tetraphenylporphinatozinc (**8d**) in the crystalline state was identified with ZnTPP.

Heating of the zinc complexes (**4d** and **8d**) in boiling *o*-dichlorobenzene resulted in the same products as those obtained by pyrolysis in the crystalline state, while the metal-free *N*-(*p*-cyanobenzoylamino)octaethylporphin was recovered unchanged under the same pyrolytic conditions. A solution of the *N*-acylaminated zinc complexes was heated in benzene or toluene. Samples were taken at intervals, and the reaction was followed spectrophotometrically. The spectral changes demonstrated isosbestic points for both zinc complexes.

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