

Preparation and Characterization of 16-Benzoylated Tetraaza[14]annulenes

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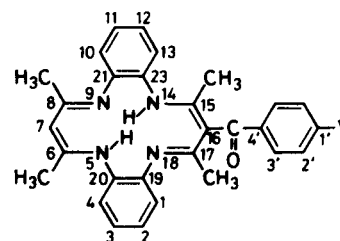
The condensation reaction between tetraaza[14]annulene (**1**) and a series of *para*-substituted benzoyl chlorides led to the 16-benzoylated corresponding products in 13-21% yields, but **1** was unreactive with alkyl acid chlorides and easily cleaved in macrocyclic framework. The mass spectra show the presence of molecular ion peaks which support the 16-benzoylated products. A strong ir band due to the C=N stretching mode of the macrocyclic moiety was observed at 1610 cm^{-1} and shifted slightly toward higher energy upon benzylation. An intense ir band which was associated with a C=O stretching mode was newly observed at 1640 cm^{-1} . The very strong absorption band about 29000 cm^{-1} was attributed to the $\pi \rightarrow \pi^*$ transition and gave a slight shift to higher frequency on benzylation. All proton signals except for methyl protons exhibit downfield shifts due to the deshielding effect of the substituted benzene ring, but the methyl proton peaks show upfield shifts due to the shielding effect caused by the magnetic anisotropy of the substituted benzene ring. The ^{13}C nmr result is also in accord with that of ^1H nmr.

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Introduction.

Although considerable effort has been expended on structural and spectral studies for tetraaza[14]annulene metal complexes [1], there are not many examples for the electrophilic substitution reaction of tetraaza[14]annulene metal complexes with various reagents. Eilmes *et al.* only published the reaction of tetraaza[14]annulene nickel(II) complexes with benzoyl chloride and glutaryl chloride up to the present time [2]. Examples of the reaction of tetraaza[14]annulene with acid chlorides are not important because of being prone to decompose with acid.

In the present research, we showed that the results of the reaction of a tetraaza[14]annulene, namely 6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (**1**), with a series of *para*-substituted benzoyl chlorides. We



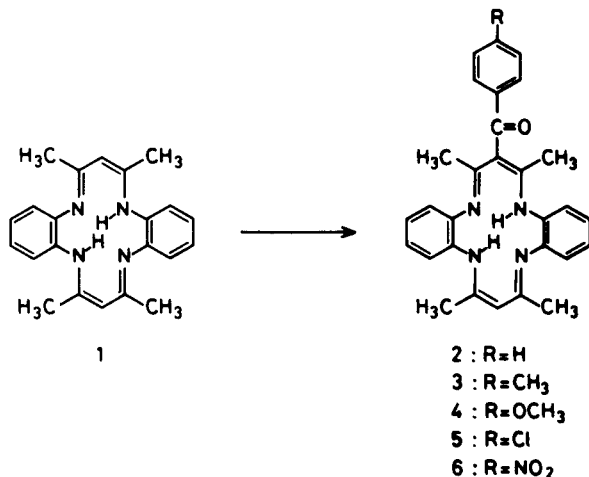
Results and Discussion.

Benzylation of Tetraaza[14]annulene.

The chelate rings in 2,4-pentanedione metal complexes undergo a number of typical reactions in aromatic systems. The hydrogen at the 3-position of the coordinated diketonate moiety is substituted by various electrophiles. Acylation, chloromethylation, dimethylaminomethylation, formylation, halogenation and nitration have been realized in this system without breakage of the chelate ring [3].

Since the electronic structure between the diiminate chelate rings of tetraaza[14]annulene and the diketonate chelate ring of 2,4-pentanedione is very similar, both structures are supposed to possess similar reactivity patterns. Consequently, this type of substitution was observed for the tetraaza[14]annulene nickel(II) complexes which gave the corresponding acylated products with a variety of acyl chlorides [2].

However, the 7,16-positions of the metal free tetraaza[14]annulene (**1**) are also found to be a reactive nucleophilic center and to be reactive with a number of aryl acid chlorides. The condensation reaction between **1** and a series of benzoyl chlorides in a 2:1 molar ratio was performed in refluxing acetonitrile and led to the 16-benzoylated corresponding products **2-6** in 13-21% yields. The analytical data for **1-6** are collected in Table I. Elemental



also characterized the spectral properties of the present products, that is, monosubstituted tetraaza[14]annulenes **2-6** by way of mass, infrared, electronic and nmr spectroscopy.

Table I
Elemental Analyses for Tetraaza[14]annulene and its Nickel(II) Complex

Formula	Compound No.	Carbon %		Hydrogen %		Nitrogen %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
$C_{22}H_{22}N_4Ni$	1-Ni	65.88	65.50	5.49	5.59	13.98	13.72
$C_{22}H_{24}N_4$	1	76.74	76.36	6.98	7.19	16.28	16.12
$C_{29}H_{26}N_4O$	2	77.65	77.48	6.29	6.54	12.49	12.41
$C_{30}H_{30}N_4O$	3	77.89	77.93	6.54	6.85	12.11	11.89
$C_{30}H_{30}N_4O_2$	4	75.29	75.66	6.32	6.59	11.70	11.91
$C_{29}H_{27}N_4OCl$	5	72.11	72.09	5.64	5.90	11.60	11.77
$C_{29}H_{27}N_5O_3$	6	70.57	70.66	5.51	5.67	14.19	14.19

Table II

Characteristic IR Absorption Bands for Tetraaza[14]annulene and 16-Benzoylated Tetraaza[14]annulenes [a]

Compound No.	Substituent Group (R)	ir band (cm^{-1})	
		ν C=O	ν C=N
1			1610
2	H	1640	1620
3	CH ₃	1640	1620
4	OCH ₃	1640	1620
5	Cl	1640	1620
6	NO ₂	1640	1620

[a] Measured by the potassium bromide disk method at room temperature.

analyses of crystalline samples of **2-6** were in agreement with compounds for the formula monobenzoylated tetraaza[14]annulenes. Metal coordination is not necessary for electrophilic substitution of **1**. Nevertheless, the reaction of **1** with alkyl acid chlorides did not occur and resulted in rupture of the macrocyclic framework. This seems to indicate that the coordinate nickel(II) ion protects the feasible nucleophilic nitrogen centers from attack by electrophiles and is allowed to undergo electrophilic substitution at the methine carbon atom of **1** alone.

Mass Spectra.

The EI mass spectra for benzoylated tetraaza[14]annulenes **2-6** exhibit the presence of a molecular ion M^+ at m/z 448, 462, 478, 482 (^{35}Cl) and 493, respectively, as given in the Experimental. These peaks are the base peaks in each mass spectrum and a good fit is obtained between the calculated and observed isotopic distributions. Further, these prominent parent peaks support 16-benzoylated products. The masses of the major fragment at m/z 344 in all products correspond to $[M-RC_6H_4CO+H]^+$ and the fragment peaks at m/z 433, 447, 463, 467 (^{35}Cl) and 478 also correspond to $[M-CH_3]^+$, respectively.

Vibrational Spectra.

The characteristic ir bands are compiled in Table II. A strong band due to the stretching mode of the C=N bond without benzoylation turns up at 1610 cm^{-1} . The band is most sensitive to benzoylation among the absorption peaks appearing in the sodium chloride range and shifts significantly to higher frequency on benzoylation. A strong absorption band at 1640 cm^{-1} is obtained for all benzoylated tetraaza[14]annulenes and attributed to the C=O stretching mode [4]. The band is little affected by changing the *para*-substituent in the benzoyl group and is always observed at 1640 cm^{-1} . This seems to indicate that the electronic effect of tetraaza[14]annulene ring is greater in magnitude than that of the *para*-substituent group.

Electronic Spectra.

The tetraaza[14]annulenes exhibit an extremely intense absorption band (ϵ 47000) at 29000 cm^{-1} in the visible area which is reasonably attributable to a $\pi \rightarrow \pi^*$ transition within a macrocyclic molecule. The band indicates a slight shift to higher frequency on benzoylation and has an increasing tendency on its hypsochromic shift in the follow-

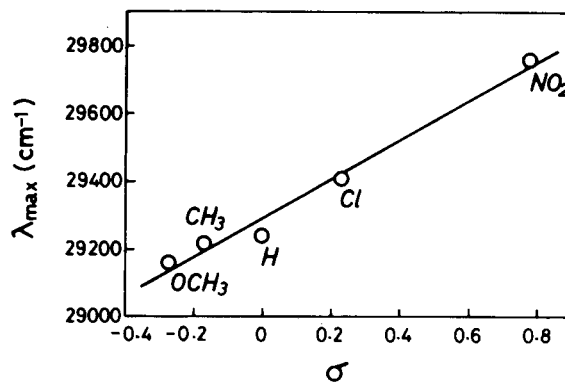


Figure 1. Correlation between λ_{max} values and σ constants for the *para*-position of benzoylated tetraaza[14]annulenes in *N,N*-dimethylformamide.

Table III

Proton NMR Data for the Tetraaza[14]annulene and Benzoylated Tetraaza[14]annulene [a]

Compound No.	Methyl			Methine 7-H	Aromatic	Amine	
	15,17-CH ₃	6,8-CH ₃	CH ₃ (benzoyl group)			5-NH	14-NH
1	2.13 (s)	2.13 (s)		4.87 (s)	6.99 (br)	12.6 (br)	12.6 (br)
2	1.97 (s)	2.12 (s)		4.91 (s)	7.01-8.12 (m)	12.9 (br)	13.8 (br)
3	1.96 (s)	2.12 (s)	2.44 (s)	4.90 (s)	7.01-8.01 (m)	13.0 (br)	13.5 (br)
4	1.97 (s)	2.12 (s)	3.89 (s)	4.91 (s)	7.01-8.11 (m)	12.8 (br)	13.6 (br)
5	1.96 (s)	2.12 (s)		4.90 (s)	7.03-8.04 (m)	13.0 (br)	13.8 (br)
6	1.98 (s)	2.12 (s)		4.91 (s)	7.05-8.42 (m)	13.0 (br)	14.0 (br)

[a] Chemical shifts in ppm from internal TMS. Measured in chloroform-d. Multiplicity of a proton signal is given in parentheses after δ -value: s = singlet, m = multiplet, br = broad singlet.

ing order: **6** > **5** > **2** > **3** > **4**. This implies that the electronic effects of a *para*-substituent in the benzoyl group are transmitted to the tetraaza[14]annulene. As illustrated in Figure 1, there is a systematic correlation between λ max values and σ constants [5]. The increasing order of λ max values is compatible with that of σ constants. Successful application of Hammett linear free-energy functions to benzoylated tetraaza[14]annulenes shows that λ max values are correlated with inductive effects of the substituents.

NMR Spectra.

Proton nmr data and their assignments for macrocycles **1-6** are listed in Table III. The amine proton peaks of the 5- and 14-positions for **1** are equivalent and broad singlets. On the other hand, the amine proton peaks at the 5- and 14-positions of **2-6** are nonequivalent and show downfield shifts by 0.2-0.4 ppm (5-position) and 0.9-1.4 ppm (14-position) upon benzoylation. The magnitude of downfield shifts for the 5-position is much smaller than that observed for the 14-position. This is primarily due to the fact that the amine group at the 5-position is placed further from the adjacent substituted carbonyl group, which provides magnetic anisotropy. On benzoylation the aromatic proton signals lead to downfield shifts and are split into multiplets with a lowering of symmetry. These downfield shifts are attributed to the deshielding effect owing to the substituted benzene ring. The 7-methine proton peaks for **2-6** are also shifted downfield by 0.03-0.04 ppm. The much smaller downfield shift seems to indicate that the methine group is placed further from the substituted benzene ring. The 15- and 17-methyl proton peaks show the upfield shifts by 0.15-0.17 ppm upon benzoylation, as seen in **2-6**. The methyl groups are subjected to the shielding effect caused by the magnetic anisotropy of the substituted benzene ring. The proton signals for other methyl groups placed at the 6- and 8-positions are hardly shifted on benzoylation.

Carbon-13 nmr data and their assignments for **1-6** are summarized in Table IV. All carbon signals for **1** exhibit a singlet, but the methyl, methine, 6-, 8-, 15- and 17-positions signals for **2-6** are observed as a 1:1 doublet. These peaks were analysed as two signals produced by the different chemical shift with the lowering of symmetry judging from off-resonance decoupling data. The methyl carbon signals bound to the 15- and 17-positions show the upfield shifts which are associated with the shielding effect due to the substituted benzene ring. The other carbon signals are shifted downfield on benzoylation. The new carbon signals for the carbonyl group and the phenyl group on the basis of benzoylation are freshly observed at 196-199 ppm and 124-163 ppm, respectively. This result is in agreement with the corresponding proton nmr spectral behavior.

EXPERIMENTAL

All melting points were determined on a Yanaco MP-S3 micro melting point apparatus. Mass spectra were performed on a Jeol JMS-DX 300 gas chromatograph-mass spectrometer at 70 eV using a direct inlet system. Infrared spectra in the region of the 400-4000 cm^{-1} were taken on a Hitachi 260-30 spectrophotometer at room temperature as potassium bromide pellets. Electronic spectra covering the 13000-37000 cm^{-1} range were carried out with a Shimadzu UV 200S double beam spectrophotometer for *N,N*-dimethylformamide solutions at room temperature. Proton and carbon-13 nmr spectra were recorded on a Jeol JNM-FX 60 spectrometer using tetramethylsilane as an internal reference standard in chloroform-d and chemical shifts are reported in ppm.

4-Chlorobenzoyl chloride (0.83 g), acetonitrile (400 ml) and **1** (3.24 g) were reacted as described above to yield 0.38 g of ocherous prisms (17%), mp 272-275° dec; ir: ν C=C 1555 cm^{-1} ; ms: m/e (relative intensity) 485 (11.0), 484 (38.2), 483 (35.3), 482 (100), 470 (8.1), 469 (27.2), 468 (24.5), 467 (73.9).

16-(4-Nitro)benzoyl-6,8,15,17-tetramethyldibenzo[b,*i*][1,4,8,11]-tetraazacyclotetradecine (**6**).

4-Nitrobenzoyl chloride (0.62 g), acetonitrile (400 ml) and **1** (2.30 g) were reacted as described above to yield 0.40 g of red prisms (21%), mp 258-260° dec; ir: ν C=C 1560, ν NO₂ 1520, 1345 cm^{-1} ; ms: m/e (relative intensity) 495 (6.4), 494 (33.3), 493 (100), 479 (27.8), 478 (85.4).

REFERENCES AND NOTES

- [1a] H. Hiller, P. Dimroth and H. Pfitzner, *Ann. Chem.*, **717**, 137 (1968); [b] E.-G. Jaeger, *Z. Anorg. Allg. Chem.*, **364**, 177 (1969); [c] F. A. L'Eplattenier and A. Pugin, *Helv. Chim. Acta*, **58**, 917 (1975); [d] V. L. Goedken, S.-M. Peng, J. M. Norris and Y. Park, *J. Am. Chem. Soc.*, **98**, 8391 (1976); [e] D. R. Neves and J. C. Dabrowiak, *Inorg. Chem.*, **15**, 129 (1976); [f] M. C. Weiss, G. Gordon and V. L. Goedken, *Inorg. Chem.*, **16**, 305 (1977); [g] A. Pezeshk, F. T. Greenaway and G. Vincow, *Inorg. Chem.*, **17**, 3421 (1978); [h] Y. Nishida, A. Sumita, K. Hayashida, H. Ohshima, S. Kida and Y. Maeda, *J. Coord. Chem.*, **9**, 161 (1979); [i] M. C. Weiss and V. L. Goedken, *Inorg. Chem.*, **18**, 274 (1979); [j] K. Sakata, M. Hashimoto, N. Tagami and Y. Murakami, *Bull. Chem. Soc. Japan*, **53**, 2262 (1980); [k] V. L. Goedken and J. A. Ladd, *J. Chem. Soc., Chem. Commun.*, 142 (1982); [l] K. Sakata, H. Nakamura and M. Hashimoto, *Inorg. Chim. Acta*, **83**, L67 (1984); [m] V. L. Goedken, H. Ito and T. Ito, *J. Chem. Soc., Chem. Commun.*, 1453 (1984); [n] K. Sakata, M. Hashimoto and T. Naganawa, *Inorg. Chim. Acta*, **98**, L11 (1985); [o] K. Sakata, Y. Hayashida, M. Hashimoto, K. Terada and Y. Kato, *Inorg. Chim. Acta*, **105**, L25 (1985); [p] A. R. Cutler, C. S. Alleyne and D. Dolphin, *Inorg. Chem.*, **24**, 2276 (1985); [q] H. Bastian and E. Breitmaier, *Chem. Ber.*, **118**, 2565 (1985); [r] C.-H. Yang and V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 1101 (1986); [s] C. Floriani, S. Ciurli, A. Chiesi-Villa and C. Guastini, *Angew. Chem., Int. Ed. Engl.*, **26**, 70 (1987); [t] S. Ciurli, E. M. Meyer, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 281 (1987); [u] K. Sakata, Y. Hayashida, S. Yanagida, M. Hashimoto and Y. Kato, *Inorg. Chim. Acta*, **134**, 269 (1987); [v] C. Floriani, M. Mazzanti, S. Ciurli, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1361 (1988); [w] P. Berno, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1409 (1988); [x] K. Sakata, T. Naganawa, M. Hashimoto, H. Iyehara Ogawa and Y. Kato, *Inorg. Chim. Acta*, **143**, 251 (1988); [y] K. Sakata, T. Annoura and M. Hashimoto, *Inorg. Chim. Acta*, **150**, 153 (1988).
- [2a] J. Eilmes and E. Śledziewska, *Bull. Acad. Pol. Sci.*, **26**, 441 (1978); [b] J. Eilmes, D. Pelan and E. Śledziewska, *Bull. Acad. Pol. Sci.*, **28**, 371 (1980); [c] J. Eilmes, *Polyhedron*, **4**, 943 (1985); [d] J. Eilmes, *Polyhedron*, **6**, 423 (1987).
- [3a] J. P. Collman, *Angew. Chem. Int. Ed. Engl.*, **4**, 132 (1965); [b] J. P. Collman, "Transition Metal Chemistry", Vol 2, Marcel Dekker, Inc., New York, 1966.
- [4] R. M. Silverstein, G. C. Bassler and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 4th Ed, Wiley, New York, 1981.
- [5] N. B. Chapman and J. Shorter, "Advances in Linear Free Energy Relationship", Plenum, New York, 1972.