Phthalocyanine Analogues. Part 1. Synthesis, Spectroscopy, and Theoretical Study of 8,18-Dihydrodibenzo[*b*,*l*]-5,7,8,10,15,17,18,20-octa-azaporphyrin and MNDO Calculations on its Related Hückel Heteroannulene

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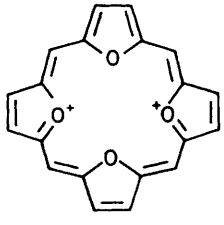
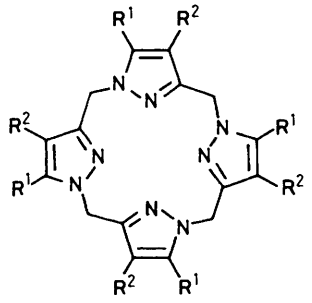
Three hemiporphyrazines containing two 1,2,4-triazole subunits, namely the *N,N'*-unsubstituted, the *N,N'*-didodecyl-, and *N,N'*-diphenyl-substituted derivatives, have been synthetised and fully characterized (m.s., u.v., and n.m.r.). In particular, high-resolution solid-state ^{13}C n.m.r. spectroscopy has proved to be a suitable method for the study of this highly insoluble class of compounds, giving valuable information on their tautomerism. An MNDO theoretical study (fully optimized geometries) has been carried out in order to understand why the didehydro derivative (**7**) (an 18π-electron aromatic porphyrin) is much less stable than the corresponding *N,N'*-unsubstituted hemiporphyrazine (**6**). The explanation lies in the peculiar structure of 1,2,4-triazoline-3,5-di-imine that one triazoline ring of (**7**) must adopt in order to allow a fully conjugated system. This structure has also been calculated, and shows a strong tendency to lose bound fragments (molecular dinitrogen and the azomethyne ylide $HN=\overset{+}{C}-NH-\overset{-}{C}=NH$).

The major interest in natural products containing porphyrin structures (*e.g.* chlorophylls, haemoglobin, and cytochromes) derives from their participation in biological processes of paramount importance, such as photosynthesis, electron, oxygen, or carbon monoxide transport, enzyme catalysis, and the regulation or control of metabolites. Quite surprisingly, the search for new molecules related to the planar, 18π-electron heteroaromatic structure of porphyrin—the bridged annulene[1] of nature—has been almost entirely limited to the azaporphyrins, with one or more nitrogen atoms at the *meso* bridges.[2] Substitution of other atoms in the system is much less common, and even the simpler tetraoxaporphyrin dication (**1**), with



(**1**)

oxygen atoms instead of nitrogen (the furan analogue of porphyrin) has been reported only recently by Vogel and co-workers.[1] Compound (**1**) is a remarkably stable, planar compound with u.v., i.r., and n.m.r. spectra closely resembling those of porphyrin. In terms of Hückel's rule, (**1**) must be considered as an 18π-electron aromatic system. Another example of a porphyrin analogue containing different heterocycles is the tetrapyrazole system (**2**), developed by Tarragó and co-workers.[3] Some derivatives of (**2**) display interesting complexing properties, and (**2**; R^1 = Me, R^2 = NH_2) has been found to extract alkali-metal ions more efficiently than dibenzo-18-crown-6, though in a less selective

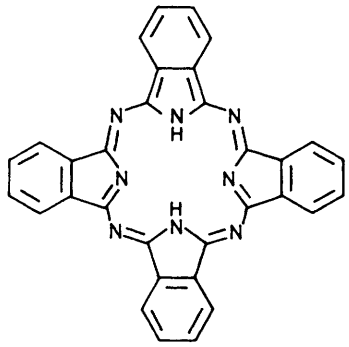


(**2**)

way. In spite of these merits, (**2**) can not be actually considered a porphyrin analogue, but as a non-conjugated porphyrinogen analogue, unable to aromatize owing to the bridgehead position of four of its pyrazole nitrogen atoms.

Phthalocyanine (**3**) and its metal complexes, obtained by template condensation of isoindolinedi-imine or phthalonitrile, represent undoubtedly the best known derivatives of tetraazaporphyrins (of great importance in the dyestuff industry and for the development of new conducting materials).[4] On the other hand, condensation of isoindolinedi-imine with a range of *meta*-oriented aromatic or heteroaromatic diamines yields the so-called hemiporphyrazines, a family of macrocycles related to phthalocyanines, in which isoindole alternates with other rings.[5] However, all hemiporphyrazines described to date are 'non-Hückel'[2] systems. For example, (**4**) has a cross-conjugated structure, and its metal complexes (**5**) display an antiaromatic extended conjugation of 20π-electrons.[6] Detailed *X*-ray diffraction data show that the parent neutral ligand (**4**) and some metal complexes (**5**; M = Mn, Co, Cu, and Zn), are planar structures, whereas the hydrate of (**4**) and the complex (**5**; M = Ni) have a pronounced saddle shape.[7]

Among the hemiporphyrazines, the bis-triazole derivative (**6**)



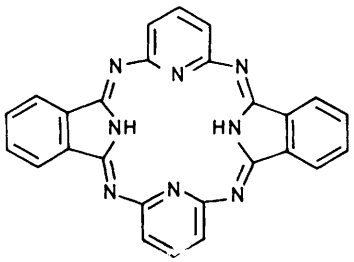
(3)

results from the condensation of isoindolinedi-imine or phthalonitrile with 1,2,4-triazole-3,5-diamine (guanazole).[8,9] In terms of the Hückel rule, this compound appeared to be an intriguing molecule, since a single oxidation could result in a fully-conjugated, 18π-electron porphyrinic structure (**7**). Tautomers (**6a**, **b**) or (**7a**, **b**) can be considered as the most representative of the many tautomeric forms that could be written for both (**6**) and (**7**), respectively. Owing probably to its extremely low solubility in most solvents, the experimental data supporting structure (**6**) were limited to i.r. spectra and microanalysis, in which the found value for hydrogen deviated more than 1% from the calculated value.[9] Obviously, this can not differentiate (**6**) ($C_{20}H_{12}N_{12}$) from (**7**) ($C_{20}H_{10}N_{12}$). Although some theoretical calculations were also performed by Honeybourne,[10] these were devoted to study of the columnar stacking of (**6**) and other macrocyclic ligands in order to develop new semiconductor materials, and were not concerned with the present problem. We decided, therefore, to undertake a more detailed structural study of compound (**6**). In order to compare the intrinsic stabilities of (**6**) and (**7**), theoretical calculations on these structures were also performed.

Results and Discussion

Synthesis and Characterization.—Triazolohemiporphyrazine (**6**) was synthetised from phthalonitrile or isoindolinedi-imine and guanazole, in 73 and 84% yields, respectively, by a modification of previously reported procedures.[8,9] This compound was found to be quite insoluble in almost all common solvents, so that purification up to an analytical grade was achieved by successive trituration with different alcohols (see the Experimental section). In this way, an amorphous brownish powder of molecular formula $C_{20}H_{12}N_{12}\cdot H_2O$ was obtained. The molecular ion at *m/z* 420 was also consistent with structure (**6**) proposed for the compound. Crystallization from trifluoroacetic acid (TFAA) gave the trihydrate as a microcrystalline, bright orange powder. However, all attempts to grow crystals suitable for *X*-ray structure determination were unsuccessful. Use of wet TFAA afforded only phthalimide and guanazole, even at room temperature, showing the Schiff-base character of the macrocycle.

In order to distinguish structure (**6**) from its oxidized derivative [the heteroannulene (**7**)] and also to enhance the



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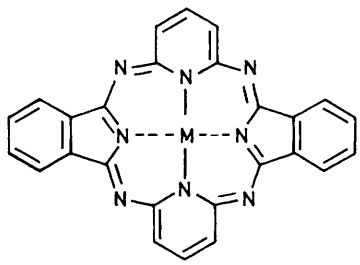

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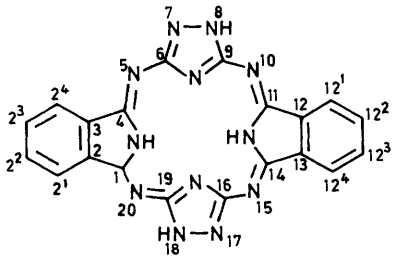
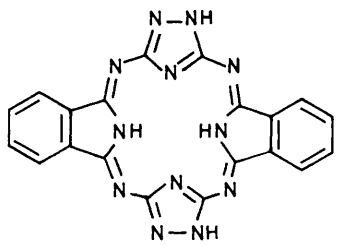
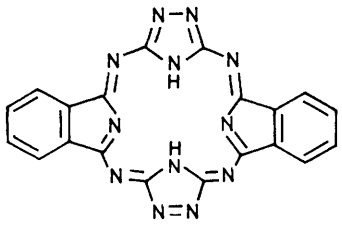


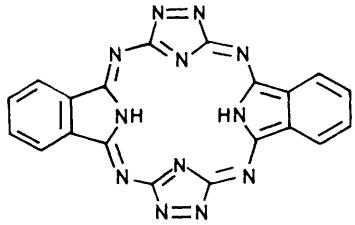
(6a)



(6b)



(7a)

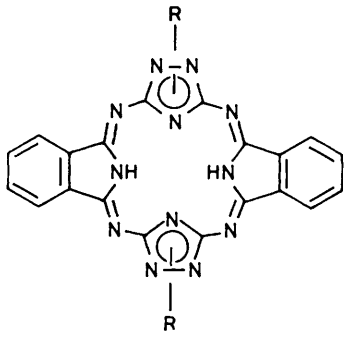


(7b)

Table 1. Values of δ_C (ppm) for compounds (**6**), (**11**), and (**12**).

Compound	(6)	(11a)	(11)	(11b)	(12)
Solid state	170.9 (C-5)	170.7 (C-1)		174.7, 173.5 (C-1, C-3)	
	163.0 (C-7)				161.5 (C-3)
	156.6 (C-10)				157.8 (C-5)
	135.3 (C-4a)	137.3 (C-3a)		139.6, 135.7 (C-3a, C-7a)	
	132.8 (C-2)	132.0 (C-5)		135.7, 129.9 (C-5, C-6)	
	122.6 (C-1)	122.0 (C-4)		123.6, 120.7 (C-4, C-7)	
TFAA	155.7 (s, C-5)		164.6 (s, C-1)		
	153.8 (s, C-7)				148.0 (C-3)
	135.3 (d, C-4a)		136.4 (d, C-5)		
	128.0 (s, C-2)		125.6 (s, C-3a)		
	124.3 (d, C-1)		125.6 (d, C-4)		
$(CD_3)_2SO$			169.9 (s, C-1)		
					158.6 (C-3)
			136.6 (s, C-3a)		
			130.6 (d, C-5)		
			121.1 (d, C-4)		

solubility of the hemiporphyrazine system, we prepared both the didodecyl derivative (**9**), by heating equimolar amounts of isoindolinedi-imine and 1-dodecyl-1,2,4-triazole-3,5-diamine (**8**), and the diphenyl derivative (**10**).[8] Compounds (**9**) and (**10**) (mixtures of regioisomers) are examples of fixed models for structure (**6**), since they cannot be oxidized to the corresponding annulenes.

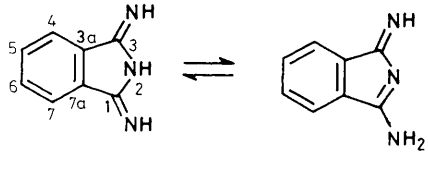


(**9**) R = n-$C_{12}H_{25}$

(**10**) R = Ph

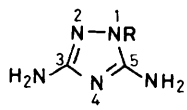
A comparison of the u.v. spectra (TFAA) of (**6**) and (**9**) (see the Experimental section) clearly revealed the similarity in their electronic structures. Bathochromic shifts of *ca.* 12 nm observed for the absorptions of compound (**6**) at 323 and 337 nm [335 and 349 nm in (**9**)] are in good agreement with the normal shifts observed upon *N*-alkylation in 1,2,4-triazole and other azoles.[11]

The ^{13}C n.m.r. spectrum of (**6**), determined both in the solid state and in TFAA, was assigned with the aid of isoindoline-1,3-di-imine (**11**) and guanazole (**12**) as model compounds (Table 1). In the solid state, isoindolinedi-imine was found to be a mixture of tautomers (**11a**) and (**11b**) (major). On the other hand, guanazole (**12**) existed exclusively as a 1*H*-tautomer, with



(**11a**)

(**11b**)



(**8**) R = n-$C_{12}H_{25}$

(**12**) R = H

well separated signals at 157.8 (C-5) and 161.5 (C-3) ppm. The mean value of these shifts (159.6 ppm) is quite similar to the value in solution (158.6 ppm in dimethyl sulphoxide). The solid-state shifts, however, are in excellent agreement with those found for the parent 1,2,4-triazole: 143.9 ($\Delta\delta$ = +13.9 ppm) and 148.0 ($\Delta\delta$ = +13.5 ppm).[12] As the values displayed in Table 1 clearly indicate, the solid-state spectrum of (**6**) represents an almost perfect combination of (**11a**) and (**12**). The triazole rings in (**6**) must therefore be 1*H*-tautomers, although *syn–anti* regioisomers (**6a**) and (**6b**) are probably present.

A looser correlation was observed in TFAA solution for the quaternary carbon atoms of (**6**) and of the model compounds (**11**) and (**12**), probably due to different protonation sites in the macrocycle and in the free-amine containing models.

The ^{13}C n.m.r. spectra of the *N*-substituted derivatives (**9**) (TFAA and chloroform) and (**10**) (TFAA) were more complex than the spectra of (**6**), due to the fact that these compounds were actually (1 : 1) mixtures of *syn* and *anti* regioisomers, so that most signals were split in the spectra. However, the mean values of these split signals closely correspond to those found for (**6**).

Theoretical Calculations.—Calculations were performed at a semiempirical level, the size of the molecules under consideration preventing the use of more accurate methods. Thus, geometric parameters were fully optimized by the MNDO method,[13] minimizing the corresponding heats of formation. Some symmetry constraints were introduced: *e.g.* C_{2h} and C_{2v} symmetries were adopted for tautomers (**6a**, **b**) respectively, whereas a D_{2h} symmetry was imposed on tautomers (**7a**, **b**). The resulting optimized structures, their charge distributions and bond-order patterns are shown in Figures 1 and 2.

The optimized structures of the oxidized derivatives (**7a**, **b**) and, in particular, the almost constant length of bonds involving the bridging nitrogen atoms reveal the existence of an inner 18π-electron aromatic ring. However, it must also be pointed out that the C–N distances for the azole rings are longer than in isolated triazole rings, whereas the N–N bonds are considerably shorter.[14] This could indicate that in these oxidized forms the interaction between the N–N fragment and the rest of the system is very weak. This is also consistent with a bond order less than one having the calculated charge distribution. In fact, it is quite significant that the charge at the nitrogen atoms of the N–N bonds is almost zero, as if it were a dinitrogen molecule loosely bound to the rest of the macrocyclic framework. This would lead to an unstable overall molecular system. In good agreement with this prediction was the experimental evidence

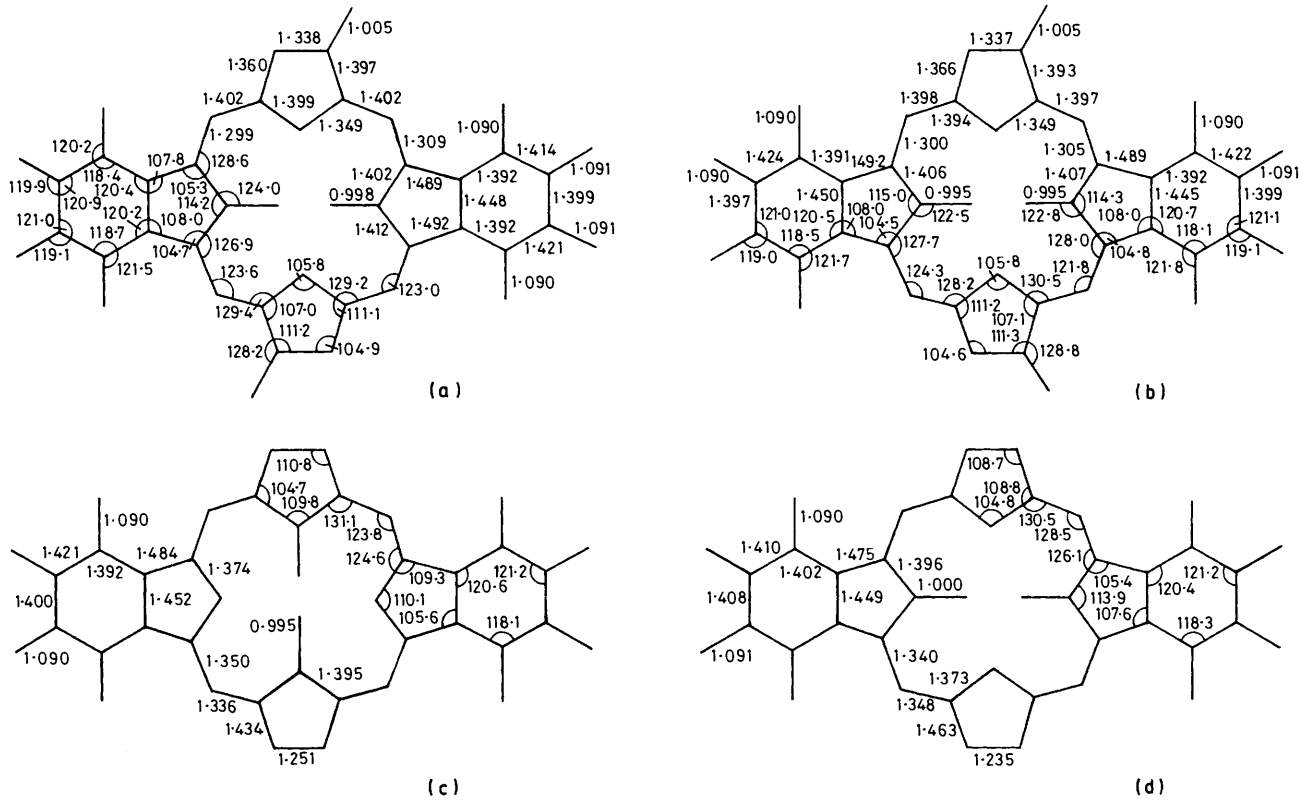


Figure 1. MNDO optimized bond lengths (Å) and bond angles (°) for: (a) (**6a**); (b) (**6b**); (c) (**7a**); and (d) (**7b**).

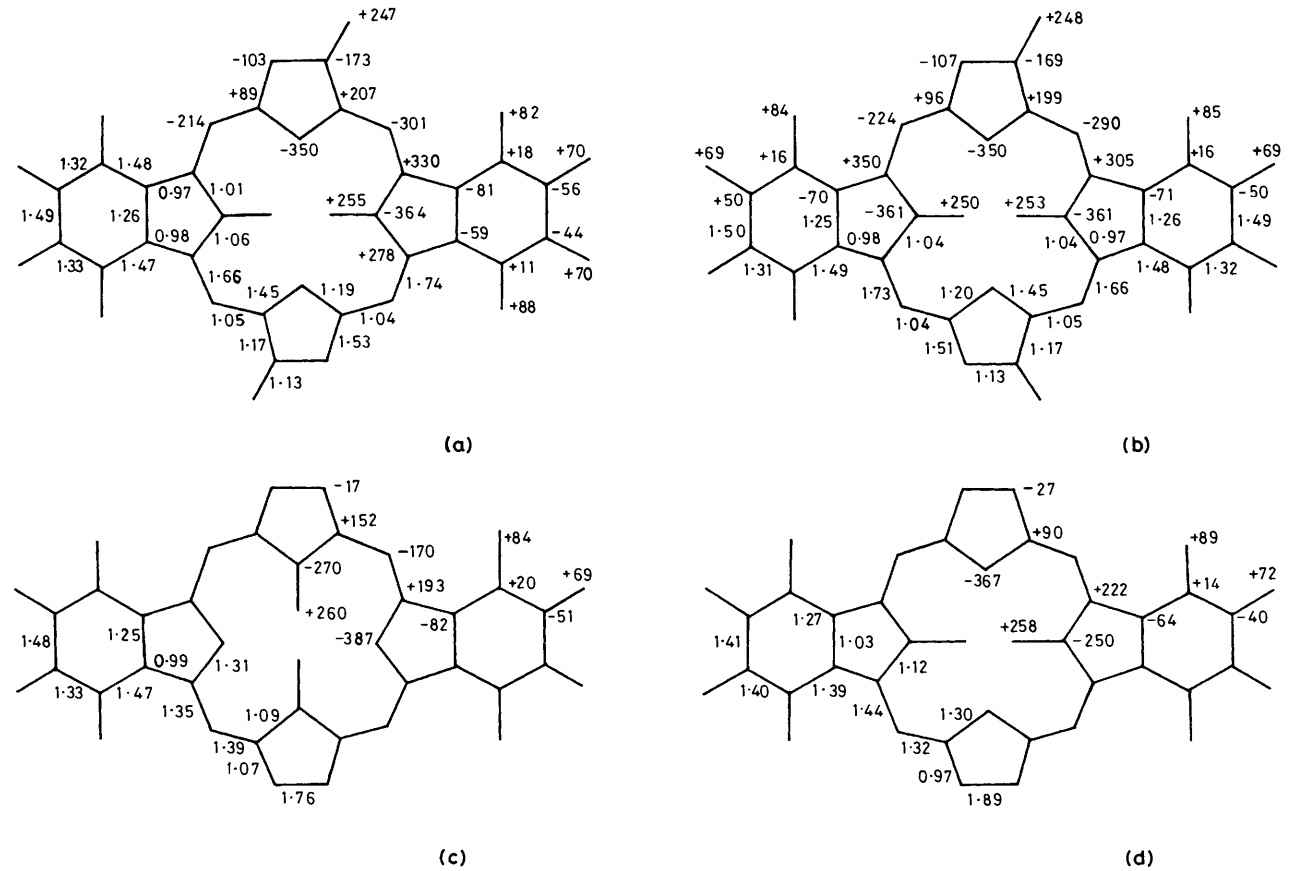


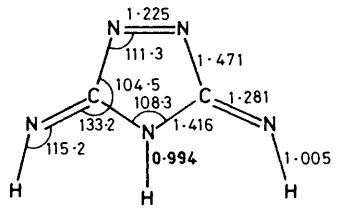
Figure 2. MNDO calculated atomic charge densities (in millielectrons) and bond orders for: (a) (**6a**); (b) (**6b**); (c) (**7a**); and (d) (**7b**).

shown above, and also a comparison of the calculated heats of formation (Table 2), which show that both reduced species (**6a**) and (**6b**) were of about the same stability and considerably more stable than the corresponding oxidized counterparts (**7a**) or (**7b**).

To confirm this destabilizing effect, we also performed MNDO calculations on molecule (**13**), which was used as a model for the azole subunit present in (**7a**). The optimized geometry of (**13**) is shown in Figure 3. Although bond lengths and angles were found to be quite similar in (**7a**) and (**13**), the effects mentioned above were even stronger in the latter. For instance, the N–N bond length was somewhat shorter, whereas C–N bonds were correspondingly longer, contributing to a smaller interaction of the N–N bond with the rest of the molecular fragment. Most significantly, the structure found for compound (**13**) was very close to that reported by Gleiter *et al.* for 4-methyl-1,2,4-triazoline-3,5-dione,[15] an extremely reactive dienophile. On these grounds, one should expect similar behaviour for compound (**13**), which could be considered, as indicated above, as a dinitrogen molecule loosely bound to a $HN{=}\overset{+}{C}{-}NH{-}\overset{-}{C}{=}NH$ closed-shell fragment. To estimate the degree of instability of compound (**13**) we also evaluated its relative energy with respect to both these non-interacting closed-shell fragments, N_2 and $NH{=}\overset{+}{C}{-}NH{-}\overset{-}{C}{=}NH$. For the sake of consistency these calculations were carried out at the MNDO level, using completely optimized geometries. Our results showed that compound (**13**) was only 31.2 kcal mol^{-1} more stable than a dinitrogen molecule held infinitely apart from a $HN{=}\overset{+}{C}{-}NH{-}\overset{-}{C}{=}NH$ system. Therefore, in agreement with our prediction, when the new triazole system is formed, the C–N bonds should be very weak.

Table 2. MNDO total energies (atomic units) and heats of formation (kcal mol^{-1}) of compounds (**6**) and (**7**).

Compound	Total energy	Heat of formation
(**6a**)	−191.383 69	231.72
(**6b**)	−191.382 67	232.16
(**7a**)	−190.241 47	295.14
(**7b**)	−190.248 51	290.53



(**13**)

Figure 3. MNDO optimized bond lengths (Å) and bond angles (°) for (**13**).

The low stability of compound (**13**) was also clearly indicated by a consideration of its higher-energy molecular orbitals (Figure 4). There were mainly two kinds of MO: those with a main atomic orbital contribution centred at N-1 and N-2, and those mainly localized on the $HN{=}\overset{+}{C}{-}NH{-}\overset{-}{C}{=}NH$ framework. Among the former were the $\psi_{17}(b_2)$ and $\psi_{12}(a_1)$ MOs, which are essentially the same combination as those defining ψ_{15} and ψ_{16} but involving the N-1 and N-2 lone pairs, and $\psi_{13}(b_1)$ MO, which is mainly N(1)–N(2) π-bonding and slightly antibonding with the rest of the molecule. Among the latter was the HOMO, $\psi_{18}(b_1)$, a π-type antibonding MO, and the $\psi_{16}(a_1)$ and $\psi_{15}(b_2)$ MOs, which are basically in-phase and out-of-phase combinations of the exocyclic nitrogen lone pairs.

A comparison of (**13**) with the triazole subunit of macrocycle (**7a**) show that only slight distortions are observed. For example, inspection of the MOs of (**7a**) (referred to hereafter as φ_n), reveal that the MOs of the triazole rings interact very weakly with those localized on the isoindoline rings. As a consequence, most of the MOs of (**7a**) are actually the result of a pairwise interaction between the MOs of the two triazole rings of the macrocycle. Thus, the φ_{74} MO corresponds to the $(\psi_{18} + \psi_{18})$ linear combination, whereas the orthogonal combination $(\psi_{18} - \psi_{18})$ defines the φ_{64} MO (Figure 5). Something similar can be said of ψ_{15}, which yields the φ_{69} and φ_{62} MOs of (**7a**) through an out-of-phase $(\psi_{15} - \psi_{15})$ and an in-phase $(\psi_{15} + \psi_{15})$ interaction, respectively. Finally, the linear combinations $(\psi_{14} + \psi_{14})$, $(\psi_{13} + \psi_{13})$, $(\psi_{13} - \psi_{13})$, $(\psi_{12} + \psi_{12})$, and $(\psi_{12} - \psi_{12})$ yield for MOs φ_{67}, φ_{57}, φ_{54}, φ_{50}, and φ_{49}, respectively.

Conclusions

The stability of compound (**7**) is the resultant of two opposing forces: the porphyrin-type aromaticity of the aza-annulene and the antiaromatic character of the triazolinedi-imine structure. Our experimental results, as well as the calculated energy values, suggest that the latter is stronger: aromaticity and antiaromaticity are more important concepts in small rings than in large ones. In structure (**7**), the major cause of instability seems to be the N=N bond present in one triazole subunit. Since analogues of (**7**) with C=C double bonds *e.g.* phthalocyanine

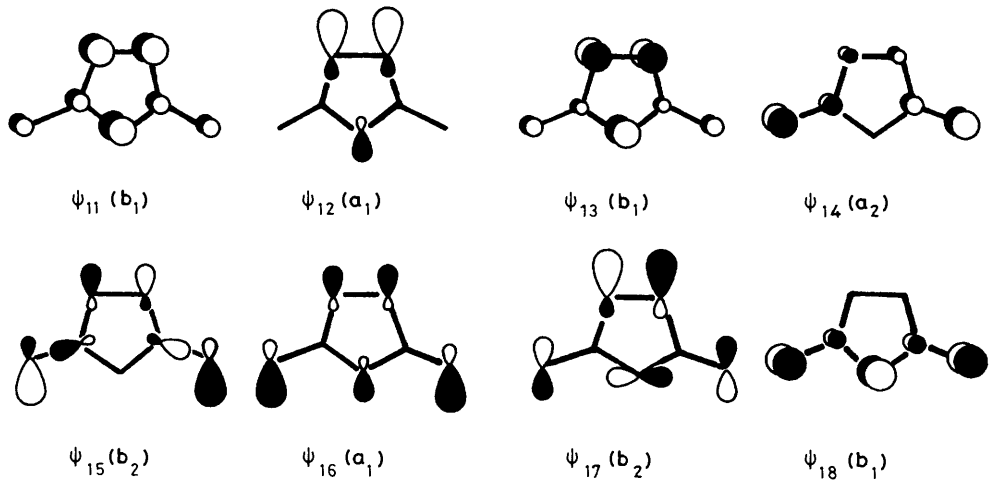


Figure 4. Schematic drawing of the highest occupied molecular orbitals of (**13**).

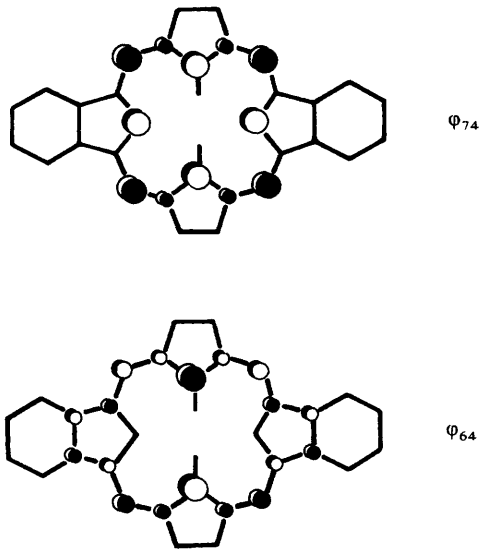
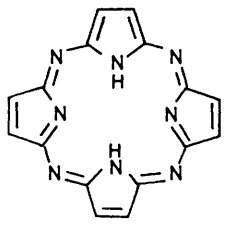
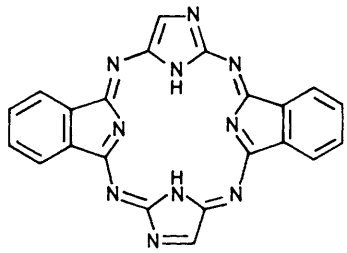


Figure 5. Schematic representation of the φ_{74} and φ_{64} molecular orbitals of (**7a**), showing that they are linear combinations of the highest occupied molecular orbitals (ψ_{18}) of (**13**).



(**14**)



(**15**)

(**3**) or the tetra-azaporphyrin (**14**)[16] are well known stable structures, one may anticipate that a hemiporphyrazine containing two imidazole subunits instead of triazoles would have more opportunity to be oxidized to the as yet unknown hexa-azaporphyrin (**15**) which contains C=N double bonds.

Experimental

M.p.s are uncorrected. Electron impact (e.i.) (70 eV) and FAB (*m*-nitrobenzyl alcohol matrix, ionization by xenon atoms, 8 kV) m.s. spectra were determined on a Varian MAT 312 and Finnigan HSQ-30 instruments, respectively, incorporating an SS 300 MS datasystem. For the recording of i.r. and u.v. spectra, Perkin-Elmer 257 and Kontron Uvikon 820 instruments were used, respectively. N.m.r. spectra (^1H and ^{13}C) were recorded on a Bruker WP 200 SY instrument, and c.p./m.a.s. ^{13}C n.m.r. spectra on a Bruker MSL 400. Elemental analyses were carried out in the Instituto de Química Orgánica General, CSIC, Madrid. Thin layer plates were visualized by u.v. light or iodine. 3-Iminoisoindolenin-1-amine (iminoisoindoline) (**11**) and 1,2,4-triazole-3,5-diamine (guanazole) (**12**) were purchased from the Aldrich Chemical Co., and used as received without further purification.

8,18-*Dihydrodibenzo*[b,l]-5,7,8,10,15,17,18,20-*octa-azaporphyrin* (**6**).—(A) *From* 3-*iminoisoindolenin*-3-*amine* (**11**). A mixture of (**11**) (0.58 g, 4 mmol) and 1,2,4-triazol-3,5-diamine (**12**) (0.40 g, 4 mmol) was boiled for 24 h in 2-ethoxyethanol (8 cm^3). The resulting brown solid was filtered, washed with 2-ethoxyethanol, and triturated with hot ethanol (50 cm^3). The yield was 0.74 g (84%), m.p. > 350 °C (Found: C, 55.2; H, 3.4; N, 37.8. $C_{20}H_{12}N_{12}\cdot H_2O$ requires C, 54.8; H, 3.2; N, 38.4). Recrystallization from TFAA and successive washing with acetic acid and ethanol afforded the trihydrate, m.p. > 350 °C (Found: C, 51.0; H, 3.4; N, 35.8. $C_{20}H_{12}N_{12}\cdot 3H_2O$ requires C, 50.6; H, 3.8; N, 35.4); $\lambda_{max.}$(TFAA) 260, 323sh (log ε 4.4 dm^3 mol^{-1} cm^{-1}), 337 (4.5), 355 (4.5), 374 (4.4), 420sh (3.5), 446sh (3.3), and 482sh nm (3.1); $\nu_{max.}$(KBr) 3 300, 3 150, 3 050, 2 910, 1 672, 1 639, 1 560, 1 482, 1 365, 1 310, and 1 048 cm^{-1}; δ_H([$^2H_6$]DMSO) 7.6–8.1 (8 H, m, arom.); δ_C(TFAA and solid state) (see Table 1); *m/z* (e.i.) 420 (M^+, 13%), 129 (100), and 128 (68).

(B) *From phthalonitrile.*[8] A mixture of phthalonitrile (2.58 g, 20 mmol) and 3,5-diamino-1,2,4-triazole (**12**) (2.00 g, 20 mmol) was boiled in ethane-1,2-diol (50 cm^3) for 24 h. Work-up as above afforded (**6**) (3.12 g, 73%) identical with the compound obtained by method A.

3,5-*Diamino*-1-*dodecyl*-1,2,4-*triazole* (**8**).—A general method for the alkylation of triazoles was followed[17] (sodium methoxide, dodecyl bromide). The yield was 45%. M.p. 115–117 °C (from heptane) (Found: C, 62.7; H, 11.1; N, 25.8. $C_{14}H_{29}N_5$ requires C, 62.9; H, 10.9; N, 26.2); $\nu_{max.}$(KBr) 3 340, 3 190, 2 930, 2 755, 1 660, 1 592, and 1 545 cm^{-1}; δ_H($CDCl_3$) 0.88 (3 H, t, CH_3), 1.24 (18 H, m, CH_2), 1.71 (2 H, m, CH_2CH_2N), 3.63 (2 H, t, CH_2N), 4.14 (2 H, br s, NH_2), and 4.98 (2 H, br s, NH_2); δ_C($CDCl_3$) 14.0 (CH_3), 22.6 (CH_2CH_3), 26.6, 27.0, 28.9, 29.2, 29.4, 29.5 (CH_2), 31.8 (CH_2CH_2N), 46.3 (CH_2N), 153.1 (C-5), and 159.5 (C-3); *m/z* (e.i.) 267 (M^+, 18%), 112 (80), and 99 (100).

8,18-*Didocecyl*-8,18-*dihydro- and* 8,17-*Didodecyl*-8,17-*dihydrodibenzo*[b,l]-5,7,8,10,15,17,18,20-*octa-azaporphyrin* (**9**).— A mixture of 3-iminoisoindolenin-1-amine (**11**) (0.16 g, 1.12 mmol) and 3,5-diamino-1-dodecyl-1,2,4-triazole (**8**) (0.30 g, 1.12 mmol) was boiled in 2-ethoxyethanol (9 cm^3) for 24 h. The solvent was evaporated under reduced pressure, and the residue was treated with water, then filtered and dried. Recrystallization from heptane gave (**9**) (0.15 g, 35%), m.p. 170–180 °C (decomp.) (Found: C, 68.1; H, 8.1; N, 21.8. $C_{44}H_{60}N_{12}\cdot H_2O$ requires C, 68.2; H, 8.1; N, 21.7); $\lambda_{max.}$(TFAA) 260, 335sh (log ε 4.2 dm^3 mol^{-1} cm^{-1}), 349 (4.3), 358 (4.3), 368 (4.2), 380sh (4.1), 420sh (3.7), 446sh (3.5), and 484sh nm (3.2); $\nu_{max.}$(KBr) 3 300, 2 925, 2 856, 1 667, and 1 488 cm^{-1}; δ_H($CDCl_3$) 0.86 (6 H, t, CH_3), 1.1–1.4 (36 H, m, CH_2), 1.6 (2 H, br s, H_2O), 1.88 (4 H, m, CH_2CH_2N), 4.13 (4 H, t, CH_2N), 7.55, 7.75, and 7.85 (8 H, m, arom.); δ_C($CDCl_3$) 14.1 (CH_3), 22.5 (CH_2CH_3), 26.3, 28.9, 29.2, 29.5 (CH_2), 31.8 (CH_2CH_2N), 46.6 (CH_2N), 122.5, 122.9, 131.5, 132.1, 132.2, 134.1, 134.7 (C-12^3, C-12^4, C-13, C-2, C-2^1, C-2^2), 152.7, 153.6, 154.2, 155.1, 155.6, 162.7, 163.2, and 168.2 (C-14, C-16, C-19, C-1); δ_C(TFAA) 11.0 (CH_3), 20.6 (CH_2CH_3), 24.0, 24.1, 26.7, 27.1, 27.4, 27.6 (CH_2), 30.0 (CH_2CH_2N), 46.1, 47.3 (CH_2N), 122.3, 122.7, 123.6, 124.2, 125.1, 128.3, 131.2, 132.0, 132.6, 134.0, 134.7, 136.6 (C-12^3, C-12^4, C-13, C-2, C-2^1, C-2^2), 151.7, 152.1, 152.5, 153.8, 154.8, 154.9, and 156.2 (C-14, C-16, C-19, C-1); *m/z* (e.i.) 758 (12%), 757 (52), 756 (M^+, 100), 602 (25), 601 (38), 433 (15), and 421 (19); *m/z* (FAB) 757 ($M^+ + 1$).

8,18-*Diphenyl*-8,18-*dihydro and* 8,17-*Diphenyl*-8,17- *dihydrobenzo*[b,l]-5,7,8,10,15,17,18,20-*octa-azaporphyrin* (**10**).—This compound was prepared in 51% yield from phthalonitrile and 1-phenyl-1,2,4-triazole-3,5-diamine according to a literature procedure.[8] M.p. > 350 °C; $\nu_{max.}$(KBr) 3 320, 1 660, 1 600, 1 500, and 1 310 cm^{-1}; δ_C(TFAA) 122.3, 122.5, 123.8, 124.6, 125.1, 127.9, 128.0, 128.8, 129.5, 131.4, 131.7, 132.5, 132.8, 133.1, 134.2, 134.9, 136.9 (*N*-phenyl, C-12^3, C-12^4, C-13, C-2, C-2^1, C-2^2), 152.0, 152.1, 152.5, 153.9, 155.4, and 156.7 (C-14, C-16, C-19, C-1).

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